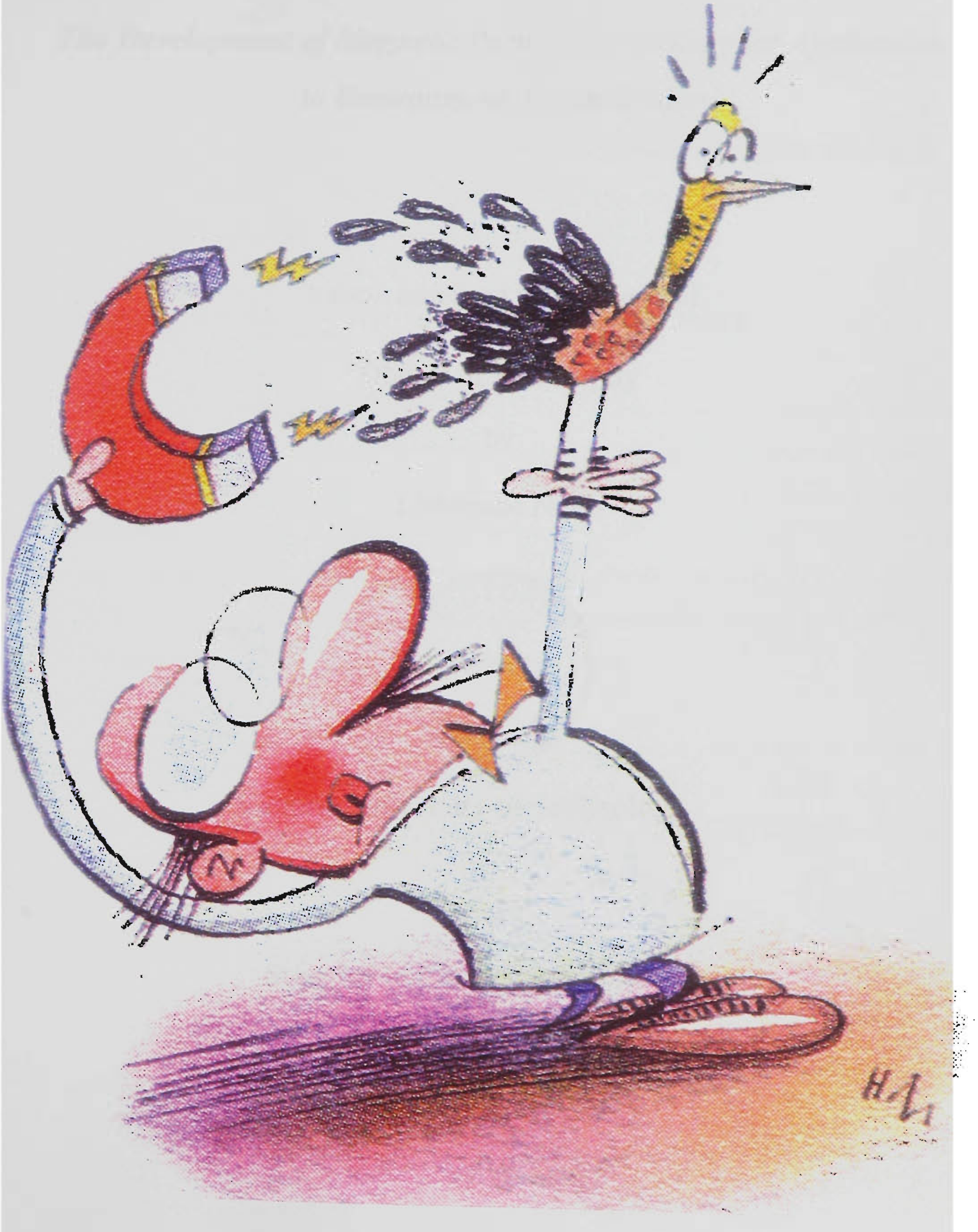

(from *Business Week Magazine*, 17 May, 1999, p. 89)

The Development of Magnetic Particle Technology for Application to Environmental Remediation

A thesis submitted for the degree of

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by

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Publications, relevant to the scope of the thesis

1. Orbell, J.D.; Godhino, L.; Bigger, S. W.; Nguyen, T. M.; Ngeh, L. N. Oil spill remediation using magnetic particles: An experiment in environmental technology, *J. Chem. Educ.*, 74, 12, 1446-1448, 1997.

2. Orbell, J. D.; Tan, E. K.; Coutts, M. C.; Bigger, S. W.; Ngeh, L. N. Cleansing oiled-feathers - magnetically, *Mar. Pollu. Bull.*, 38, 3, 219-221, 1999.

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Abstract

The potential for the development and the application of magnetic particle technology to environmental and wildlife remediation has been explored. Initial studies have been carried out on the ability of iron particles with polyethylene (PE) or polyvinylchloride (PVC) to magnetically harvest various contaminants. In this context, methods have been developed for the production of research quantities of particles of different sizes and with various textures. The pick up characteristics for a variety of contaminants have been experimentally and theoretically investigated. In particular, a mathematical model for the characteristic adsorption isotherm has been developed and several efficiency parameters have been defined. The effects of the nature of the substrate from which the contaminant is removed and the contaminant hydrophobicity and viscosity have also been investigated. The ability of PE and PVC coated particles in the remediation of soil contaminated with various pesticides has been explored. Uncoated iron particles have also been found to be effective in the remediation of various contaminants. In particular, iron powder was found to be almost 100% effective in the magnetic harvesting of various contaminants from a glass substrate.

The demonstrable success of iron powder in the magnetic harvesting of various contaminants prompted an investigation into its ability to cleanse oiled feathers. A methodology was developed for *in vitro* studies on duck, penguin and seagull feather clusters. Iron powder was found to be very effective in the cleansing of such feathers for a variety of contaminants. Furthermore, the development and application of an empirical mathematical model has allowed the efficiency of oil removal to be compared for different feathers on the same bird and for the same feathers between different birds. In particular, the model allows for the calculation of an initial removal efficiency, which is of relevance for the development of a field protocol based on such technology. The relationship between removal efficiency and contaminant viscosity has also been investigated.

The *in vitro* studies on the use of iron powder to cleanse oiled feathers have been extended to studies of the plumage of duck and penguin carcasses and, to a limited extent, of live birds. The results are promising and reflect those carried out on feather clusters. This clearly demonstrates the feasibility of using iron powder as a dry cleansing agent for the removal of contaminants from the plumage of whole birds. The empirical model has been employed to develop efficiency parameters for such experiments. The problem of removing weathered oil contamination by this method has been investigated *via* the use of various pre-conditioning agents. These experiments have been carried out *in vitro* and on the plumage of a whole bird. Of all pre-conditioning agents tested, olive oil was found to be the most promising.

A method has been developed for the assessment of feather damage by an analysis of feather microstructure using digital imaging. Initially, the possibility of using the hooklet extension as a microstructural indicator was explored. Although this parameter was discounted as a candidate, some interesting trends in hooklet extension emerged which are suggestive of its role in feather curvature. Additional insights into the role of the hooklets in the maintenance of coherency of the feather vane and the water repellency of the feather were also obtained. A procedure was developed for measuring the coherency of a feather vane (i.e. feather damage) with a single parameter. This procedure is based on a mathematical analysis of a two dimensional grid which models the feather vane. The mathematical model indicates that such a method would be highly sensitive. These ideas were born out in experimental tests on real feathers which were damaged in a controlled way using a range of detergent concentrations. The calculated damage parameter was found to be directly proportional to the detergent concentration. This parameter could also be used to demonstrate quantitatively that cleansing oiled feathers with iron powder effectively restores them to their original condition.

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Abbreviations

AGAL	Australian Government Analytical Laboratories
C	Percentage removal of the contaminant from carcass feathers
Cbs (Pn)	Breast feathers of Carcass (Penguin)
Cbk (Pn)	Back feathers of Carcass (Penguin)
Cbs (Du)	Breast feathers of Carcass (Duck)
Cbk (Du)	Back feathers of Carcass (Duck)
Cbs (Sg)	Breast feathers of Carcass (Seagull)
Cbk (Sg)	Back feathers of Carcass (Seagull)
D	Indicator of feather damage
DDT	Dichloro-diphenyl-trichloroethane
E_1	Removal efficiency of contaminants from petri dishes
E_2	Removal efficiency of contaminants from *in vitro* feathers based on particles to chemical ratio
E_3	Removal efficiency of contaminants from *in vitro* feathers based on numbers of treatments.
E_4	Efficiency removal of contaminants from carcass feathers based on numbers of treatments.
Emulsion S	50% Oil C/seawater by volume.
F	Percentage removal of contaminants from *in vitro* feathers
Fbs (Pn)	*In vitro* breast Feathers (Penguin)
Fbk (Pn)	*In vitro* back feathers (Penguin)
Fbs (Du)	*In vitro* breast Feathers (Duck)
Fbk (Du)	*In vitro* back Feathers (Duck)
Fbs (Sg)	*In vitro* breast Feathers (Seagull)
Fbk (Sg)	*In vitro* back Feathers (Seagull)
GC	Gas chromatography
H	Peak height
K	Efficiency constant
kF_o	Efficiency of contaminant removal
N	Number of treatments
Oil A	Mobil Super XHP 20W-50, 1993 formulation
Oil B	Moderately heavy crude oil, Mobil Oil, Australia

Oil C	Light crude oil, Esso Australia
Oil D	Light crude oil, Shell Australia Limited
%CV	Percentage coefficient of variance
P	Percentage removal of chemicals from petri dishes
PE	Polyethylene
PINP	Philip Island Nature Park
PVC	Polyvinylchloride
R	Particle to chemical ratio by weight
r^2	Linear regression coefficient
SE	Solvent extraction
SFE	Supercritical fluid extraction
$W_{1/2}$	Half-width
WOC	Weathered, oil-contaminated

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1.2 Magnetic Particle Technology and Magnetic Separation

- 1.2.1 Uncoated and Surface-Treated Magnetic Particles
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- 1.2.3 Coated (or Encapsulated) Magnetic Material

1.3 References

1.1 Introduction

Magnetism has been known and exploited for centuries. The first known natural magnets, "loadstones", which are essentially magnetic iron oxide deposits, were discovered by the ancient Chinese and Greek civilisations. These materials were found to always point in one direction when allowed to rotate freely. This led to the development of the magnetic compass in China in the middle ages, arguably the first practical application of magnetism. In the seventeenth century it was discovered that the earth itself is a giant magnet with north and south poles; and in the early nineteenth century the relationship between magnetism and electricity was discovered. At this time, a more theoretical understanding of the phenomenon of magnetism and electricity began to emerge. The stage was then set for dramatic technological advances with the discovery, by Michael Faraday in 1830, that a changing magnetic field produced a current in a coil of wire (electromagnetic induction). This discovery led to the generation and exploitation of electric power.

The twentieth century witnessed an even more dramatic increase in the understanding of the phenomenon of magnetism and to technological applications in a wide range of areas such as electronics, nuclear magnetic resonance spectroscopy and materials science. Less sophisticated (but equally useful) applications of magnetism include the use of electromagnets in scrap yards and waste sorting.

Although elemental iron is traditionally considered to be the "stuff of magnets", many other materials exhibit magnetic properties including those containing nickel and cobalt (Setchell, 1985), and more recently, even organic materials (Miller & Epstein,1998). Nonetheless, many applications are still based on iron even though the magnetic strength of iron magnets is relatively low. There is an increasing demand for stronger magnets with a higher magnetic field and smaller size. As long ago as 1931, Mishima developed a new class of magnetic materials based on aluminum-iron-nickel alloys known as Alni materials (Hadfield, 1962). The addition of cobalt to the Mishima system produced the commonly known Alnico magnets (O'Connor, 1993). Cobalt provides more temperature stability to these magnets. Alnico alloys have now reached a stage where there is no further improvement of their properties. However, there still remains a requirement and a demand for further development.

In 1952, the Philips Electronics Company developed a unique class of magnetic materials known as "ceramic ferrite magnets" or "ceramic magnets". These materials are based on the elements barium, strontium or lead, which are combined with iron oxides. They are made by powder metallurgical methods, similar to those used to produce pottery, hence the reference to "ceramic" (Campbell, 1994). The term "ferrite" refers to the presence of iron oxide in these materials. Like most ceramic materials, they are characteristically hard and brittle. Ceramic magnets have a number of advantages including inexpensive raw materials and a relatively simple manufacturing process. Furthermore, they are chemically stable and light-weight with a relatively strong magnetic field. These magnets are more commonly used than Alnico magnets, but have the disadvantage of the magnetic strength decreasing at temperatures above 200°C (Valenzuela, 1994).

In the late 1950s, researchers began to investigate other classes of magnetic materials with a view to further enhancing various properties. It was known that rare earth elements such as La, Ce, Pr, Sm and Y readily form alloys with transition metals such as Fe, Ni, or Co (Campbell, 1994). After extensive research, it was found that the optimum alloy was samarium-cobalt (1:5). The magnetic field strength of a samarium-cobalt magnet is approximately twice that of an Alnico magnet and six times that of a ferrite magnet (Moskowitz, 1995).

Despite the successful development of these magnets, which are far superior to existing ferrite and Alnico magnets, the high cost of samarium and cobalt limits their usage. For this reason investigations were focused on using iron in place of cobalt with a variety of rare earth elements, but they were found to have undesirably low operating temperatures (Campbell, 1994).

In the early 1980s, it was found that by incorporating boron into the neodymium-iron system, the operating temperature could be extended up to 300°C (Strnat, 1987). Neodymium is considerably more abundant than samarium, which coupled with the use of iron as the transition metal, greatly reduces the cost compared to the samarium-cobalt systems. However, in contrast to samarium-cobalt magnets, the magnetic properties of Neodymium-iron-boron (Nd-Fe-B) magnets deteriorate rapidly with increasing temperature (Mitchell, 1985; Jakubovics, 1987). Nd-Fe-B is the better choice up to 300°C, but for temperatures above 300

°C, samarium-cobalt will generally give superior performance (Andriessen & Terpstra, 1989). Nd-Fe-B magnets are now considered the most powerful permanent magnets in common usage (Herbst, 1993).

The most important advantage of more powerful magnetic materials is the potential for minaturization of devices. However, in spite of advances in the development of magnetic material, many permanent magnets are very hard and brittle. This led to an interest in so-called "bonded magnets". The bonded magnets produced commercially are based primarily upon ferrite and Nd-Fe-B (Nesbitt & Wernick, 1973; Croat, 1997). These magnets are produced by encapsulating a magnetic powder in a polymer or resin and then moulding them to the final shape. They are developed at low cost for applications such as refrigerators, toys and door gaskets. The relative magnetic strengths of some of the common magnets is given in Table 1.1.

Table 1.1 : Comparison of the relative magnetic strength of different types of common magnets.

Types of magnets	**Magnetic field strength/Oersted**
The Earth	6.25
Alnico	400 - 2000
Ferrite and ceramic	1800 – 3400
Samarium-cobalt	5000 - 7000
Neodymium-iron-boron	8000 - 11000

In 1991 the first organic-containing materials to exhibit magnetic characteristics were developed (Miller & Epstein, 1998). Several classes of "organic magnets" based on the tetracyanoethenide radical anion, $[TCNE]^{-}$, have been reported to bond with metals such as V, Mn, Fe, Co and Ni. For example, when diphenyl vanadium, $V(C_6H_6)_2$, is reacted with tetracyanoethylene (TCNE) in dichloromethane, an amorphous product, $V[TCNE]_2.\frac{1}{2}CH_2Cl_2$ isolated. This material is magnetic up to 77 °C. However, it is readily decomposed by exposure to air. The production technique has been improved by preparing thin films of $V[TCNE]_2$ in the gas phase, thus eliminating the solvent which tends to react with vanadium (Pokhodnya *et al.*, 2000). Further improvement can be achieved by stabilising the material with a protective coating to eliminate the degradation of the film in air.

Some naturally occurring iron oxides such as magnetite (Fe_3O_4) and maghemite (γFe_2O_3) possess magnetic properties which have been exploited in various applications such as sewage treatment. These properties have also been exploited in iron oxide/polymer composites. Magnetic particles based on such material are extensively used in chemical and biochemical separations (Cunningham, 1992) and have also been used in oil remediation (Chun & Park, 2001). In addition to their magnetic properties, an additional requirement for these materials in that their surfaces have an affinity (either naturally or by functionalisation) for a chemical of interest.

Although often referred to as magnetic, such materials more strictly termed paramagnetic. This means that the materials are attracted by a magnetic field, but do not retain the magnetism when the field is removed. This property is particularly useful for biochemical applications (Safarik *et al.*, 1995; Sinclair, 1998). In contrast to paramagnetic materials, ferromagnetic materials are attracted to a magnetic field and have the ability to remain magnetised when the field is removed (Moskowitz, 1995). Such properties might find specific application in the production of permanent magnets and in the coagulation of environmental contaminants such as oil in water using magnetic particles.

1.2 Magnetic Particle Technology and Magnetic Separation

The concept of magnetic particle and magnetic separation technology is not new. A patent relating to the clean-up of oil spills have been documented as long ago as 1981 (Wessman, 1981). This work outlines an idea for applying oil-absorbing magnetic particles to oil contamination in variety of circumstances and suggests a means of subsequent magnetic harvesting (see Figure 1.1).

Magnetic separation has a number of advantages over other techniques, including, for example, centrifugation. Various applications will be discussed in detail in this chapter. Magnetic particles which are currently available or under development can be divided into three broad categories: (ii) uncoated and surface-treated magnetic particles, (ii) particles impregnated with magnetic particles and (iii) coated (or encapsulated) magnetic particles.

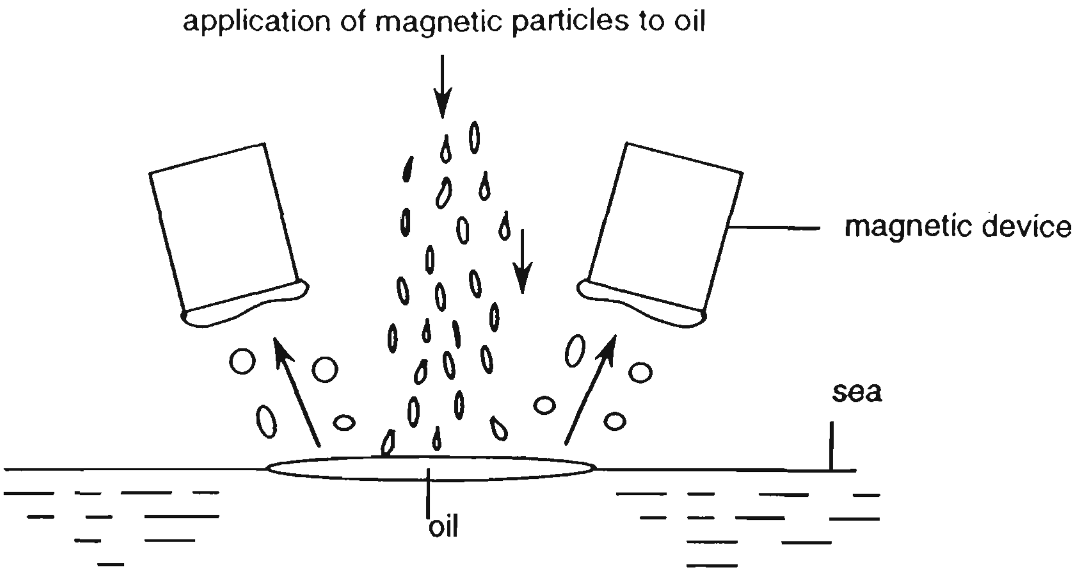


Figure 1.1 : Schematic diagram of method and device for collecting oil magnetically (Adapted from Wessman, 1981).

1.2.1 Uncoated and Surface-Treated Magnetic Particles

During research on the application of polymer-coated magnetic particles to oil spill remediation at Victoria University, it was discovered that uncoated steel "isoshot" pellets (iron pellets), iron filings, and iron powder also had an affinity for oil (Orbell *et al.*, 1999). The attraction of oil for elemental iron is, perhaps, not surprising when one considers that oil is used routinely as a lubricant for moving metal parts. This led to the suggestion that uncoated iron particles might be applicable to oil spill remediation. The initial experiments were conducted on iron pellets which are commercially available. These are used in "shot-blasting", and are cheap, highly magnetically susceptible and produced in a variety of grades that are characterised by different particle size distributions, ranging from 0.45 to 1.59 mm average diameter. Iron filings (average maximum diameter, 0.30 mm) and iron powder (average maximum diameter, 0.10 mm) are also commercially available.

Initial studies on the affinity of iron powder, iron pellets and iron filings for engine oil were carried out by the Victoria University research group in 1997. The results of the percentage oil pick-up were very promising, ranging from 74% to 99% depending on the particle size distribution. The application of iron powder for the removal of other contaminants will be discussed in detail in Chapters 2 and 3.

Other uncoated magnetic particles generally refer to naturally occurring powdered (micron size) magnetite (Fe_3O_4), and other powdered magnetic iron oxides such as goethite and maghemite (γ-Fe_2O_3). The particle surface may be chemically treated or modified for the attachment of surface-active groups. Examples of such surface manipulation are given later.

An example of the application of uncoated magnetic particles where their surface has been chemically activated is their use in water purification and sewage treatment. The Commonwealth Scientific and Industrial Research Organisation (CSIRO), Australia, has developed a process for water clarification and decolourisation based on magnetite particles (Anderson *et al.*, 1983; Priestly, 1990; Booker *et al.*, 1991).

Conventional processes in water purification and sewage treatment generally rely on aerobic biological oxidation. (Rittmann, 1987; Lapara & Alleman, 1999). However, the cost of treatment to meet health standards is a concern. Therefore, there is a need to develop new technologies to reduce the cost of sewage treatment. The CSIRO (Sirofloc) process uses a combination of efficient physico-chemical clarification with rapid anaerobic biological digestion. As a consequence, treatment costs have been reduced.

This technology is currently used in a pilot sewage treatment plant in Sydney at Malabar. It was reported that 87% of suspended solids, 90% oil and grease, 99% bacteria, 89% phosphate, 60% COD, 50% BOD and up to 89% heavy metals are removed within 15 min (Bolto, 1996). This process has also been used in water treatment plants in Western Australia, Tasmania, and overseas, including the United Kingdom, and Taiwan (Bolto, 1996, Bolto, personal communication, 2000). Other researchers have successfully used this method in the removal of colour and turbidity from water in situ (Kolarik, 1983) and from river water in water treatment plants (Anderson & Priestley, 1983).

The "Sirofloc" process involves the addition of magnetite particles to effluent. Magnetite can act as an efficient adsorbent and the magnetic properties can be exploited to enhance sedimentation in the treatment process. There are three steps in the treatment of effluent.

The first step is a pre-treatment step. Naturally occurring magnetite (Fe_3O_4) is generally negatively charged due to the presence of silica, a common contaminant of mineral matter, and this reduces the efficiency of the process. Pre-treatment involves the washing of the magnetite particles with sodium hydroxide to remove the silica and other impurities from the surface to leave a clean metal oxide.

The second step involves acidification of the magnetite particles to positively charge their surface. Acidic magnetite of particle size 1-10 μm is used as a 1% w/w slurry at pH 5-6. Impurities, such as colloidal and coloured particles are generally negatively charged and hence adsorb to the surface of the positively charged magnetite. The loaded magnetite is then subjected to magnetic field, which promotes settling.

The third step involves the subsequent treatment of loaded magnetite with sodium hydroxide to raise the pH to 11-12. The magnetite surface now becomes negatively charged and attached impurities are released. Thus, the magnetised particles can act as an adsorbent at low pH, and can be regenerated at high pH for reuse.

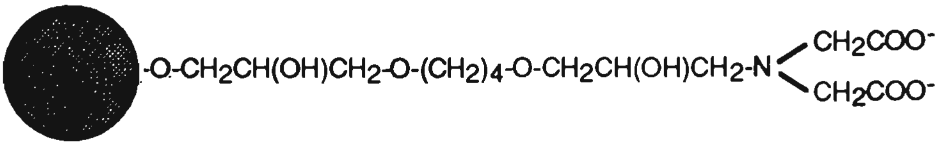
The equations for the acidic and alkaline treated magnetite particles are shown below.

$$\mathrm{Fe-OH + H^+ \leftrightarrow Fe-OH_2^+} \quad \text{(Acidic conditions)}$$

$$\mathrm{Fe-OH + OH^- \leftrightarrow Fe-O^- + H_2O} \quad \text{(Alkaline conditions)}$$

Following the same principle, Sakai *et al.*, (1991) have investigated the effect of the application of iron oxide powder and a gradient magnetic field (generated by an electromagnet) on sedimentation in the activated sludge process for sewage treatment. Their studies have shown that the application of iron oxide powder and a gradient magnetic field have increased sedimentation by 36 times over the control.

Other magnetic particles may also be prepared where the surface is "functionalised" by covalently attaching molecules such as silane and carboxylate groups. For example, preparation of an amine terminated iron oxide can be carried out in situ according to a patented procedure (Josephson, 1987), Figure 1.2. Iron oxide can be precipitated by reacting a solution containing $FeCl_2$ and $FeCl_3$ with sodium hydroxide. Preparation of amine-terminated iron oxide particles may then be carried out by mixing the iron oxide particles with aminopropyltriethoxy silane. These amine terminated iron oxide particles can be used for the preparation of magnetic chelator particles (Halling & Dunnill, 1979, O'Brien *et al.*, 1996; Shen *et al.*, 1996). These functional chelator supports are used for binding with a substrate such as antibodies. The loaded particles are separated with a permanent magnetic device.



$$\text{-O-CH}_2\text{CH(OH)CH}_2\text{-O-(CH}_2)_4\text{-O-CH}_2\text{CH(OH)CH}_2\text{-N}\begin{matrix} \text{CH}_2\text{COO}^- \\ \text{CH}_2\text{COO}^- \end{matrix}$$

Figure 1.2 : Amine terminated iron oxide particles

1.2.2 Polymer Particles Impregnated with Magnetic Material

Particles impregnated with magnetic material have been developed and used extensively for chemical and biomedical applications (Wang & Shah, 1987). The particles are usually produced in sizes ranging from an average of 100 Å to 1000 µm. In general, this class of particle is polymer-based and impregnated with iron oxide. For example, An invention relating to the synthesis of magnetic polymeric particles and functional polymeric particles has been described in the patent literature (Chang *et al.*, 1987; Chang & Colvin, 1989). These magnetic polymers are generally produced *in situ* by adding a saturated solution of iron(II) and iron(III) ions to preformed porous polymer particles and allowing the ions to impregnate or diffuse into the pores. Porous particles provide a greater surface area for adsorption or binding to substrates. The rate of diffusion increases with temperature. The impregnation step is usually carried out at a temperature from 20 °C to 50 °C. A basic reagent such as sodium hydroxide is added to the solution to convert the metal ions to magnetite (Fe_3O_4) and and/or maghemite (γ-Fe_2O_3).

The preparation of impregnated functional hydrophilic polymers *in situ* has also appeared in the patent literature (Chang *et al.*, 1987). They are formed from a solution of 25% to 95% of water-soluble mono-unsaturated monomer mixture. These include amino, carboxyl, aldehyde or hydroxyl substituted acrylic monomers. These hydrophilic polymers are often used for biological use as they are generally more specific and have functional groups available for covalent bonding to substrates such as antibodies.

Impregnated polystyrene particles of exactly the same size have been made under normal gravity (Ugelstad, 1979). Uniformity of particle size is considered important since non-uniform particles tend to clump together or bind non-specifically to other surfaces (Chang *et al.*, 1987). Uniform particles in the size range 0.5-100 μm have been commercially produced. These polystyrene particles can be magnetised by the impregnation of iron oxide (γ-Fe_2O_3) throughout. A commercial example of these magnetic polymer particles is Dynabeads^{TM}, which are used for biomedical applications such as immuno magnetic separation. Dynabeads are functionalised by covalently attaching molecules such as antibodies to the surface. The functionalised surface is then recognised by a target such as an antigen which subsequently binds, Figure 1.3. The Dynabeads/target materials are then magnetically harvested. A schematic diagram showing the immunomagnetic separation of antigens using Dynabeads is shown in Figure 1.4.

Figure 1.3 : Binding of antigen to functionalised surface of a Dynabead (from Dynal booklets).

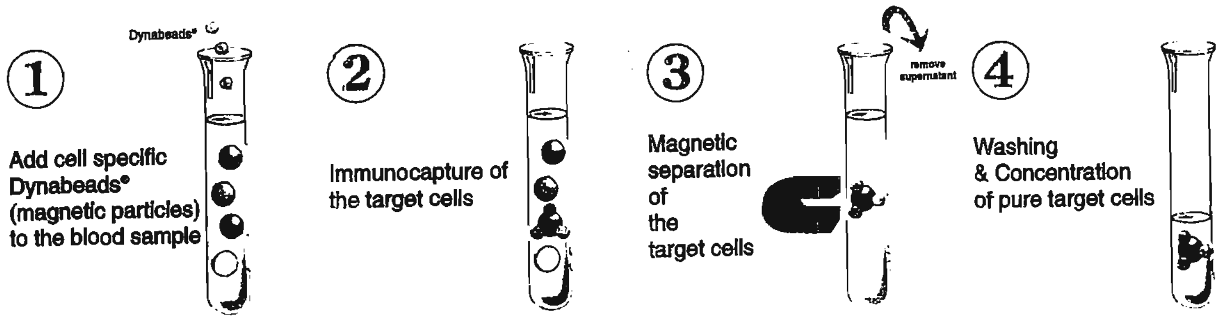


Figure 1.4 : Schematic diagram showing the magnetic separation of antigen using Dynabeads (from Dynal booklets).

Recently magnetic polyvinyl butyral microbeads were prepared from a commercial resin, Mowital^{TM} B30HH (polyvinyl butyral) in uniform and spherical form over a size range of 125 to 250 μm (Tanyolac & Ozdural, 2000). A solvent evaporation technique was employed for the production of these particles. Magnetite particles of mean diameter of less than 40 μm were successfully embedded in the polymer particles during polymerisation by an elaborate technique. Spherical particles with high magnetic quality were realised. The particle surface contains an abundance of active sites containing hydroxyl groups. This may be functionalised by glutaraldehyde for biomagnetic separation.

Following the same principle, functional magnetic particles have also been used in areas such as the magnetic separation of cancer cells (Wang *et al.*, 1993), separation of radioactive materials (Nunez *et al.*, 1996), as catalyst supports (Wang *et al.*, 2000), and in diagnosis (Nakamura & Matsunaga, 1993). Functional magnetic particles have also been used in the determination of pesticides in water and soil (Lawruk *et al.*, 1993, Hottenstein *et al.*, 1996).

Other methods for producing an oil-adsorbing magnetic material have been developed and patented (Nicolaides, 1996). Magnetic powder such as ferrite powder (Sr-ferrite, or Ba-ferrite), or magnetite (Fe_3O_4), or powder of iron, with an average particle size range of 0.5 μm to 500 μm is impregnated into a mixture of polymers. Polymer such as polyurethane provides a high specific surface area ≥ 2 m^2/kg with high absorbent capacity. This magnetic material produced under the trade name Cleanmag^{TM}, is granular, porous and suitable for oil spill clean-up and oil recovery from the sea and the environment. The material was reported to absorb all kinds of oil, but not water. It has the ability to form aggregates after absorption of the oil thus preventing expansion of the oil-spill area due to their low mobility in water. After oil absorption the oil-laden material will remain afloat thus allowing the contaminants to be collected using permanent magnet conveyor belt systems. It is reported that this material could achieve 100% recovery of the spilled oil from water. The material can be applied or sprayed by aerial or naval means.

1.2.3 Coated (or Encapsulated) Magnetic Material

Plastics such as polyethylene (PE) are known to attract oil. Indeed, a well-known classroom experiment using PE beads to produce fresh water from contaminated oily water is shown in

Figure 1.5. Here, oily water is poured into a funnel containing PE beads. The oil contaminant is adsorbed onto the PE beads and fresh water is collected as filtrate.

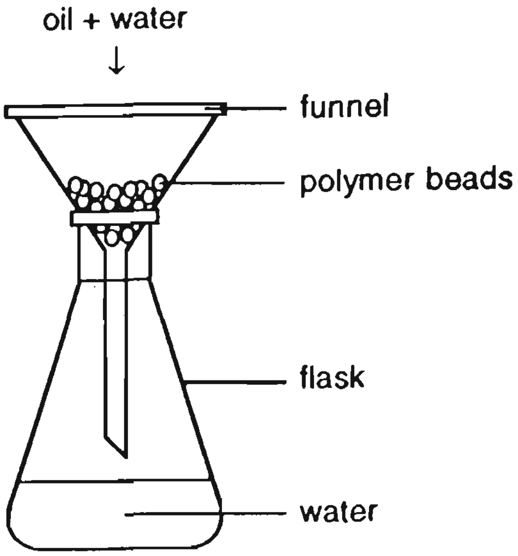


Figure 1.5 : Schematic diagram of an apparatus for separating water from oil.

It is a short step from this experiment to surmise that plastic particles with a magnetic core could provide an effective means of magnetically harvesting oil contamination, Figure 1.6. Such technology might find a particular application to circumstances such as contaminated foreshore. In this regard the development of iron particles coated with oil adsorbing polymer was pioneered in early 1992 at Victoria University. Preliminary tests using very crude materials such as polyethylene coated iron wire and gave encouraging pick-up values of 40% for engine oil.

For "proof of principle" investigations, two types of polymer-coated magnetic particles were manufactured; polyethylene-coated magnetic particles (PE-coated particles) and polyvinyl-coated magnetic particles (PVC-coated particles). The iron core was an isoshot pellet (described previously, Section 1.2.1) of an average size 1.0 mm. Experiments on pellets of smaller sizes ranging from 0.1-0.5 mm were also carried out.

The production and applications of these polymer-coated magnetic particles will be discussed in detail in Chapter 2.

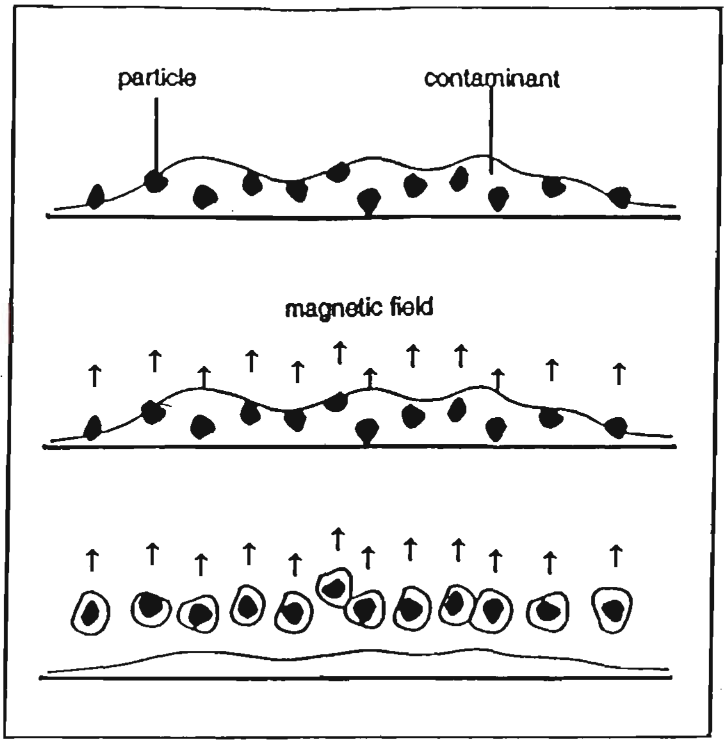


Figure 1.6 : Schematic diagram of oil-laden magnetic particles being magnetically harvested.

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Chapter 2 Application of Magnetic Particles to Oil and Chemical Remediation

2.1 The Application of Polymer-Coated Magnetic Particles to the Removal of Contamination

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- 2.2.1 Materials and Equipment
- 2.2.2 Production of the Polymer-Coated Magnetic Particles
  - 2.2.2.1 Fluidised Bed Apparatus
  - 2.2.2.2 Manufacturing Process
- 2.2.3 Characterisation of Particles
  - 2.2.3.1 Particle Size Distribution
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2.5 The Application of Elemental Iron to Oil Remediation

- 2.5.1 Investigating the Affinity of Iron Powder for Oil Contaminants
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2.6 Conclusions

2.7 References

2.1 The Application of Polymer-Coated Magnetic Particles to the Removal of Contamination

One of the aims of this research is to explore the manufacture of chemical adsorbing polymer-coated magnetic particles at low cost from readily available materials. A strategy for the manufacture of such material was advanced as follows. Commercially produced iron pellets[1] are cheap, highly magnetically susceptible and are characterised by different size distributions. These form the basis for a magnetic core which can, in principle, be coated (or encapsulated) with an appropriate polymer such as polyethylene (PE) or polyvinylchloride (PVC), which has an affinity for various contaminants, particularly oil.

Attention was turned to devising a method for coating these particles. In order to produce research quantities it was decided to try a coating method analogous to that used in industry to coat iron wire with PE (Wiredex Wire Products Pty. Limited, Clayton, Victoria, Australia), namely, the heated iron is immersed in a fluidized bed of polymer powder.

2.2 Experimental Details

2.2.1 Materials and Equipment

The following materials were used for preliminary investigations: polyethylene (PE) powder (Courtney Polymers, Dandenong, Australia) and polyvinylchloride (PVC) powder (Plascoat Systems Limited, Surrey, United Kingdom), grade 4612-05A of PE and grade PC-80-ES of PVC; a muffle furnace for heating the iron pellets; an air compressor; a "laboratory magnetic tester" (Figure 2.1) made by Alpha Magnetics, Victoria, Australia; a mechanical shaker for removing excess polymer powder or loose flakes of polymer from the surface of the magnetic particles; microscope for examination of the magnetic particles; hot air gun; iron powder, Hoganas, C100.29, Sweden; steel "isoshot" pellets (Barton Abrasive Ltd., West Midlands, United Kingdom), grades S330; commercial iron "isoshot" pellets (iron pellets) of different grades (Ervin Industries, Ann Arbor, MI). The mesh sizes and estimated average particle sizes of these pellets are listed in Table 2.1.

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[1] So-called "isoshot", used in shot-blasting.

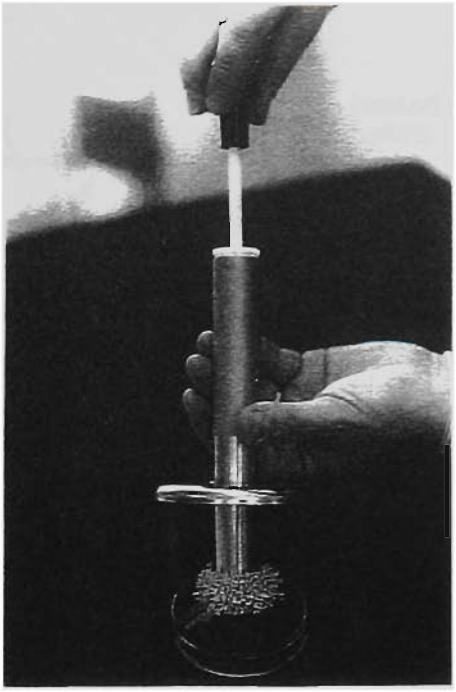

Figure 2.1 : Laboratory Magnetic Tester for harvesting oil-laden magnetic particles

Table 2.1 : The mesh size and particle size of iron pellets.

Particle grade	Mesh size (mm)	Estimated average particle size (mm)
S110	0.30-0.60	0.45
S230	0.60-1.00	0.80
S330	0.85-1.40	1.13
S460	1.18-2.00	1.59

2.2.2 Production of the Polymer-Coated Magnetic Particles

2.2.2.1 Fluidised Bed Apparatus

An apparatus for producing a fluidized bed of polymer powder is shown in Figure 2.2. The apparatus was constructed from a cylindrical metal bucket (25 cm diameter × 25 cm in height). An air-porous ceramic plate was fitted to the inside wall of the bucket about 5 cm from the bottom. Compressed air was admitted to the bucket through a 5-mm diameter air inlet situated near the bottom of the container.

About 2 kg of polymer powder was placed on top of the porous plate and the powder was fluidised by passage of compressed air through the air inlet.

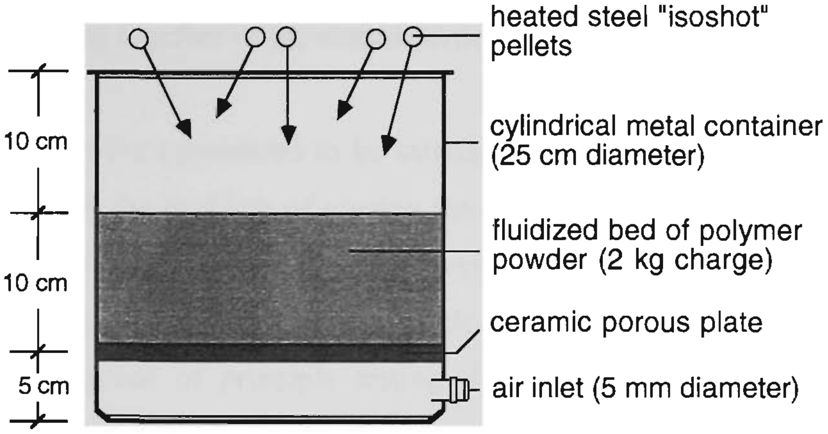

Figure 2.2 : Schematic diagram of fluidised bed apparatus

2.2.2.2 Manufacturing Process

To manufacture a stock of coated pellets, 5 g of the iron pellets (grade S330 - average particle size 1.0 mm) was placed in a porcelain crucible and heated in muffle furnace to ca. 650 °C. The heated iron pellets were then scattered into a fluidised bed of polymer (Figure 2.2) using magnetised tweezers. This was achieved by striking the loaded tweezers on the rim of the container. As the heated pellets were scattered onto the fluidised bed, the heat from these pellets caused the polymer to melt and coat onto their surface. It was important to carry out this operation promptly to minimise heat loss from the pellets prior to their contact with the polymer. The operation was repeated with 5 g batches until the desired quantity of coated particles was produced.

After turning off the air, the coated pellets (particles) were magnetically harvested from the polymer powder and placed in a conical flask. The particles were agitated for approximately 5 min using a mechanical shaker to remove loose flakes of polymer from their surface. Two types of polymer powder, polyethylene (PE), and polyvinylchloride (PVC) were used to coat the iron pellets in this way.

When the method was applied to iron pellets of a smaller size (grades S110 or S230), the coating process was found to be less successful. Two major factors contributed to this. Firstly, the smaller size particles cannot retain sufficient heat to affect melting of the polymer grains at their surface. Secondly, the particle size distributions of the PE and PVC "powders" (e.g for PVC, 90% is between 0.075 - 0.150 mm in diameter) ultimately produce coated particles that have a granular appearance. This not only reduced their ability to fuse to the hot surface, but in the case of PE presented a physical obstruction to complete coverage. All of these factors also contributed to the clumping together of the coated particles in some instances.

Since the S330 particles were considered to be satisfactorily coated for research purposes, it was decided not to pursue the problem of coating the smaller particles. This is, however, an ongoing goal of the research group at Victoria University. Thus for physical integrity of the polymer coating and adequate surface coverage, grade S330 pellets were used for subsequent experimental work and proof of principle testing. It must be emphasised that these are preliminary studies and the experiments would obviously be improved with more control over the particle size distributions.

2.2.3 Characterisation

2.2.3.1 Particle Size Distribution

The particle size distributions for both PE and PVC-coated particles were determined. Approximately 200 PE and PVC-coated particles of grade S330 were placed on a petri dish. A photocopy of a section of a ruler was taped onto the petri dish for measurement purposes. The particles were examined under a microscope (100× magnification), and photograph taken. Between 100 and 150 particles from each of photographs were selected and their diameters measured. Figure 2.3 shows that the sizes of both PE and PVC-coated particles are normally distributed. The average diameter for PE and PVC-coated particles was found to be 1.20 mm and 1.35 mm respectively.

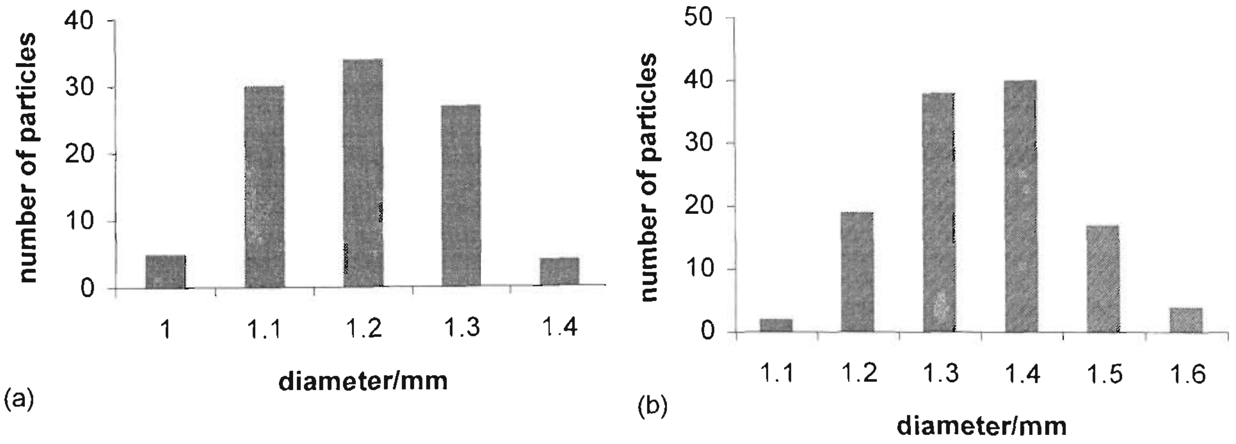

Figure 2.3 : A size distribution for: (a) PE-coated particles and (b) PVC-coated particles.

2.2.3.2 Scanning Electron Micrograph Examination of Particles

Observation under an electron microscope shows that a PE-coated particle has a granular surface texture and a PVC-coated particle exhibits a smoother, globular texture, Figure 2.4.

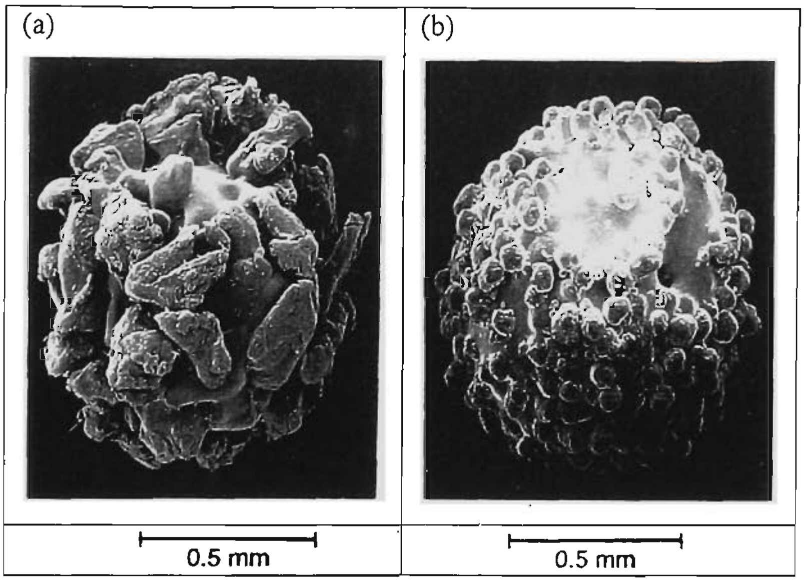

Figure 2.4 : Scanning electron micrographs of: (a) PE-coated particles and (b) PVC-coated particles.

2.2.4 Particle Encapsulation

Microscopic examination of the PVC-coated particles revealed that they had sufficient polymer coating with adequate surface coverage, Figure 2.4(b). This is related to the lower melting point of PVC (sintered at 185 °C).However, examination of the PE-coated particles revealed that loose flakes were protruding from the surface (sintered at 149 °C). An attempt was made to improve the surface integrity of the granular PE-coated particles in a number of ways. An apparatus based on a "crystal spherising chamber" (Bond, 1951) was initially trialled, Figure 2.5, but the method achieved limited success. Several other techniques were also trialled with limited success. These included solvent treatment and exposure to a stream of hot-air. These techniques were not pursued further for the purposes of this thesis. For "proof of principle" investigations the PVC-coated particles and the more granular PE-coated particles shown in Figure 2.4 were produced in research quantities.

In order to modify surface texture for further "proof of principle" experiments, a baking technique was used. This method is analogous to the standard industrial process where a heated iron substrate such as a frame from a coat hanger is dipped into a fluidised bed containing polymer powder. The heat from the iron substrate causes the polymer powder to melt onto their surface. The coated substrate is then baked at a controlled temperature and the surface becomes smooth.

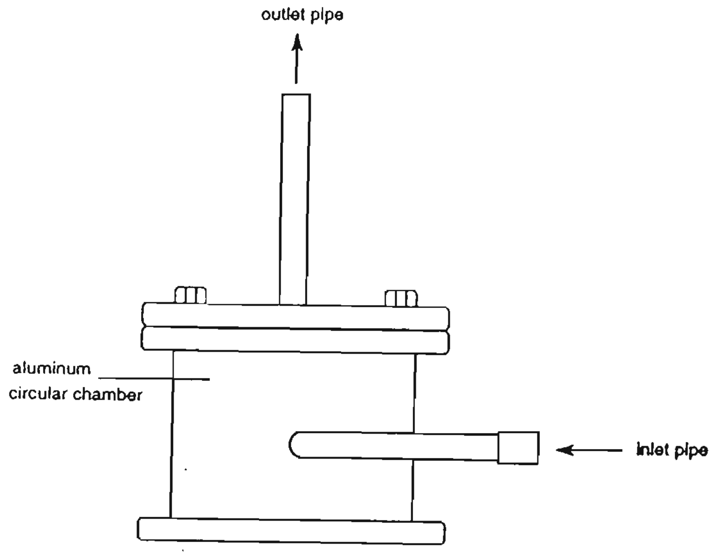

Figure 2.5 : Apparatus based on a crystal spherising chamber.

Two methods were employed in the baking process. The first method involved heating 1g of PE-coated particles on a wire gauge in a muffle furnace at 150 °C for 5 min. The second method involved the heating and agitation of a glass petri dish containing 1 g of PE-coated particles in a muffle furnace at 150 °C.

The baking method appears to have more success. The upper surface is encapsulated quite successfully. However, the bottom surface appears flat and slightly charred. Further improvement of the baking method has been undertaken to reduce the charred flat surface of the particles. This was done by strict control of experimental conditions, especially temperature. A petri dish containing some PE-coated particles was placed in a muffle furnace and gently shaken at 150 °C for 10 min. This improves the surface integrity of the particles, Figure 2.6. For a given weight of baked PE-coated particles, they have less surface area compared to the PE-coated particles. The method was considered satisfactory for the production of research quantities of "smoothed" particles.

Generally, the baking method appears to produce particles with improved surface integrity. However, the production of baked particles is very time-consuming and as it produces particles having a smaller surface area, this means that more particles would be required for affinity studies. Thus PE-coated particles were used for all subsequent experimental work.

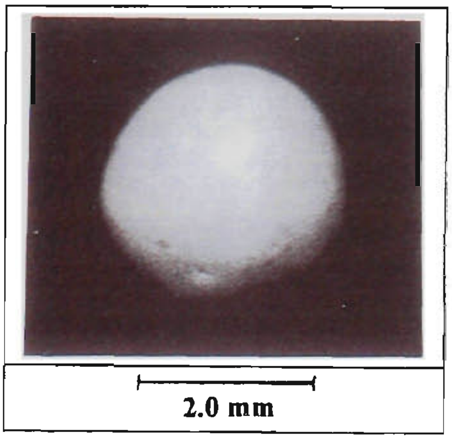

Figure 2.6 : Baked PE-coated particles.

2.3 Methodology for Removing Chemicals and Oil

Note:

Unless otherwise stated: (i) all raw data are presented on the CD ROM attached, (ii) all chemical and oil pick-up experiments were conducted at 25 °C.

A fixed quantity of a chemical (e.g. 1.0 g) was placed into a pre-weighed (w_1) petri dish, which was then re-weighed (w_2). PE-coated particles were applied to the chemical and the petri dish was re-weighed (w_3). The particle-to-chemical ratio is defined as the mass of particles over the mass of chemical of interest. In the case of the adsorption of oil, R is the particle-to-oil ratio and this may be calculated using equation (2.1).

$$R = (w_3 - w_2) / (w_2 - w_1) \tag{2.1}$$

The particle/chemical mixture was left in the petri dish for approximately 5 min. The chemical-laden particles were harvested magnetically, Figure 2.1. The petri dish was re-weighed (w_4) and the percentage of chemical harvested by the particles, P was determined according to equation (2.2):

$$P = [(w_2 - w_4) / (w_2 - w_1)] \times 100 \tag{2.2}$$

The procedure was repeated in batches for increasing values of R until a maximum value of P was achieved, P_c, for a maximum value of R_c. The above procedure was carried out with 5 replicates in all subsequent experiments. A sample calculation using equation (2.2) is presented in Appendix 2.1. The equations for the error analysis are presented in Appendix 2.2.

Based on the raw data of various chemicals documented in Appendix 2.3 values of P versus R were plotted. The plots typically increase and reach a plateau at critical value of P and R_c. In their profiles, the plots range between two extremes represented by Figure 2.7(a) (near "ideal" behaviour) and Figure 2.7(b) ("non-ideal" behaviour). From this point such profiles will be referred as an adsorption isotherm.

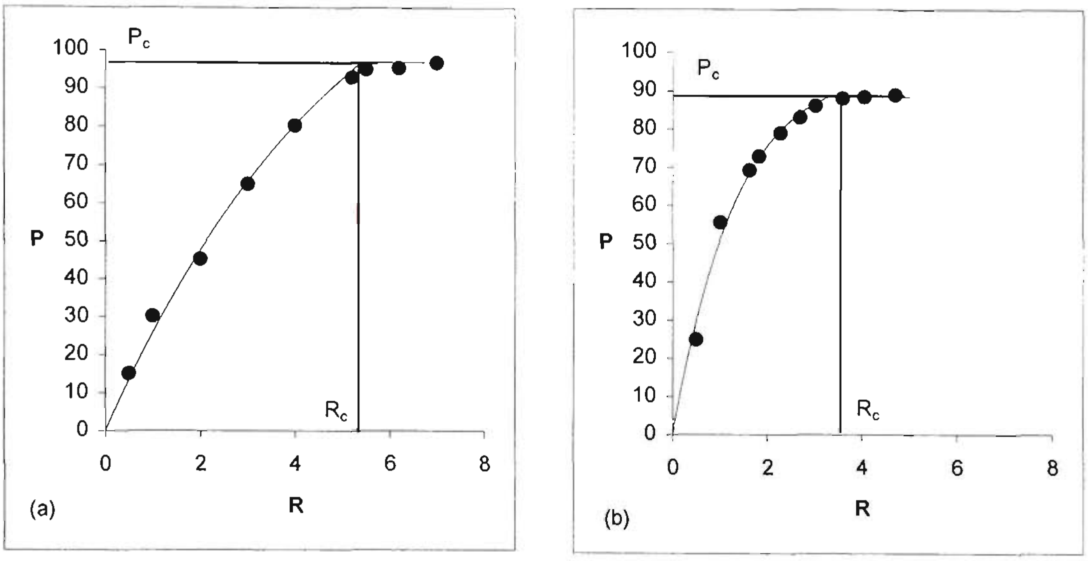

Figure 2.7 : Computer-generated fit (solid line) for the two extremes of data represented by: (a) triethylamine value of $\alpha_o = 1.33$ and (b) iodobenzene value of $\alpha_o = 3.28$; filled circles are the experimental data, Section 2.3.3. The α_o values are discussed in Section 2.3.1.1.

In the "ideal" system each particle picks up a certain quantity of chemical, and so upon the addition of successive particles, a linear increase in the total amount of chemical that is picked up is expected. Under these conditions the value of P would be expected to vary linearly with R up to the critical value P_c, which corresponds to R_c, Figure 2.7(a). The value of R greater than R_c is the saturated region where no more chemical can be adsorbed by the particles.

For "non-ideal" systems, each particle picks up an amount of chemical that is disproportionately larger than that expected in the idealised case. The amount that is picked up also depends on the number of particles that are added to the system. Under these conditions the value of P varies non-linearly with R up to the critical value P_c. Hence a convex curvature of the isotherm compared with the idealised case is observed, Figure 2.7(b). Again, values of R $> R_c$ define the saturated region.

In the preliminary studies, where a range of different particles and substrates were used, it was observed that the vast majority of isotherms deviate from the ideal case. In order to better understand the physical basis for this phenomenon a mathematical model was developed to fit the full range of experimental data obtained.

2.3.1 Mathematical Modelling of the Adsorption Isotherm

2.3.1.1 Derivation of an Iterative Numerical Procedure

The adsorption of a chemical on magnetic particles can be mathematically modelled by considering the amount of chemical each particle can adsorb in the presence of other particles. The particle-to-chemical ratio, R, is given by equation (2.3):

$$R = nm_1/m_2 \tag{2.3}$$

where n is the number of particles, m_1 is the average mass of one particle, and m_2 is the mass of chemical used in the experiment. At the critical particle-to-chemical ratio, R_c, equation (2.4) applies:

$$R_c = n_c m_1/m_2 \tag{2.4}$$

where n_c is the critical number of particles which are responsible for the critical (maximum) percentage adsorption, P_c. The average mass of chemical, m_s, which can be adsorbed by a single particle can be calculated as follows:

$$m_s = P_c m_2/(100n_c) \tag{2.5}$$

Substituting equation (2.4) in equation (2.5)

$$m_s = P_c m_1/(100R_c) \tag{2.6}$$

Upon the step-wise addition of up to n_c particles in an ideal or "well-behaved" system, each particle will adsorb an amount of chemical equal to m_s and the percentage adsorption, P(n), after the addition of n particles is given by equation (2.7) for n in the range $0 \leq n \leq n_c$:

$$P(n) = (nM_s/m_2) \times 100 \tag{2.7}$$

Under these conditions the value of P(n) varies linearly with n up to the critical value P_c which corresponds to n_c. Using equations (2.3), (2.6) and (2.7), the simple function P(R) can be confirmed for values of R in the range $0 \leq R \leq R_c$:

$$P(R) = RP_c/R_c \tag{2.8}$$

where P_c is the maximum critical value of P at a corresponding critical value R_c.

In many real systems, the viscous nature of the liquid to be adsorbed and the complex surface interactions between the liquid and the particles means that disproportionately larger amounts of the liquid adhere to the particles at lower values of R compared with values of R close to R_c.

The capacity of the particles to adsorb an excess loading of chemical in the early stages of the adsorption isotherm can be modelled by introducing a parameter $\alpha(n)$ which is the fractional excess of chemical a particle can adsorb in the presence of n particles. The value of $\alpha(n)$ may be generated by an empirical function and depends on the number of particles present at any point in the adsorption process.

In non-ideal cases, the percentage adsorption, P(n), is given by equation (2.9):

$$P(n) = (M_n/m_2) \times 100 \tag{2.9}$$

where M_n is the mass of oil adsorbed by n particles in a non-ideal system. The value of M_n may be related to $\alpha(n)$ as shown in equation (2.10) and may be calculated by an iterative process for values of n in the range $1 \leq n \leq n_c$:

$$M_n = M_{(n-1)} + M_s(n)\alpha(n) \tag{2.10}$$

where M_0 is zero, M_{n-1} is the mass of chemical adsorbed by n-1 particles, and $m_s(n)$ is the average mass of oil adsorbed by the n^{th} particle in the presence of n-1 particles which is iteratively adjusted to account for disproportionate adsorption. In particular:

$$M_s(n) = \left(\frac{P_c M_2}{100} - M_{(n-1)} \right) / (n_c - n) \text{ where } M_0 = 0 \tag{2.11}$$

A satisfactory fit of the experimental data can be obtained by assuming that the empirical function, $\alpha(n)$ varies linearly with n, and that the boundary conditions of (α, n) are $(\alpha_o, 1)$ and $(1, n_c)$. Under these conditions equation (2.12) can be readily derived:

$$\alpha(n) = \alpha_o + \frac{(\alpha_o - 1)(n - 1)}{(1 - n_c)} \tag{2.12}$$

Equations (2.9) to (2.12) together with equation (2.3) were used in an iterative computer program which generated the theoretical curves P(R) for given values of the adjustable parameter, α_o, Figure 2.8.

The plot in Figure 2.8 shows that for an ideal system where $\alpha_o = 1$, a linear relationship between P and R is established. However, for a non-ideal system where $\alpha_o > 1$, there is an increase in the curvature of the isotherm.

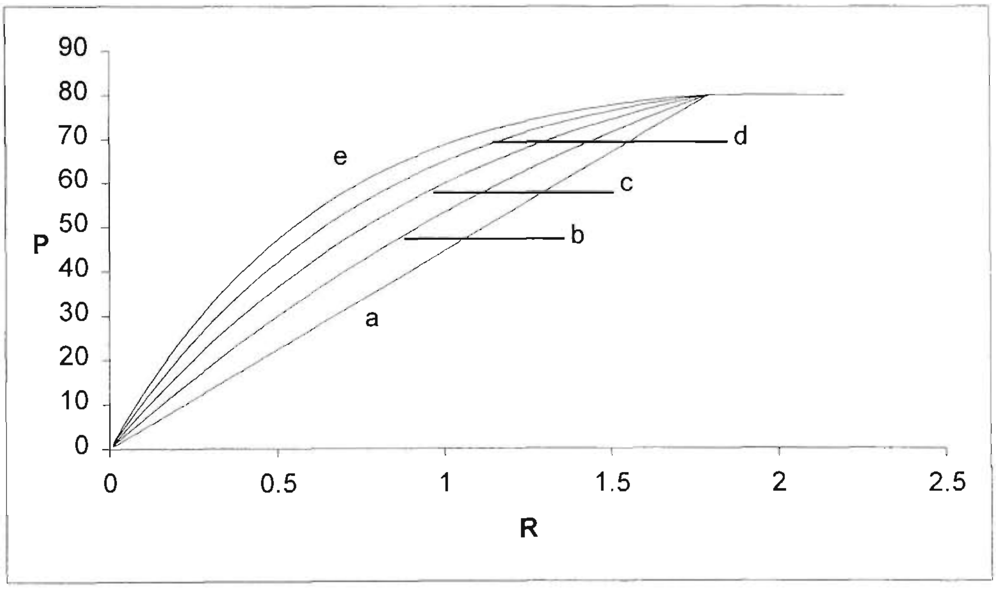

Figure 2.8 : Percentage pick-up of chemical in ideal and non-ideal systems. The theoretical isotherms were generated using the model defined by equations (2.3) to (2.12). The letters a, b, c, d and e denote $\alpha_o = 1, 2, 3, 4$ and 5 respectively.

2.3.1.2 Fitting Algorithm

The program (listed in Appendix 2.4) and its algorithm was used to find an optimum value of α_o necessary to fit each given set of experimental data by minimising the sum of the squares of the residuals, $s(\alpha_o)$, the latter was calculated in accordance with equation (2.13):

$$s(\alpha_o) = \sum_{i=1}^{n}[P(R_i,\alpha_o) - P(R_i)]^2 \qquad (2.13)$$

where $P(R_i, \alpha_o)$ is the theoretical value of $P(R_i)$ calculated for α_o and $P(R_i)$ is the experimental value of the percentage adsorption determined at the particle-to-chemical ratio, R_i.

This fitting procedure enables the optimum fit of the adsorption isotherm to be achieved by means of a single adjustable parameter, α_o, where $\alpha_o \geq 1$. For $\alpha_o = 1$, idealized adsorption occurs. Values of α_o successively greater than unity indicate greater departure from idealized adsorption behaviour.

2.3.2 Efficiency of Chemical Pick-up

2.3.2.1 Derivation of Efficiency Parameters

Two methods of determining the efficiency of pick-up of a chemical contaminant have been considered. The first method involves using an efficiency parameter E_1 which may be defined by equation (2.14):

$$E_1 = P_c/R_c \qquad (2.14)$$

where P_c is the critical value of P for a given isotherm, and R_c is the value of R that corresponds to P_c, Figure 2.7.

Clearly, this estimation of efficiency is an "average" value for the initial part of the isotherm where $0 \leq R \leq R_c$. It does not take into account the efficiency of the initial pick-up for values of R less than R_c. Indeed, E_1 will not be sensitive to systems such as that shown in Figure 2.7(b), in which there is a significant deviation from linearity in the region $0 \leq R \leq R_c$.

The second method of measuring the efficiency of chemical pick-up involves calculating the initial gradient of the adsorption curve. The initial gradient thus represents the theoretical amount of chemical picked up by one infinitesimally small particle. Consider equations (2.10), (2.11) and (2.12):

Differentiating equation (2.10), we obtain:

$$\frac{dM_n}{dn} = M_s\frac{d\alpha}{dn} + \alpha\frac{dM_s}{dn} \quad \text{, for } n = 1,\ M_o = 0, \tag{2.15}$$

Substituting equations (2.11) and (2.12) into equation (2.15), we obtain:

$$\frac{dM_n}{dn} = \frac{M_s\alpha_o}{(1-n_c)} + \alpha\frac{d}{dn}\left[\left(\frac{P_cM_c}{100} - M_{(n-1)}\right)/(n_c - n)\right]$$

$$\frac{dM_n}{dn} = \frac{M_s\alpha_o}{(1-n_c)} + \frac{\alpha P_cM_2}{100} \times \frac{d}{dn}\left(\frac{1}{(n_c - n)}\right) - \frac{\alpha d}{dn}\left(\frac{M_{(n-1)}}{(n_c - n)}\right)$$

$$= \frac{M_s\alpha_o}{(1-n_c)} - \frac{\alpha P_cM_2}{100}\ln(n_c - n) + \alpha\, M_{(n-1)}\ln(n_c - n)$$

For $n = 1$, $M_o = 0$, $M_s = \dfrac{P_cM_2}{100(n_c-1)}$ and $\alpha = \alpha_o$

$$\left(\frac{dM_n}{dn}\right)_{n=1} = \frac{P_cM_2\alpha_o}{100(n_c-1)} + \frac{\alpha_oP_cM_2}{100}\ln(n_c - 1)$$

$$= \frac{\alpha_oP_cM_2}{100}\left[\frac{1}{(n_c-1)} + \ln(n_c-1)\right]$$

$$\cong \frac{\alpha_oP_cM_2}{100}\left[\frac{1}{n_c} + \ln(n_c)\right] \text{ as } n_c >> 1$$

$$\cong \frac{\alpha_oP_cM_2}{100}\ln(n_c) \text{ as } \ln(n_c) >> \frac{1}{n_c} \text{ if } n_c >> 1$$

Thus

$$\left(\frac{dM_n}{dn}\right)_{n=1} \cong \frac{\alpha_oP_cM_2}{100}\ln(n_c) \tag{2.16}$$

We see that

$\left(\dfrac{dM_n}{dn}\right)_{n=1}$ is proportional to α_o.

Thus the initial gradient of the adsorption isotherm is proportional to α_0 and so α_0 can be used directly as a measure of adsorption efficiency.

2.3.2.2 System Characterisation

The current research is aimed at classifying different chemical/particle systems with regard to the efficiency of adsorption, and ideal or non-ideal behaviour.

Figure 2.9 demonstrates four regions which characterise the relationship between the efficiency and α_0. They are classified as follows: (i) high efficiency and ideal system, (ii) high efficiency and non-ideal system, (iii) low efficiency and ideal system, and (iv) low efficiency and non-ideal system.

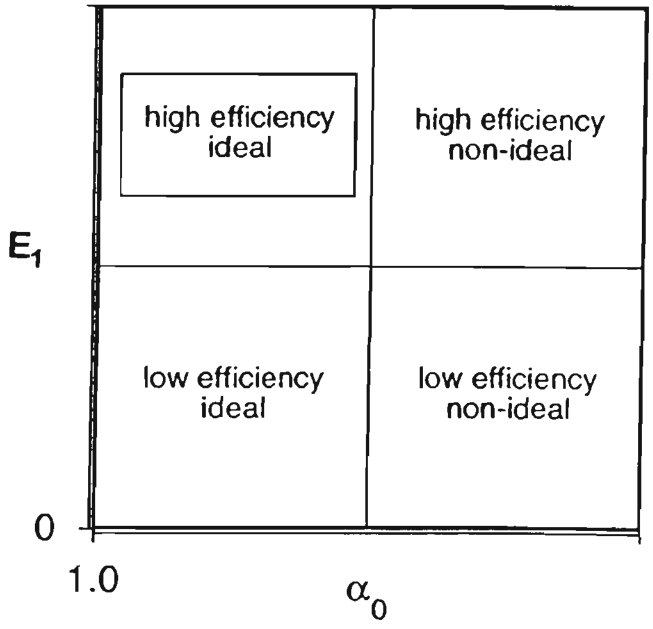

Figure 2.9 : Four regions which characterise the relationship between the efficiency and α_0.

2.3.3 Fitting Experimental Data with Model

For computer fitting purposes the average mass for a single PE-coated particle was determined. Two hundred PE-coated particles were weighed and the average mass for a single particle was found to be 0.0820 g.

The P and R data including the P_c and R_c values obtained for the affinity of a compound using PE-coated particles was entered into the computer fitting program. The program determines the value of α_0 associated with the optimum fit to the experimental data.

The computer fitting procedure was tested on a variety of compounds. Values of α_o and E_l for these and other compounds are tabulated in Table 2.2. Literature values of viscosity and surface tension at 20 °C (Dean, 1992; Weast, 1999) are also given in Table 2.2 for comparison.

Table 2.2 : The tabulation of the parameters α_o, E_l, viscosity, η and surface tension, γ, for the pick-up of various contaminants using PE-coated particles. Individual profiles are documented in Appendix 2.3.

Chemicals	$\bar{P}$	R_c	E_l	α_o	η /cp	γ /dyne cm^{-1}
triethylamine	97.0	5.4	18.6	1.36	0.38	22.7
bromobenzene	94.0	3.5	26.9	2.30	1.20	36.5
cyclohexane	95.0	3.5	27.1	1.95	0.98	27.6
ethylbenzene	93.0	3.7	25.1	2.15	0.67	31.5
iodobenzene	88.5	3.3	26.8	3.28	1.74	41.5
m-dichlorobenzene	95.0	3.6	26.4	2.57	1.05	35.4
m-xylene	91.5	3.9	23.5	1.71	0.62	31.2
2-pentanone	95.5	4.7	20.3	1.45	0.47	25.7

Figure 2.7 shows plots generated by the computer-fitting program for triethylamine and iodobenzene. The triethylamine graph displays a near-ideal behaviour for which $\alpha_o \cong 1$. The iodobenzene graph displays a non-ideal behaviour for which $\alpha_o > 1$. For triethylamine, in the initial stages, each particle picks up the same amount of chemical, resulting in an almost linear increase of the isotherm. For iodobenzene, in the initial stages, excess compound is picked up by particles, resulting in a curvature of the isotherm. In the later stages, the graph appears to plateau. This is due to the saturation of compounds by the particles. Other compounds also show a non- ideal behaviour, Table 2.2.

2.3.4 Estimation of the Range of Efficiency Parameters

In order to estimate P_c, R_c(min) and α_o(max) the following procedure is carried out. From our experience with all the chemical/polymer systems we have examined, the lowest R_c determined is 3.2. Given that the maximum theoretical value of P_c is 100%, an estimate of the maximum value of E_l is approximately 30. Thus a distinction can be made between "high efficient ideal" and "low efficient ideal" at $E_l \cong 15$.

In the wide range of systems we have studied, the maximum observed value of α_0 is ca. 3. Thus it is reasonable to propose that the α_0 value for the chemical/polymer systems is $1 \leq \alpha_0 \leq 3$. This enables a distinction to be made between "high efficient ideal" and "high efficient non-ideal" at $\alpha_0 \cong 2$. The data are mainly situated in both the "high efficiency ideal" and "high efficiency non-ideal" regions, Figure 2.9.

2.3.5 Comparison of Efficiency Parameters, Viscosity and Surface Tension

A comparison between α_0 and the efficiency parameter E_l and using PE-coated particles is shown in Figure 2.10 for eight different compounds that were tested. At low α_0 values, oil pick-up is proportional to the number of particles and so adsorption behaviour is linear. Thus in cases where adsorption is linear it has been shown, Figure 2.7(a), that E_l is an adequate indicator of efficiency. Thus for low α_0 values there should be a good correlation between α_0 and E_l as shown by the linear plot in Figure 2.10. As α_0 increases, the E_l parameter is expected to be a less reliable indicator of efficiency and a departure from linearity between α_0 and E_l occurs, Figure 2.10. In this sense, Figure 2.10 is consistent with previous findings that the reliability of E_l as an indicator of efficiency decreases as the system becomes less ideal.

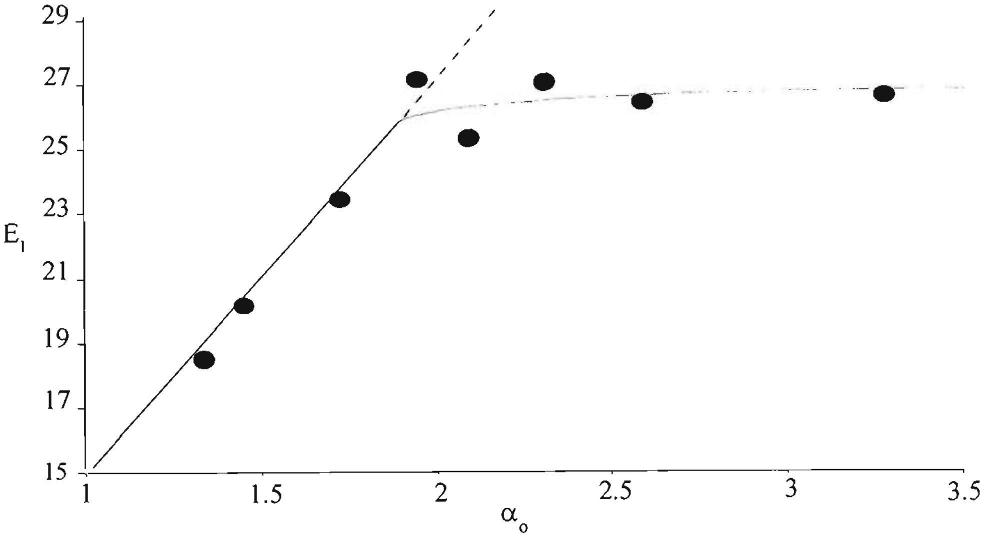

Figure 2.10 : A plot of efficiency parameter E_l versus α_0 for PE-coated particles.

Figure 2.11 shows that a plot of α_0 versus viscosity is reasonably linear with the intercept close to unity. This is consistent with the notion that the system approaches ideal behaviour as the viscosity approaches the theoretical case of having a value of zero.

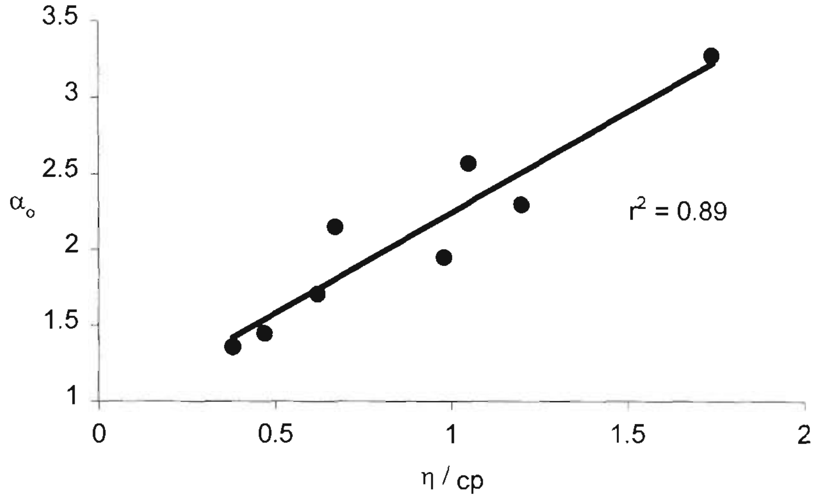

Figure 2.11 : A plot of α_o versus viscosity,η, for PE-coated particles.

A comparison between the surface tension, γ, of the compounds tested and α_o was also carried out. The plot in Figure 2.12 shows a correlation between α_o and surface tension γ. An extrapolation of the regression line to the point where α_o = 1 (ideal behaviour) yields a corresponding value of the surface tension of 17.3 dyne cm^{-1}. The surface tensions of most organic compounds found in the literature have values greater than 20 dyne cm^{-1} (Weast, 1999). It is therefore expected that experiments for the pick-up of organic compounds will show varying degrees of non-ideal behaviour. Compounds with surface tension of less than 20 dyne cm^{-1} are expected to behave ideally. However, these are very volatile materials and thus no experimental work could be carried out to determine their α_o values.

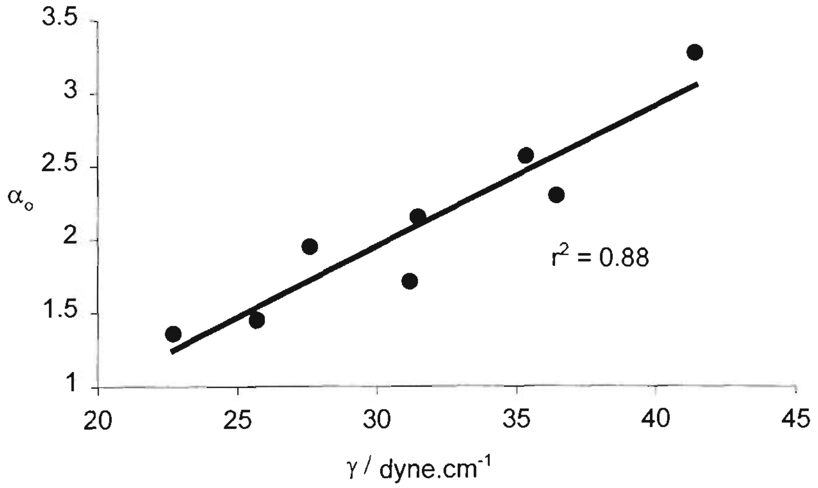

Figure 2.12 : A plot of α_o versus surface tension, γ.

Based on the literature values of viscosity and surface tension at 20°C, the relationship between viscosity and surface tension of eight different compounds was investigated. The plot in Figure 2.13 shows a correlation between viscosity and surface tension. Thus it appears both viscosity and surface tension contribute to the curvature of the isotherm resulting in an increase in α_o above unity. It is apparent that the value of α_o is dependent on the: (i) viscosity of the oil, (ii) surface tension, (iii) extent of interaction between oil and substrate, and (iv) particle size and/or surface area.

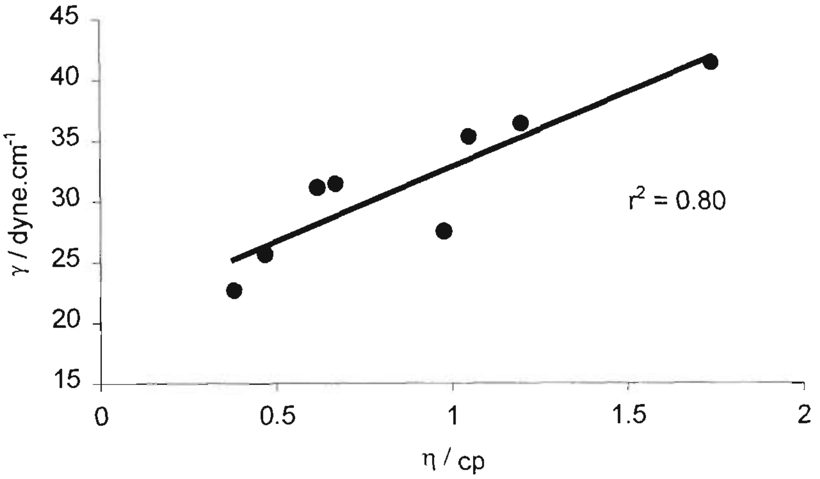

Figure 2.13 : A plot of surface tension, γ versus viscosity, η.

2.3.6 Properties that Affect the Pick-Up of Contaminant

The effects of contact time, coating type, surface texture, nature of substrate and contaminant hydrophobicity on pick-up were investigated.

2.3.6.1 Contact Time

To conduct these investigations, both PE and PVC-coated particles (grade 330S) were employed, with Oil A (Mobil Super XHP 20W-50, 1993 formulation) used throughout. The affinity of both PE and PVC-coated particles for Oil A over times ranging from 1 min to 1000 min was investigated by tracking the value of P at a value of $R > R_c$ for both PE and PVC (Godinho *et al.*, 1993). Even though, for the Oil A tested, the contact time required for optimal pick-up appeared to be almost instantaneous, this might not be the case for other types of contaminants. Therefore, a contact time of 5 min was deemed to be more than sufficient to allow maximum absorption for all the contaminants investigated.

2.3.6.2 Coating Type

The affinity of both PE and PVC-coated particles for Oil A is shown in Figure 2.14. The data listed in Table 2.3 show that the PE-coated particles are more efficient than PVC-coated particles in the pick-up of Oil A as indicated by their higher E_l and α_o values. An explanation of the relatively superior pick-up for the PE-coated particles over the PVC-coated particles requires consideration of the attractive forces involved. However, studies were not undertaken to investigate the nature of the interaction between the compounds and the particles.

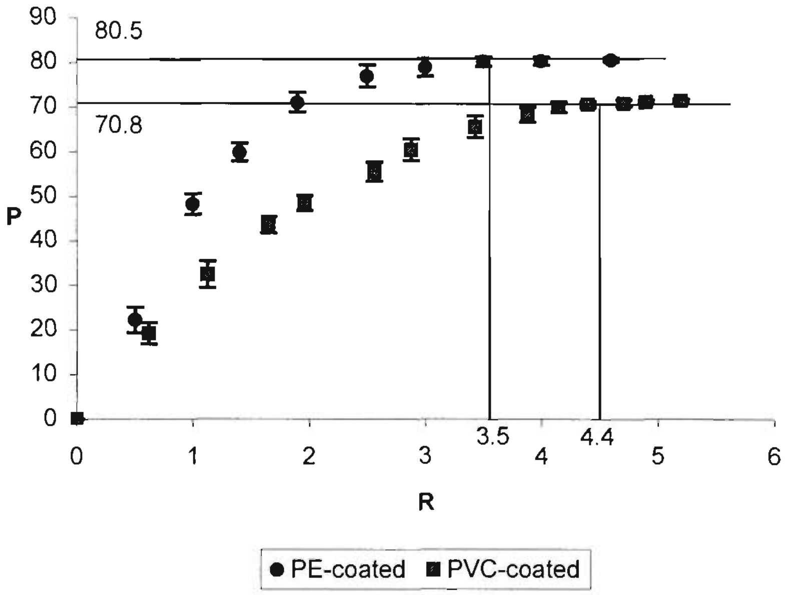

Figure 2.14 : The affinity of polymer-coated particles for Oil A. Error bar represents 95% confidence intervals for 5 replicates. The raw data are documented in Appendix 2.5.

Table 2.3 : The P_c, R_c, E_l and α_o parameters for Oil A.

Particles	**P_c**	**R_c**	**E_l**	α_o
PE-coated	80.5	3.5	23.0	3.06
PVC-coated	70.8	4.4	16.1	2.51
Baked PE-coated	79.5	5.7	14.1	2.75

2.3.6.3 Texture / Surface Modification

As mentioned previously in Section 2.2.4, surface modification by the baking method has altered both surface integrity and texture, achieving complete encapsulation. A comparative pick-up of Oil A using two types of particles: non-baked PE-coated particles and baked PE-coated particles is shown in Figure 2.15.

The parameter P for Oil A using baked PE-coated particles shows that the initial pick-up of oil is much lower than the granular PE-coated particles and that the baked particles have a greater critical value for R_c. This may be due to the fact that baked PE-coated particles have less surface area for a given mass. Thus, it requires more baked particles to achieve the same maximum saturation that can be achieved using the non-baked particles. The maximum P values for both the granular and baked particles are similar with the latter achieving a lower efficiency as indicated by their lower E_l and α_o values, Table 2.3.

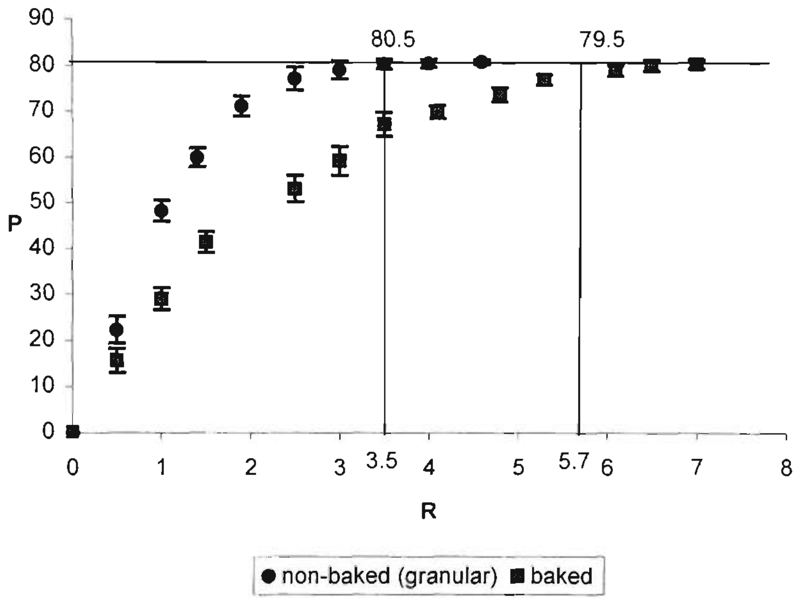

Figure 2.15 : Comparison of the percentage oil pick-up using non-baked (granular) PE-coated and baked PE-coated particles. Error bar represents 95% confidence intervals for 5 replicates. The raw data for the baked PE-coated particles are presented in Appendix 2.6.

2.3.6.4 Nature of Substrate

The pick-up of a contaminant (e.g. Oil A) is essentially a function of competition between two surfaces: (i) affinity of oil towards the particles and (ii) affinity of oil towards the surface of glass (from petri dish). Thus the nature of a substrate may influence the pick-up of oil. The following investigations were then carried out to study the affinity of oil on plastic petri dishes.

The affinity of PE and PVC-coated particles for Oil A contained in plastic petri dishes was determined using the same procedures described previously. The data for the affinity of particles for Oil A contained in plastic petri dishes are listed in Table 2.4. There appears to be little difference in the maximum pick-up using either a glass or plastic petri dish. However, the removal of oil using glass petri dishes is more efficient as reflected by their higher E_l and α_o

values. An explanation of the relative superior pick-up using a glass surface over a plastic substrate requires consideration of the attractive forces involved. However, this is beyond the scope this investigation.

Table 2.4 : The P_c, R_c, E_l and α_o parameters for the pick-up of Oil A from different types of petri dishes using PE-coated and PVC-coated particles. The experiments were carried out in 5 replicates. The raw data obtained using plastic petri dishes are given in Appendix 2.7.

Type of petri dish	PE-coated particles				PVC-coated particles			
	P_c	R_c	E_l	α_o	P_c	R_c	E_l	α_o
Plastic	79.4	5.5	14.6	2.36	70.2	6.1	11.5	1.43
Glass	80.5	3.5	23.0	3.06	70.8	4.4	16.1	2.51

2.3.6.5 Affinity for Organochlorines and the Effects of Contaminant Hydrophobicity

It is of interest to investigate the affinity of the coated particles for organochlorines since such compounds are known environmental contaminants. This also provides an opportunity to investigate the effect of increasing hydrophobicity of contaminants on pick-up, since hydrophobicity is expected to increase with an increasing number of chlorine atoms in the molecules. Chlorinated benzenes have been selected for affinity studies since these are chemically representative of the environmentally hazardous polychlorinated biphenyls (PBCs) and certain pesticides (Lawruk *et al.*, 1996; Oubina *et al.*, 1998).

Benzene, monochlorobenzene, 1,2-dichlorobenzene, and 1,2,4-trichlorobenzene were selected for study. The substituted isomers were chosen since these are all liquids at room temperature. The plots of P versus R for PE and PVC-coated particles for the pick-up of benzene and chlorinated benzenes are presented in Figures 2.16 and 2.17 respectively. The results show that: (i) the difference in the initial pick-up of these chemicals as reflected by their α_o values is immeasurably small, presumably due to the low viscosities that are involved, and (ii) as the number of chlorine atoms increases, the P value decreases, resulting in lower E_l values, Table 2.5.

Further investigations were carried out to study the relationship between the maximum pick-up of chlorinated benzenes using PE and PVC-coated particles and the size of the chlorinated benzenes. To this end, the affinity of each chlorinated benzene was accurately determined from

Figures 2.16 and 2.17 at a value of R > R_c. A maximum value of: (i) R = 4 for PE-coated particles and (ii) R = 5 for PVC-coated particles was used for the affinity study. The procedures for this investigation were carried out with 10 replicates in each case. The maximum percentage pick-up, P(max), is plotted against the number of chlorine atoms, Figures 2.18 and 2.19.

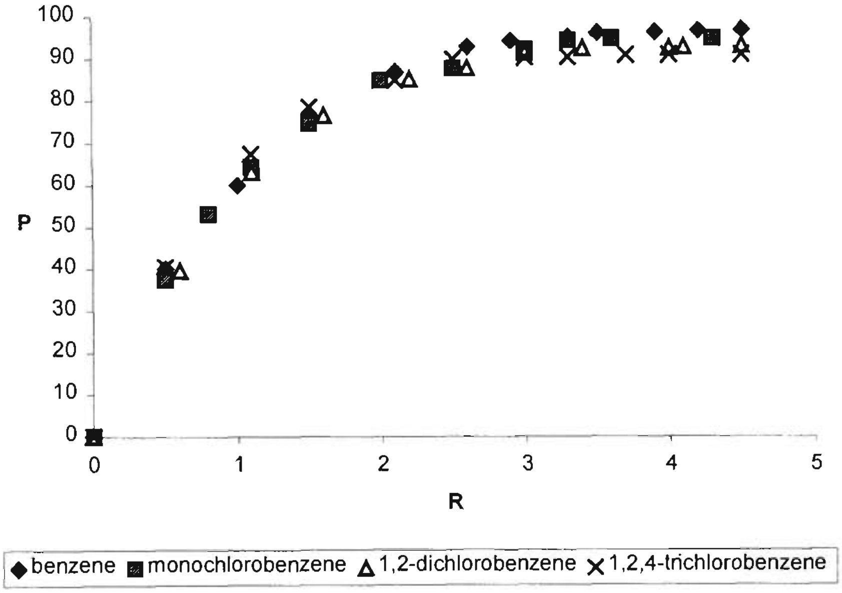

Figure 2.16 : The affinity of PE-coated particles for chlorinated benzenes. Individual profiles are documented in Appendix 2.8.

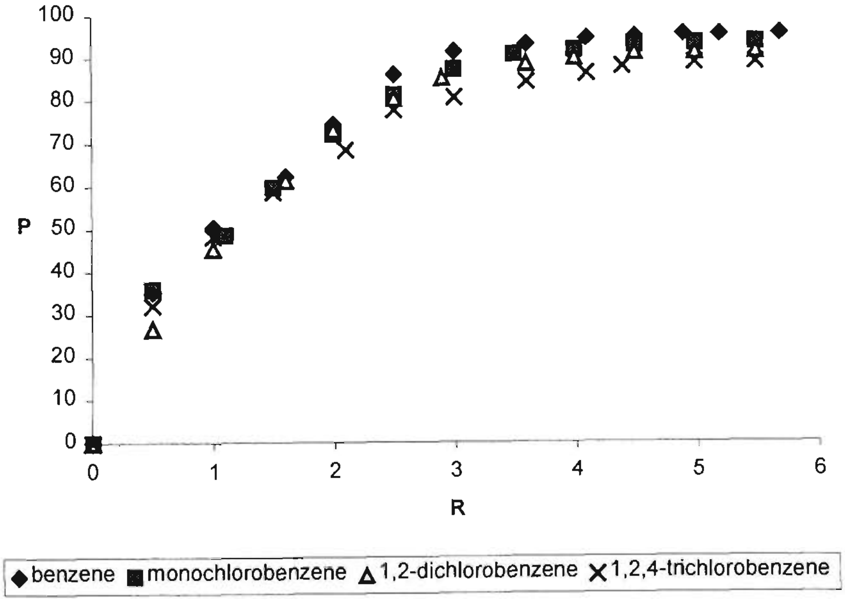

Figure 2.17 : The affinity of PVC-coated particles for chlorinated benzenes. Individual profiles are documented in Appendix 2.9.

Table 2.5 : Parameters of P_c, E_l and α_o values for chlorinated benzenes.

Chemicals	PE-coated particles			PVC-coated particles		
	P_c	E_l	α_o	P_c	E_l	α_o
benzene	97.0	25.7	2.72	95.5	19.9	2.40
monochlorobenzene	94.7	24.9	2.80	93.8	19.5	2.52
1,2-dichlorobenzene	93.0	24.5	2.73	91.3	19.0	2.46
1,2,4-trichlorobenzene	90.7	24.0	2.91	88.5	18.4	2.51

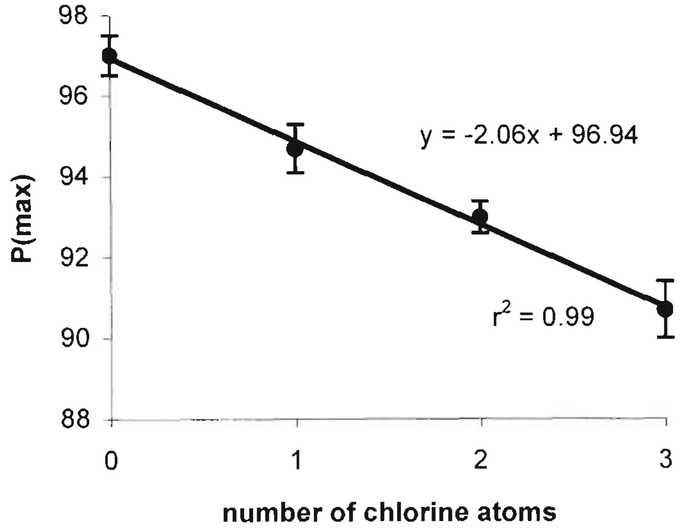

Figure 2.18 : Affinity of PE-coated particles for chlorinated benzenes. Error bars represent 95% confidence intervals for 10 replicates. The data are presented in Appendix 2.10.

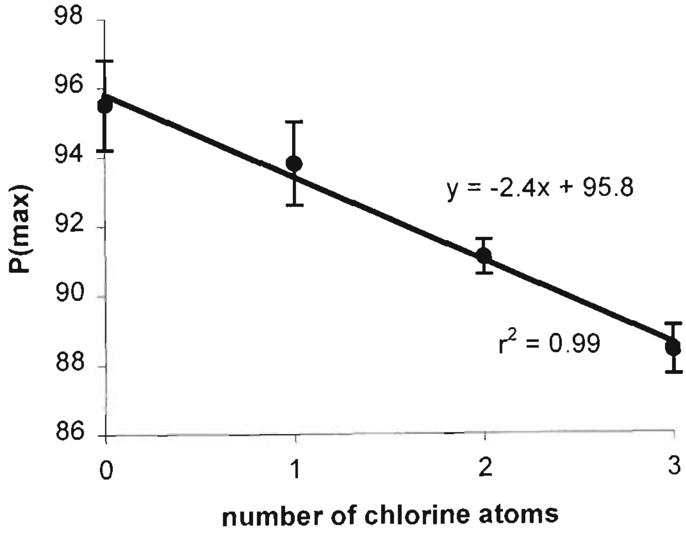

Figure 2.19 : Affinity of PVC-coated particles for chlorinated benzenes. Error bars represent 95% confidence intervals for 10 replicates. The data is presented in Appendix 2.10.

The results show that the maximum values of P for PE and PVC-coated particles in each case decrease linearly with the number of chlorine substituents. This is a surprising outcome since the hydrophobicity is expected to increase with the number of chlorine atoms. It is reasonable to expect the interaction between the polymer surface and the constituent to be of a dispersive nature (Tanaka *et al.*, 1993; Bolis *et al.*, 1997; Giasson *et al.*, 1999) and for more hydrophobicity to lead to a higher affinity. It is likely that the high overall pick-up is indeed related to the mutual hydrophobicities of the surfaces and the contaminants, but the observed decrease in pick-up with increasing hydrophobicity suggests that another factor (such as steric effects) is involved here.

In order to elucidate further the nature of the interaction, a similar study involving methyl-substituted benzenes was conducted and the results are shown in Table 2.6. A pick-up trend similar to that of the chlorinated benzenes was observed in which a linear decrease in the value of P occurs as the number of methyl substituents is increased, Figures 2.20 and 2.21. Furthermore, the hydrophobicity increases with an increase in the number of methyl groups, Table 2.7. It could be surmised from these observations that steric effects are operative, perhaps involving mesopores on the surface. However, this was not pursued further in this project. The theoretical hydrophobicity values, $\log_{10}P$ of these compounds were calculated using Hyperchem[2] software and are given in Table 2.7.

Table 2.6 : The P, R_c and E_l parameters for methyl substituted benzenes. The experiments were conducted in 5 replicates. Individual profiles are documented in Appendix 2.11.

Chemicals	**PE-coated particles**			**PVC-coated particles**		
	P_c	E_l	α_0	P_c	E_l	α_0
benzene	97.0	32.3	2.72	95.5	22.7	2.40
toluene	92.5	24.3	2.17	88.0	18.3	1.72
o-xylene	91.5	24.1	2.02	86.5	18.0	1.60
1,3,5-trimethylbenzene	88.0	23.2	1.92	82.0	17.1	1.52

The relationship between the affinity of PE and PVC-coated particles and molecular volume was also investigated, Figures 2.22 and 2.23. The results show that the maximum values for P of PE and PVC-coated particles, for both chlorinated benzenes and methyl substituted benzenes decrease linearly with an increase in molecular volume. Therefore, this trend could be related to steric effects as alluded to previously.

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[2] HyperChem is commercial molecular modeling package from Hypercube Inc., Waterloo, Ontario, Canada.

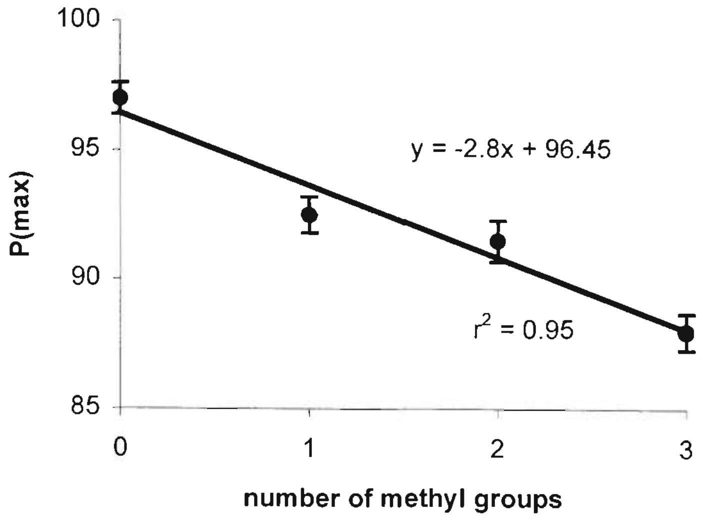

Figure 2.20 : Affinity of PE-coated particles for methyl-substituted benzenes. Error bars represent 95% confidence intervals for 10 replicates. The data are presented in Appendix 2.12.

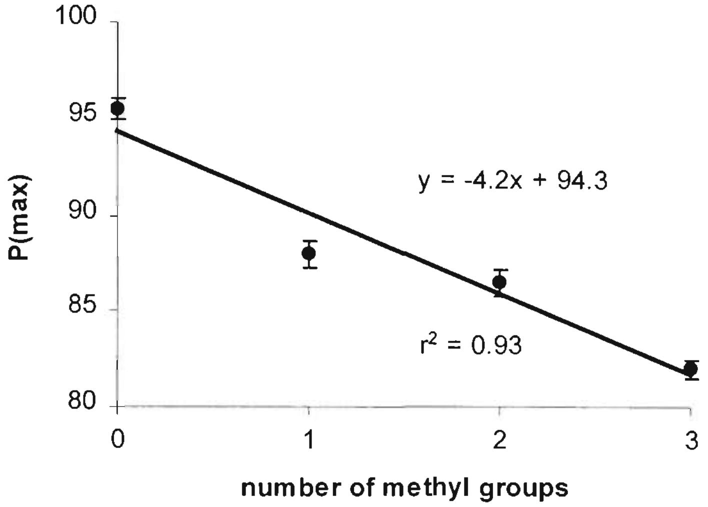

Figure 2.21 : Affinity of PVC-coated particles for methyl-substituted benzenes. Error bars represent 95% confidence intervals for 10 replicates. The data are presented in Appendix 2.12.

Table 2.7 : Hydrophobicity, $\log_{10}P$ and molecular volume (MV) parameters.

Chemicals	**$\log_{10}P$**	**MV /$Å^3$**
benzene	2.05	86.4
monochlorobenzene	2.56	101.0
1,2-dichlorobenzene	3.08	115.6
1,2,4-trichlorobenzene	3.60	130.3
toluene	2.51	384.1
o-xylene	2.98	432.0
1,3,5-trimethylbenzene	3.45	489.0

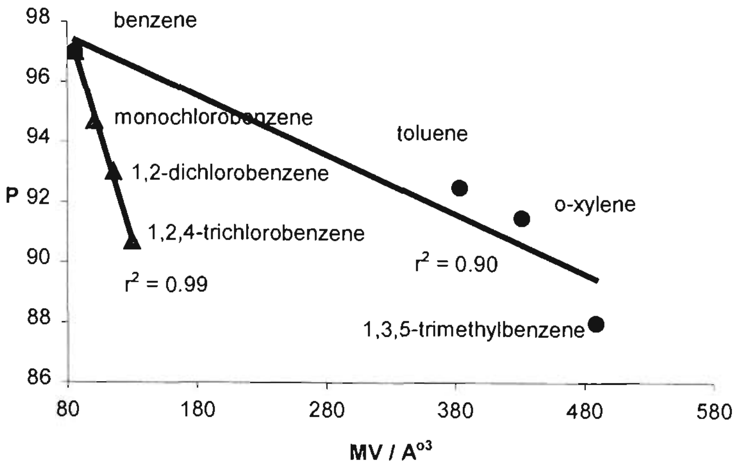

Figure 2.22: The relationship between P values and molecular volume for PE-coated particles.

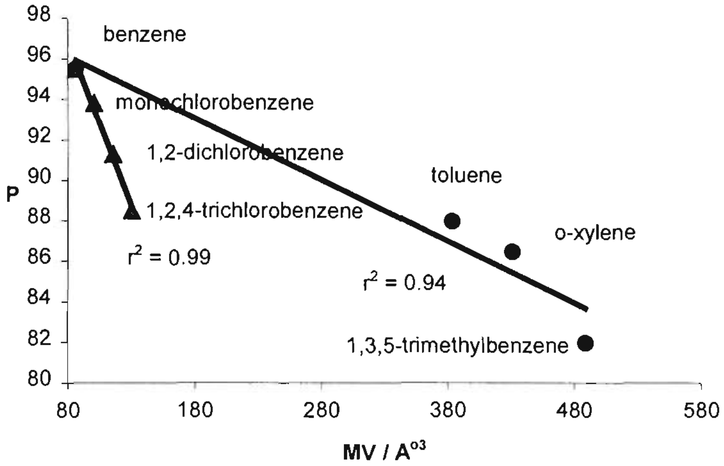

Figure 2.23 : The relationship between P values and molecular volume for PVC-coated particles.

The data in both Tables 2.5 and 2.6 show that the removal of chlorinated benzenes and methyl substituted benzenes using the PE-coated particles is slightly more efficient (higher E_l and α_o values) than their removal using the PVC-coated particles.

2.4 Removal of Contaminants from Soil Using Polymer-Coated Magnetic Particles with a Focus on Pesticides

Soil may become contaminated in many ways and with a wide variety of substances ranging from heavy metals to organochlorines. Truly practical methods of remediation must be economically feasible and not cause environmental damage. Currently there are a number of treatment technologies available for remediation of soil contamination (Shoebridge, 1993), including vapour extraction (Bohn, 1997), bioremediation (Phillips *et al.*, 2000), chemical stabilisation (Gu & Siegrist., 1997) and thermal destruction (Pope *et al.*, 2000).

One important class of environmental contaminants in soil, which has caused much public attention and concern, are pesticides. Pesticides such as dieldrin and DDT (dichloro-diphenyl-trichloroethane) are very persistent in soil and are cumulative toxins (Connell, 1981). Thus there is a need to reduce these pesticides to an acceptable level, usually less than 0.5 mg/kg (Assink & van den Brink, 1985).

Physical, chemical and biological methods have been used to remove pesticides from soil and water. The primary approach to the degradation of most pesticides is through biological treatment. The idea of using microorganisms or their enzymes to degrade pesticides in the environment is not new. Since Audus, (1950) first suggested, the use of microbes to enhance the degradation of the herbicide 2, 4-dichlorophenoxyacetic acid in soil, research has progressed significantly.

The use of enzymes to control pesticide pollution in both soils and water has been suggested (Munnecke, 1976). This is based on an observation that the enzyme parathion hydrolase, hydrolyses parathion approximately two and half times more rapidly than a chemical-based method. Likewise, other organophosphates are also hydrolysed at rates of 40 to 1000 times more rapidly than with chemical hydrolysis.

Chemical treatments of pesticides in aqueous solution have also been described (Buescher *et al.*, 1964; Robeck *et al.*, 1965; Leigh, 1969). The common chemicals used are potassium permanganate, chlorine, ozone and potassium persulfate. These studies have concluded that each pesticide must be studied individually to determine the effects of each oxidant. Moreover, organochlorine pesticides are extremely resistant to chemical treatment, especially endrin, lindane and DDT.

Powdered activated carbon has been used as an adsorbent to remove pesticides from water (Ayele *et al.*, 1989; Pirbazari *et al.*, 1991). These workers have reported a significant reduction in the level of PCBs and heptachlor in drinking water using granular activated carbon. Interestingly, magnetite particles alone can remove 70% of lindane from water (MacRae, 1985).

Both laboratory and pilot studies have shown that incineration is an effective technology for treating soils contaminated with pesticides; the contaminated soil being heated at high temperature in a closed chamber, causing the pesticides to vapourise (Troxier *et al.*, 1993).

Some of the above methods such as the biodegradation of organochlorine pesticides show great potential for the effective clean-up of contaminated sites. Others such as incineration, are not only expensive but are also known to release toxic by-products (Carpenter *et al.*, 1999). Likewise, there are limitations to using microbes for the degradation of pesticides. For instance, it may be costly and time-consuming to produce microbial cultures. Furthermore, severe conditions such as extremes of temperature, pH, soil conditions, and high concentrations of pesticides, may inhibit the activity of the microbes (Nannipieri & Bollag, 1991).

The present work advances an idea for the rehabilitation of pesticide-contaminated land utilizing chemical-adsorbing magnetic particle technology. Being a purely physical method it is anticipated that further environmental damage will be kept to a minimum and that the contaminant may be collected for destruction. It is also anticipated that the particles may be recycled for further use.

Preliminary work has already been carried out by Broadhurst *et al.*, (1993) to study the affinity of PE and PVC-coated particles for chlorinated benzenes (representative of pesticides and PCBs) in Section 2.3.9. The promising results suggest the potential of magnetic particle technology for reducing the levels of organochlorines in soil, particularly DDT and perhaps dieldrin.

2.4.1 Experimental Details

2.4.1.1 Materials and Equipment

The following materials and equipment were used: Synertrol^{TM} vegetable oil (Organic Crop Protectants Pty. Ltd.); Sep-Pak^{TM} columns (Alltech Australia, Baulham Hills, NSW, 2153); Teche Sample concentrator using nitrogen gas and a dry block heater (Ratek instruments); Varian GC/FID gas chromatograph, model 3400; a JW171 capillary column (Alltech Australia, Baulham Hills, NSW, 2153), and a sample of loam soil.

2.4.1.2 Control Studies on Soil Stock

Soil was tested for the presence of pesticides dieldrin and DDT before it was used for pesticide remediation studies. These two pesticides were chosen since they are two of the most common pesticides which have been used in Australia. The soil was ground into fine particles and air-dried in the fumehood for 24 h. Twenty grams of the dried soil was sieved, washed with 3 × 20 mL (20% v/v) ether/hexane mixture and filtered. The filtrate was concentrated to approximately 2 mL using a rotary evaporator and was placed into a Sep-Pak^{TM} column to remove any impurities. The solution was transferred to a graduated tube, concentrated to 2 mL using nitrogen gas, and 1 μL was injected into the GC. The soil revealed no detectable residues of dieldrin and DDT.

2.4.1.3 Preparation of Pesticide Standards

Having shown that the soil to be used was free of pesticide contamination, it was deemed suitable to be used for further experimentation involving spiking with the pesticides dieldrin and DDT. Since these two pesticides are solid, it was necessary to use Synertrol^{TM} (a vegetable oil) to solubilise them. In the 1960s and 1970s, Synertrol^{TM} was used by farmers to dissolve these pesticides before applications. Standard solutions were made up by dissolving solid DDT (1.10 g) and dieldrin (1.08 g) separately in 1 L Synertrol^{TM} (density = 0.832 g mL^{-1}). One millilitre of these solutions was separately diluted in 1 L Synertrol^{TM}. The concentrations of DDT and dieldrin were subsequently calculated and found to be equal to 1.32 mg/kg and 1.30 mg/kg of Synertrol^{TM} respectively.

Each standard (2 g) was placed in a Sep-Pak^{TM} column to remove Synertrol^{TM} that would otherwise contaminate the inlet of the GC. The column was eluted with 10 mL of 20% (v/v) ether/hexane mixture. The eluent was concentrated to 2 mL using nitrogen gas, and 1 μL was then injected into the GC.

The following preliminary experiments involving the application of PE and PVC-coated particles to artificially contaminated soil samples were carried out. A fixed quantity of dried soil (5 g) was placed into five pre-weighed petri dishes. To each soil sample was added 2.0 mL of Synertrol^{TM} oil containing approximately 1.0 ppm of dieldrin and DDT. Varying masses of polymer-coated magnetic particles (5, 10, 15, 20 and 25 g) were added to the each of the petri dishes respectively. The contents of each petri dish were mixed thoroughly and left to stand for 30 min. The particles were then magnetically harvested. The pesticides remaining in the soil on the petri dishes were extracted with 3 × 10 mL of 20% (v/v) ether/hexane mixture. The solution was concentrated to approximately 2 mL using a rotary evaporator and subjected to the same clean-up process using the Sep-Pak^{TM} column and eluted with 10 mL of 20% (v/v) ether/hexane mixture. The eluent was concentrated to 2 mL using nitrogen gas and 1 μL was injected into the GC.

2.4.1.4 Gas Chromatographic Analysis

Characteristic dieldrin and DDT peaks in the gas chromatograms of the pesticide extracts were analysed and a representative chromatogram is shown in Figure 2.24.

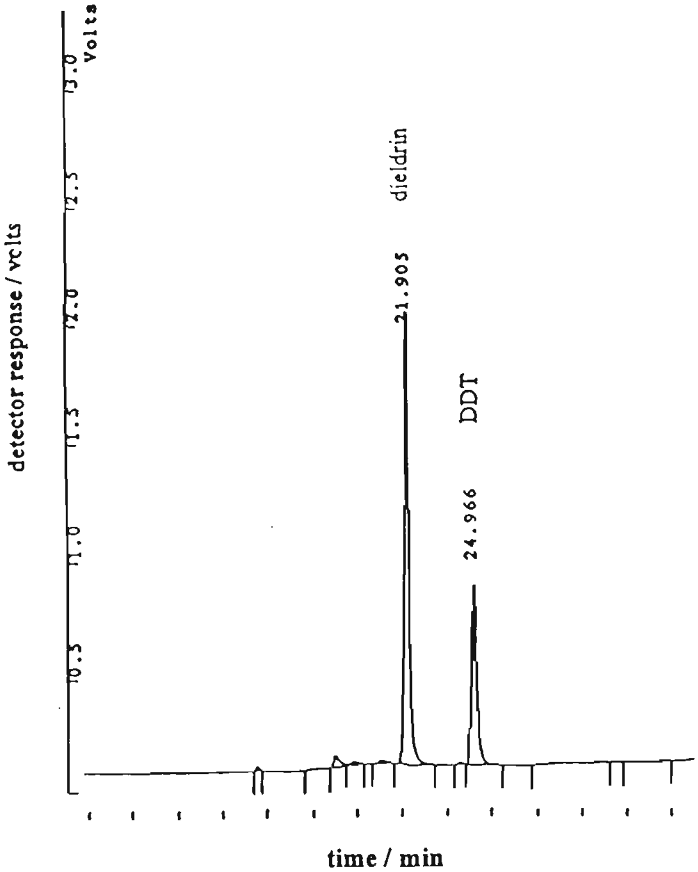

Figure 2.24: A representative GC chromatogram of the residual concentrations of dieldrin and DDT in soil.

The ratio, χ, of the integrated area under the chromatogram of each of the pesticide peaks, A_1, to the integrated area under the chromatogram of each of the pesticide standards, A_2, is given by equation (2.17):

$$\chi = A_1 / A_2 \qquad (2.17)$$

The concentration of the residual pesticide in soil, C_r, was calculated in accordance with equation (2.18);

$$C_r = A_1 / A_2 \times C_o \tag{2.18}$$

where C_o is the original concentration of the pesticide standard.

The percentage of residual pesticide remaining in a soil sample, P_r, after the magnetic harvesting process is calculated as:

$$P_r = C_r / C_o \times 100 \tag{2.19}$$

Thus the percentage of pesticide being removed from a soil sample, P_m, after the magnetic harvesting process is calculated as:

$$P_m = 100 - P_r \tag{2.20}$$

Gas chromatographic analysis was carried out using a Varian Model 3400 gas chromatograph equipped with an electron capture detector. A JW171 capillary column of 0.25 mm internal diameter, and 20 m length was used. Other parameters are: (i) injection temperature 200°C, (ii) column temperature 250 °C, (iii) detector temperature 300 °C, and program rate 200 - 250 °C at 2 °C min^{-1}.

The data for the corrected percentage removals of dieldrin and DDT in the soil samples are listed in Table 2.8. These data were used to plot the corrected percentage of pesticides versus the polymer-coated magnetic particles to soil ratio, Figures 2.25 and 2.26. For the PE-coated particles, one pick-up alone results in approximately 40% and 48% removal of dieldrin and DDT respectively. Subsequent treatments at a particle-to-oil ratio of 5.0 result in a maximum removal of approximately 73% for dieldrin and 77% for DDT. For the PVC-coated particles, one pick-up alone results in the removal of approximately 37% and 45% for dieldrin and DDT respectively. Subsequent treatments at a ratio of 5.0 result in a maximum removal of approximately 70% and 73% for dieldrin and DDT.

Table 2.8 : Percentage by weight of dieldrin and DDT removed from "Synertrol"-preconditioned soil using PE and PVC-coated particles.

PE particle/soil ratio	% dieldrin removed	% DDT removed
1	39.6	48.2
2	58.2	66.4
3	63.4	70.3
4	70.1	73.9
5	73.1	77.3

PVC particle/soil ratio	% dieldrin removed	% DDT removed
1	36.7	45.2
2	56.7	59.6
3	60.7	68.7
4	65.5	71.2
5	69.5	73.4

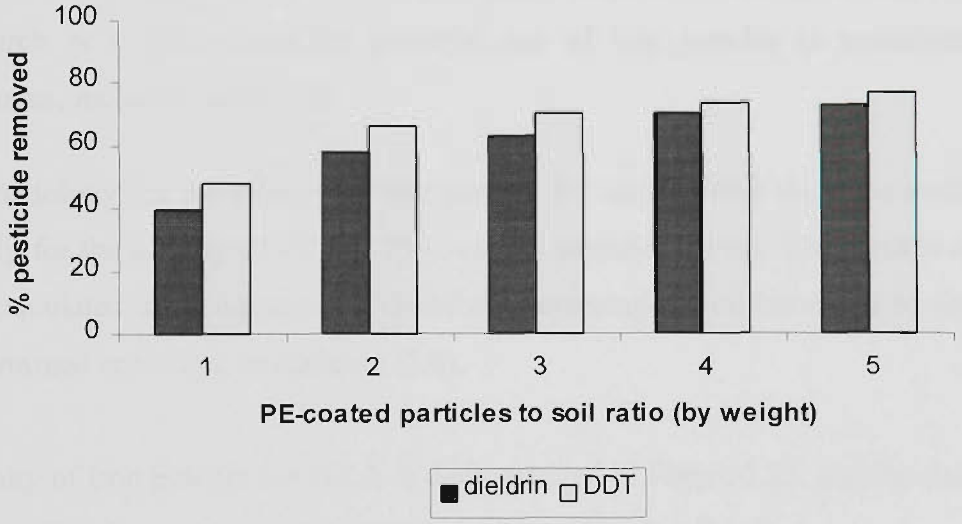

Figure 2.25 : Percentage removals of dieldrin and DDT from Synertrol^{TM}- preconditioned soil using PE-coated particles.

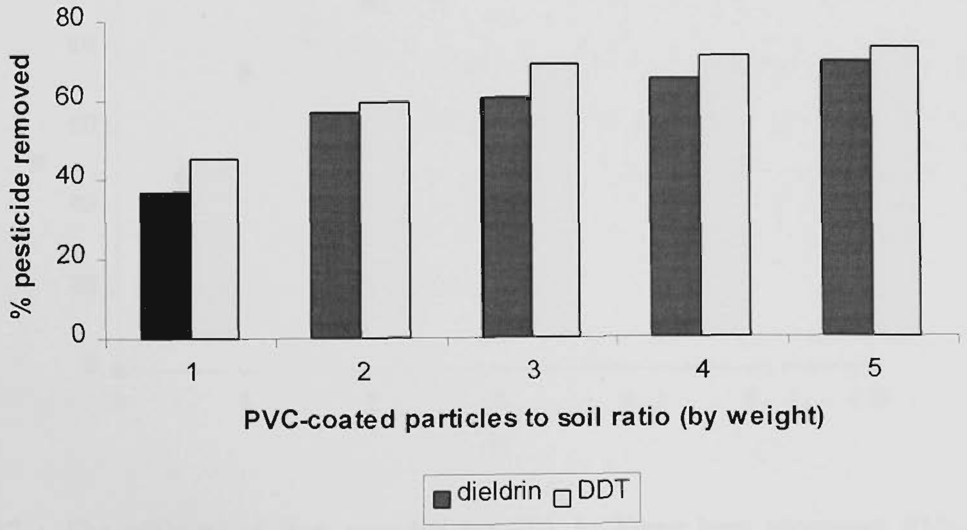

Figure 2.26 : Percentage removals of dieldrin and DDT from Synertrol^{TM}- preconditioned soil using PVC-coated particles.

2.4.2 Problems of Soil Adhesion

The preliminary work on the removal of pesticides from soil using PE and PVC-coated particles has shown promising results. However, in the process of removing solubilised pesticides from soil, there was a problem of soil adhesion to the oil and hence to the particles. It was found that between 9-20% of the soil is picked up by the oil-laden particles. Appropriate corrections were made for soil adhesion in the above studies. A possible method of reducing soil adhesion may be achieved by using less viscous oil to solubilise pesticides and this is currently being pursued by other workers.

2.5 The Applications of Elemental Iron to Oil Remediation

The affinity of iron particles for oil was previously discussed in Section 1.2.1. The next step of the research is to investigate the potential use of iron powder to remediate a range of contaminants, including crude oil.

The methodology for the affinity of iron powder for oil followed the same method described previously for the affinity of PE and PVC-coated particles for oil. The particle-to-oil ratio, R, may be calculated using equation (2.1) and the percentage of oil harvested by the particles, P, was determined according to equation (2.2).

The affinity of iron powder for Oil A is demonstrated in Figure 2.27, and the data show that a maximum oil pick-up approaching 100% may be achieved at $R > R_c$.

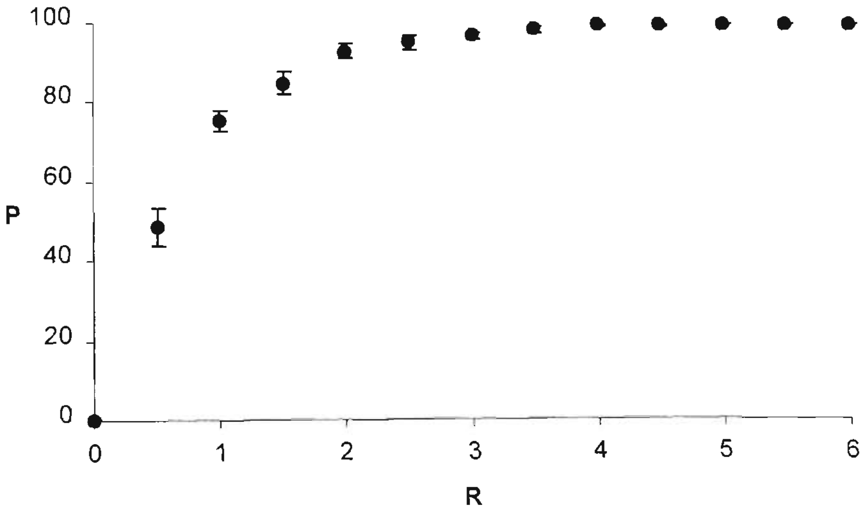

Figure 2.27 : The affinity of iron powder for Oil A. Error bars represent 95% confidence intervals for 5 replicates, Appendix 2.13.

Preliminary investigations were then conducted to explore the oil pick-up phenomenon further and the results are given in Table 2.9. The above experiment was repeated using iron filings rather than iron powder and the results show that a maximum value of approximately 86% of oil was recovered. From the data in Table 2.9, it may be seen that iron powder has a higher P_c, and smaller R_c values compared to iron filings. Moreover, iron powder is approximately twice as efficient (E_1) compared to iron filings.

From the preliminary experiments, it was surmised that the differences in P_c and R_c between iron powder and iron filings might be related to the available surface area of the particles for a given mass. The following collaborative experiments were also initiated by other workers (Tan *et al.*, 1998) using a range of iron pellets of different size distributions, namely, the S110, S230 and S460 (Table 2.1, Section 2.2). The combined results are listed in Table 2.9. The data suggest that the parameters, P_c and R_c are related to the particle size distribution of the iron particles, and thus the latter affects the shape of the adsorption profile.

Table 2.9 : The effects of different types of iron particles on the pick-up of Oil A.

Particles	**Estimated average particle size (mm)**	P_c	R_c	E_1
Iron powder	0.21	99.0	3.5	28.3
Iron filing	0.30	86.0	6.0	14.3
S110	0.45	88.0	9.4	9.4
S230	0.80	83.0	10.2	8.1
S460	1.59	73.5	13.6	5.4
Magnetite	0.15	95.5	5.0	19.2

The data listed in Table 2.9 were used to construct a plot of P_c versus the estimated average particle size, Figure 2.28. The value of P_c decreases with an increase in the average estimated particle size. As expected, the value of R_c increases with an increase in the average estimated particle size. The data for magnetite particles were excluded from the pick-up plots since magnetite is essentially iron oxide.

It must be emphasised that these are preliminary studies and the experiments would obviously be improved with more control over the particle size distributions. Further interpretation of these parameters with respect to the physical chemistry involved is not the focus of this project and is being pursued by other workers. The nature of the affinity between the oil and the iron surface is complex. It cannot be assumed that the nature of the surface of the iron powder and that of the iron filings is identical. Indeed, factors such as the relative extent of surface oxidation could well affect the maximum pick-up.

However, some preliminary work was carried out on what may be considered to be the extreme oxidized case, i.e. magnetite (Fe_3O_4). Figure 2.29 shows the pick-up profile for magnetite itself. The value for P_c in this case is only slightly lower than that of iron powder, but is substantially higher than that for iron filings. Thus it is evident that magnetite could also be used to recover oil.

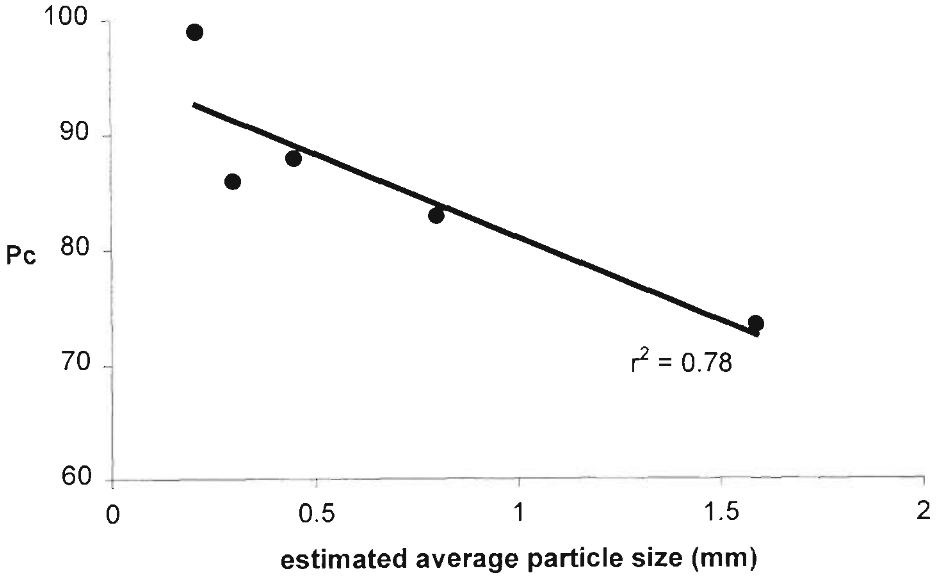

Figure 2.28 : A plot of P_c versus estimated average particle size.

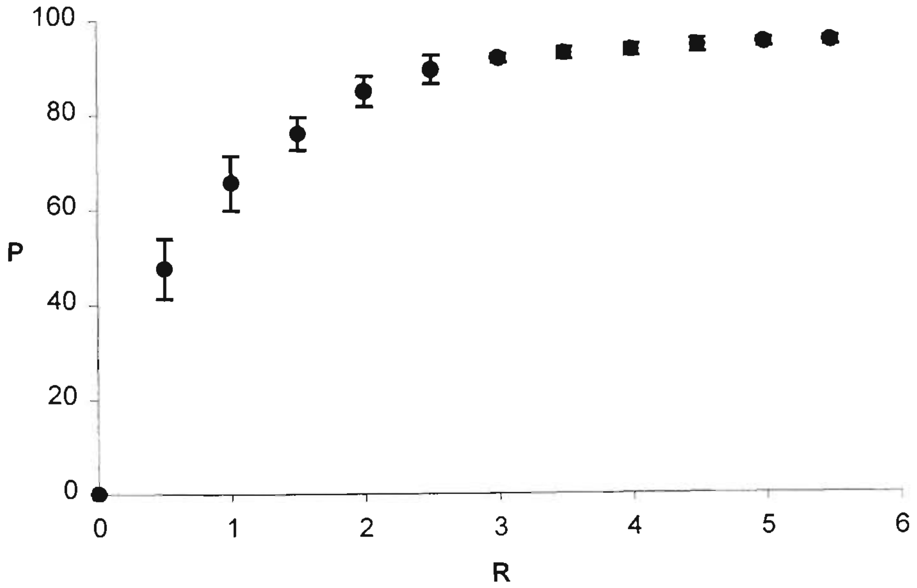

Figure 2.29 : The affinity of magnetite for Oil A. Error bars represent 95% confidence intervals for 5 replicates. The data are presented in Appendix 2.14.

2.5.1 Investigating the Affinity of Iron Powder for Oil Contaminants

The experiments in Section 2.5 were carried out on Oil A only. The methodology was extended for iron powder alone to Oils B, C, D, and emulsion S. Prior to the investigations on the affinity of various oil contaminants, viscosity measurements were carried out using the Brookfield Synchrolectric Viscometer. An appropriate speed of the viscometer was selected and a spindle with an appropriate size was placed in a 125 mL beaker containing some oil. Ten measurements were recorded and the results for the viscosity measurements for each oil contaminant are presented in Table 2.10. An example of the calculation for the determination of the viscosity measurements for Mobil Super XHP 20W-50 (Oil A) is shown in Appendix 2.15.

Table 2.10 : Viscosity (η), P, R_o, E_l and α_o parameters for a variety of contaminants. The error analyses associated with E_l and α_o values are presented in Appendix 2.16.

Contaminants	**η/cp**	**P_c**	**R_c**	**E_l**	α_o
Oil A	425.5	98.9 ± 0.4	4.2 ± 0.3	23.6 ± 1.8	5.4 ± 0.2
Oil B	115.5	97.9 ± 0.9	4.2 ± 0.3	23.4 ± 1.9	5.0 ± 0.2
Oil C	11.4	98.3 ± 1.6	5.1 ± 0.3	19.2 ± 1.4	3.3 ± 0.1
Oil D	13.0	97.9 ± 0.6	5.2 ± 0.3	18.9 ± 1.1	3.1 ± 0.1
Emulsion S	_	96.7 ± 0.6	5.2 ± 0.2	18.8 ± 0.9	3.1 ± 0.1

Figure 2.30 shows that the light crude oils (C and D) have relatively low P values compared to the more viscous oils (A and B, respectively). Therefore, it appears that the higher viscosity oils tend to have higher initial values of P. However, a maximum value for P of approximately 98% was eventually achieved for all the oils used. Thus it would appear that the value of P_c, for all of the oils tested is effectively independent of the oil type.

2.5.2 The Efficiency of Contaminant Removal Using Iron Powder

The data listed in Appendix 2.13 were used to plot the affinity of iron powder for all oil systems versus R. For each oil, five replicate plots were constructed, and from each plot, the values P_c and R_c were determined graphically. This enabled the efficiency parameter E_l to be calculated using the equation $E_l = P_c / R_c$. The average values of P_c, R_c, and E_l are listed in Table 2.10.

The data in Table 2.10 show that the most viscous oil (Oil A) has the highest efficiency value (E_I), followed by the moderately viscous oil (Oil B). Oils C and D have the lowest efficiency values due to their low viscosities. Although it was not possible to conduct viscosity measurement for emulsion S, it would appear from the handling of this material that it is less viscous than Oils A and B. This assumption is supported by the efficiency value for emulsion S which is less than that of Oils A and B, but comparable to Oils C and D.

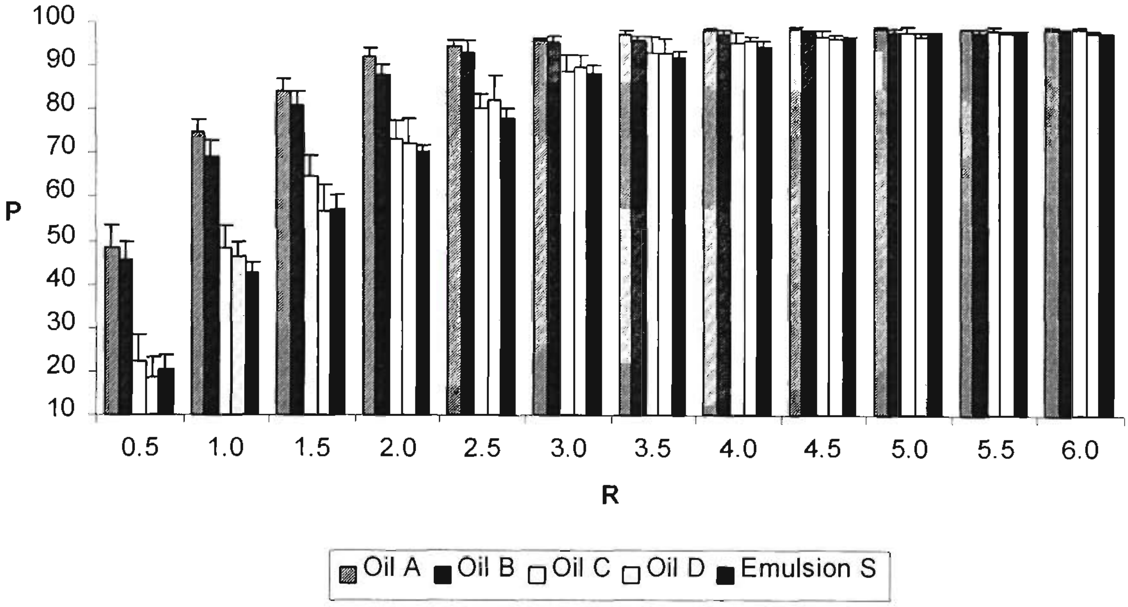

Figure 2.30 : The affinity of iron powder for a variety of oils. Error bars represent 95% confidence intervals for 5 replicates. Individual profiles are documented in Appendix 2.13.

2.5.3 Fitting Experimental Data to the Model

In order to determine the α_0 values for the removal of oil by iron powder, it was necessary to calculate the average mass of a particle of iron powder used in the process. The average mass of an iron powder particle was found to be 3.05×10^{-4}g and the calculation of this is presented in Appendix 2.17. The average mass of a single particle of iron powder is small and so it was necessary for purposes of implementing and speeding the iterative numerical procedure of the computer fitting software to use a cluster of iron powder particles. In this case, the computer fitting program was adapted so as to consider a cluster of 400 iron powder particles as a single absorbing entity.

The mathematical model was tested on Oils A, B, C, D, and emulsion S. For each oil, five replicate plots were generated by the computer-fitting program to obtain the α_0 values. The average α_0 value for each oil was subsequently determined and the errors associated with the

α_o values are presented in Table 2.10. The detailed calculations for these values are presented in Appendix 2.16. For each oil, the data for each of the five replicates were used to test the applicability of the mathematical model. Figure 2.31 shows a plot of the average percentage removal of Oil A together with the optimum computer fit. Similar plots for the other oils are presented in Appendix 2.18.

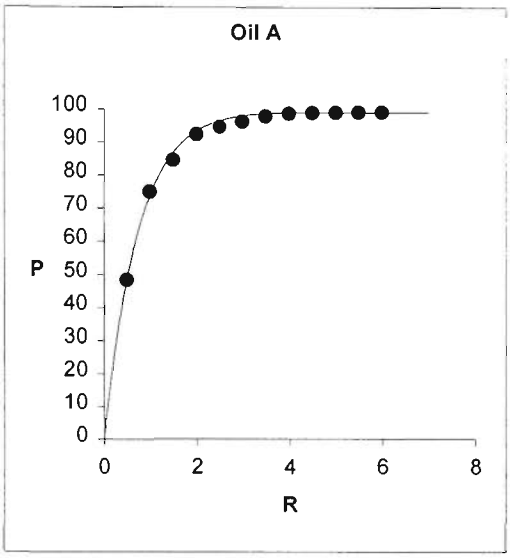

Figure 2.31 : Computer-generated curve fit for Oil A where $\alpha_o = 5.4 \pm 0.2$.

The errors associated with efficiency of the oil pick-up parameters E_l and α_o confirm the observations that were made previously concerning the respective reliabilities of these parameters, Section 2.4.2. In particular, for these highly non-ideal systems the parameter E_l is a somewhat insensitive indicator of efficiency as it can only distinguish between the efficiencies of the viscous oils (i.e. Oils A and B) and the relatively less viscous oils (i.e. Oils C and D) at the 95% confidence level. On the other hand, the α_o values indicate that there is a significant difference between the pick-up efficiencies of all of the oils at the 95% level. Moreover, both the E_l and α_o values indicate that the more viscous oils are adsorbed more efficiently by iron powder than the less viscous ones. This observation has also been made in studies of the removal of oil from oil filters where it was found that the more viscous oil adhered more strongly to the metal than the less viscous ones (Peaslee & Roberts, 1998). The adsorption of the emulsion S is of low efficiency when compared with the oils in the series.

2.6 Conclusion

The production of research quantities of PE and PVC-coated particles for "proof of principle" investigations was carried out using grade S330 iron pellets. The polymer-coated particles were applied to the removal of various "contaminants". The pick-up characteristics range between two extremes, represented by near "ideal" and "non-ideal" behaviour. A mathematical model was developed in order to gain insights into the physical basis for the pick-up phenomenon. Two different kinds of efficiency parameters of pick-up have been developed. The parameter E_l represents the maximum removal efficiency which can be achieved, and α_o represents the initial efficiency of pick-up. A numerical value of E_l is determined from the experimental data and α_o is determined from the experimental data fitting algorithm. A correlation was found between α_o and the viscosity.

Various properties which affect the pick-up of contaminants were investigated. It was found that the nature of the coating materials, the surface texture and the nature of the substrate influence the pick-up of contaminants. In particular, it was found that PE-coated particles are more efficient (E_l and α_o) than PVC-coated particles in the pick-up of a representative oil; the pick-up of the same oil using granular PE-coated particles is more efficient (E_l and α_o) than when PE-coated particles with a smooth surface is used; the removal of a representative oil from a glass substrate is more efficient than removal from a plastic substrate. The effects of contaminant hydrophobicity on pick-up were also investigated. Preliminary results indicate that the efficiencies of pick-up of chlorinated benzenes and methyl-substituted benzenes decrease as the size of the molecule increases. This seems counter-intuitive, since with increasing size the hydrophobicity increases and one might expect the affinity to increase. It was surmised that in addition to hydrophobicity, other factors such as steric effects could be involved.

The ability of PE and PVC-coated particles to remove the pesticides dieldrin and DDT from soil was explored. It was found that although an encouraging extent of removal could be achieved, the major problem with this technique is soil adhesion to the particles.

Iron powder was found to have a high affinity towards a range of contaminants with a pick-up from a glass substrate approaching 100% being achievable. The effects of different particle size distributions of iron particles on the pick-up of a representative oil were investigated. The results show that there is a linear decrease in the oil pick-up with an increase in the average particle size. The more viscous oils show a higher initial pick-up of contaminants than that of the lighter oils and the sea water/oil emulsion. However, a maximum value of approximately 98% was eventually achieved for all contaminants used. Thus for the contaminants used here the ultimate removal is independent of the type of contaminant. Using the mathematical model the efficiency of contaminant removal was determined. Numerical values of the efficiency parameters E_1 and α_o, indicate that the more viscous oils are adsorbed more efficiently by iron powder than the less viscous ones and the sea water/oil emulsion.

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Chapter 3 Application of Magnetic Particle Technology to the *in vitro* Cleansing of Contaminated Feathers

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- 3.1.2 Alternative Cleansing Approaches

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3.1 Introduction

Crude petroleum and refined petroleum may be accidentally, or even deliberately, released into the environment from a number of sources. These include tanker accidents, the deliberate discharge of bunker oil from ships, and oil leaks in offshore operations (Yang *et al.*, 2000). Marine birds are probably the most noticeable and recognized victims of such incidents. For example, just after midnight on 24 March, 1989, the supertanker "Exxon Valdez", sailed off-course in a 16 km wide channel at Prince William Sound near Valdez, Alaska, and hit submerged rocks on a reef, creating one of the most damaging oil spills in history. It was estimated that the oil killed up to 695,000 birds (including 144 bald eagles), up to 5,500 sea otters, 30 seals, 23 whales, and an unknown number of fish and other aquatic species (Miller, 1994; Schmidt, 1997).

A more recent example in Australia involved the bulk carrier "The Iron Baron", which went aground at Low Head in Northern Tasmania on 10 July 1995 (Hull *et al.*, 1998). An unknown number of Little Penguin (*Eudyptula minor*) were contaminated with bunker fuel oil. It was estimated that the bunker oil killed more than four thousand penguins. A total of 1,894 penguins contaminated with the oil were rescued and cleaned, of which 65 eventually died.

3.1.1 The Development of Cleansing Agents for Oil-Contaminated Wildlife

Undoubtedly, the effectiveness of cleansing agents is of primary importance in the treatment of oiled birds. Serious studies on the treatment of oiled birds began in the late 1960s (Clark, 1969), although most early attempts to clean and rehabilitate large numbers were of dubious value. Mortality was over 75% and in many cases was close to 100% (Clark & Kennedy, 1968; Orr, 1971). For example, on 18 January 1971, two oil tankers collided near San Francisco and 1.2 million gallons of No. 2 bunker oil were spilled into the sea (Smith, 1973). Approximately 1285 oiled water birds were cleaned, of which only 198 birds survived (85% mortality). From the late 1970s onwards, techniques for rehabilitating oiled birds have improved markedly (Jenssen & Ekker, 1989; Jessup, 1998).

In the 1970s, the most popular method to clean oiled birds was to use organic cleansing solvents such as Shell Sol 70^{TM} (Naviaux & Pittman, 1973; Williams, 1978). This solvent, on w/w basis, consists of paraffins (98.9%), aromatics (0.4%), and olefins (0.7%) and is reported to be effective, safe, and completely removable from the feathers by evaporation. Another hydrocarbon solvent, Arklone P^{TM}, developed by ICI Limited, has a low boiling point and an anaesthetic property, and is reported as being successful for cleansing birds, resulting in a plumage that remains watertight (Clark & Gregory, 1971).

In general, most of these cleansing solvents are toxic to some degree and can also be irritants (Jenssen, 1994). For example, in contrast to earlier findings by Naviaux and Pittman (1973) and Williams, (1978), Shell Sol 70^{TM} was reported to be toxic to birds and humans alike (Perry *et al.*, 1978; Smail, 1978). In these studies, over 90% of all birds cleansed with petroleum solvents died within 12 h, apparently from inhaling vapours or from skin contact. In addition, birds cleansed with organic solvents have to be kept up to several months before they are ready for release. This disadvantage has led to the development of methods that use surfactant-based cleansing agents.

In the 1970s, British researchers demonstrated that simple dish-washing detergents are preferable to organic solvents (Smail, 1978). Other detergents such as Amber Lux^{TM}, a biodegradable industrial detergent, was also used successfully to clean oiled birds. The introduction of surfactants has improved the survival rate of oiled birds (Randall *et al.*, 1980), and under ideal circumstances, birds can be released in a matter of days instead of several months.

Continuing research has resulted in the development of more efficient surfactant formulations for cleansing oiled birds in order to reduce cleansing time and to improve the degree of restoration of the insulative properties of the plumage. In the late 1980s, an even more efficient surfactant, Taski-Profi^{TM}, was developed (Jensen & Ekker, 1989). This represented an advance in reducing the cleansing time and improving the thermal insulation of the feathers. Such an increase in efficiency would be expected to reduce stress to birds and result in their earlier release.

In the 1990s other such cleansing agents were developed. For example, a formulation developed by Bassères *et al.*, (1994) removed 90% of oil from standard duck feathers compared with 30% removal in control tests. The normal metabolic rate was recovered one day after cleansing and thermal insulation was restored four days after cleansing.

In 1995, a method for evaluating the efficiency of various types of surfactants used for removing petroleum contaminants from feathers was developed (Bryndza *et al.*, 1995). An "oil" consisting of thirteen polycyclic aromatic hydrocarbons, representative of components present in light crude oils and diesel fuel, was formulated. This has been used as a standard contaminant to assess the removal of oil by different surfactants. An evaluation of detergent efficiency can thus be determined. In general, it was found that shampoos and various dishwashing detergents were suitable, with Dawn™ dish washing detergent being the most effective tested in this and other studies (Gilardi & Mazet, 1999).

Currently, rescue and rehabilitation methods have greatly improved. This has been primarily due to the development of new and more effective surfactants as oil removal agents, advances in nutritional supplementation, husbandry practices, medical evaluation, and biomedical treatments. Post-treatment protocols have also been improved to a great extent. However, in spite of these advances the conservational value of bird rescue and rehabilitation has been questioned (Schmidt, 1997).

Studies have shown that although surfactants may effectively cleanse the plumage of oil, they contribute to the wetting of the feathers, and thus contribute to the mortality rate when the birds are released (Clark & Gregory, 1971; Perry *et al.*, 1978). In addition, the washing process itself may severely stress the bird, damaging the essential microstructure of the feathers and lowering the bird's ability to survive (Briggs *et al.*, 1997). For example, a typical surfactant-based (3% v/v) cleansing protocol used by Bassères *et al.* (1994), involves three washings with large volumes of warm water (40 °C). This includes 2 min per washing, and 5 min per rinsing for each wash. The bird is then rinsed continuously until the water is free of oil. Such a protocol stresses the bird and is very time consuming and costly. Often, during oiled bird rescue operations, the mortality rate can be further exacerbated by the oil not being removed rapidly enough. Therefore, in developing new protocols, the factors to consider are: (i) efficiency in terms of rapid removal of contaminant and cleansing agent (especially initial removal), (ii) nature of the cleansing agent (non-toxic and non-irritant), (iii) stress to the bird, (iv) cost, (v) labour intensity, and (vi) portability of equipment.

Advances in handling, transportation, housing, and stabilization of oiled birds have also improved since the late 1960s. Various current protocols relating to the treatment of oiled birds are discussed in Chapter 4.

3.1.2 Alternative Cleansing Approaches

Recalling that iron materials have an affinity for oil and, in particular, that iron powder has been applied successfully to oil spill remediation (see Section 2.5; Tan *et al.*, 1998), it was proposed that iron powder might be a suitable dry cleansing agent for oiled feathers. If successful, this method would obviate the need for the use of warm water and drying, and could ensure the complete removal of the cleansing agent itself. This is vital during the cleansing of the oiled birds, since removal of all of the cleansing agent is also a requirement for their successful survival (Clark & Gregory, 1971; Kerley *et al.*, 1987; Jenssen & Ekker, 1989). Furthermore, the wastes produced by the magnetic harvesting process could be contained and recycled using an appropriate method such as supercritical fluid extraction (discussed in Chapter 6).

This project has explored the feasibility of using iron powder as a cleansing agent, whereby the oil-laden powder can be removed by magnetic harvesting. The condition of the feathers after cleansing has also been investigated by an examination of the feather microstructure (discussed in Chapter 5).

3.2 Experimental Details

For *in vitro* tests on feather clusters, three different species of birds were considered, namely, the domestic duck (*Anas platyrhynchos*), the Little Penguin (*Eudyptula minor*), and the Silver Gull (*Larus novaehollandiae*). Domestic duck feathers were chosen since they are a standard model for laboratory testing (Jenssen & Ekker, 1989; Bassères *et al.*, 1994) and they also have the advantage of being readily available in good condition. The feathers of the Little Penguin were available through collaboration with the Phillip Island Nature Park (PINP). These feathers are representative of flightless seabirds and differ from duck and seagull feathers in that they are more dense and closely packed. As such, their structure may be considered to represent a "worse case scenario" matrix.

Unlike duck and penguin feathers, which are readily available, seagull feathers had to be collected individually by searching along beaches around Port Phillip Bay[1], Melbourne, Australia. The seven Victorian locations where the feathers were collected are: (i)

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[1] Port Phillip Bay is located at latitude 38° 20', longitude 144° 30', Australia.

Williamstown, (ii) Altona, (iii) Altona Meadows, (iv) Werribee, (v) Geelong North, (vi) Portarlington, and (vii) Queenscliff.

Bound clusters of five to six bird feathers were used for *in vitro* studies. The feathers were visually inspected to ensure that they were clean and of a consistent quality. The feathers were saturated with contaminants, covered with iron powder and magnetically stripped to remove the contaminants, Figure 3.1.

Figure 3.1 : (a) oil-laden feathers, (b) oil-laden feathers covered with iron powder, (c) oil-laden feathers after cleansing with iron powder and (d) original feathers.

The following materials were used: iron powder (0.21 mm – average maximum dimension), Hoganas, C100.29, Sweden; Ajax Laboratory Chemicals, APS Finechem, NSW Australia, and a "laboratory magnetic tester" (Alpha magnetics, Victoria, Australia).

Commercial grade engine oil (Oil A), various crude oils (Oils B, C and D) and Oil C/sea water emulsion (emulsion S) were used in these studies and details of these oils are given in Table 3.1.

Table 3.1 : Viscosity values for various oils.

Oil	Details	Viscosity /cp
A	Mobil Super XHP 20W-50, 1993 formulation	425.5
B	Moderately heavy crude oil, Mobil Oil, Australia	115.5
C	Light crude oil, Esso Australia Limited	11.4
D	Light crude oil, Shell Australia Limited	13.0
Emulsion S	50% Oil C/seawater by volume.	-

The method of reverse emulsion by Bessères, (1994), was adopted in preparing emulsion S.

3.3 Removal of Contaminants Using Iron Powder

For *in vitro* studies, clusters of feathers were used as "animal analogues". Each cluster of feathers was prepared by tying five or six feathers together at the base with cotton thread, Figure 3.1(d). A cluster of pre-weighed (f_1) feathers was immersed into a given oil or the emulsion S to achieve saturation. They were then removed and allowed to drain for 10 min before being placed on a tared petri dish to be re-weighed (f_2). The feathers were then removed from the dish and the mass of the oil remaining on the petri dish was also recorded (ϕ). Hence, the mass of the oil-laden feathers, f_3, for further experiments is given by equation (3.1):

$$f_3 = f_2 - \phi \tag{3.1}$$

A known mass of iron powder was placed on a tared petri dish and weighed (m_o). A small amount of iron powder from this stock was added to the oiled feathers. The mass of iron powder remaining on the petri dish was weighed (m_1). Hence the mass of iron powder placed in contact with the feathers (m_r) is given by equation (3.2):

$$m_r = m_o - m_1 \tag{3.2}$$

The particle-to-oil ratio, R, may then be calculated using equation (3.3):

$$R = m_r / (f_3 - f_1) \tag{3.3}$$

The oil-laden iron powder was magnetically harvested from the feathers using the magnetic tester. The feathers were re-weighed (f_4) and the percentage removal of the contaminant, F was calculated according to equation (3.4):

$$F = [(f_3 - f_4) / (f_3 - f_1)] \times 100 \tag{3.4}$$

The procedure was repeated for increasing R values until a maximum percentage removal of oil from feathers, F_0 was obtained. The procedure was carried out with five replicates in each case. A sample calculation is presented in Appendix 3.1.

A plot of F, the average percentage removal of contaminant using iron powder versus R (in this case R = iron powder-to-oil ratio) for duck breast and back feathers is presented in Figures 3.2 and 3.3 respectively.

It is clear from data plotted in Figures 3.2 and 3.3 that only slight differences exist between the pick-up characteristics for the contaminants investigated. Thus there is a need to utilize a more refined analytical approach in order to differentiate between the pick-up of these contaminants. Such an approach has been applied and is discussed in Sections 3.3.1 and 3.3.2. Nonetheless, the plots for both duck breast and back feathers show that for low values of R, the removal of the less viscous Oils C and D is only slightly greater than the more viscous Oils A and B as well as the emulsion S. However, for all of the oil systems, sufficient application of iron powder cleansed the feathers to a maximum value of approximately 96%.

The results for the initial pick-up of contaminants from feathers using iron powder are different from the results for the initial pick-up of the contaminants from a glass petri dish, Section 2.5. In the latter case, the results suggest that the more viscous Oils A and B are picked-up more efficiently than the light crude Oils C and D. The different behaviour observed between the feather experiments and petri- dish experiments possibly reflects the differences in the interaction between the contaminants and the substrate.

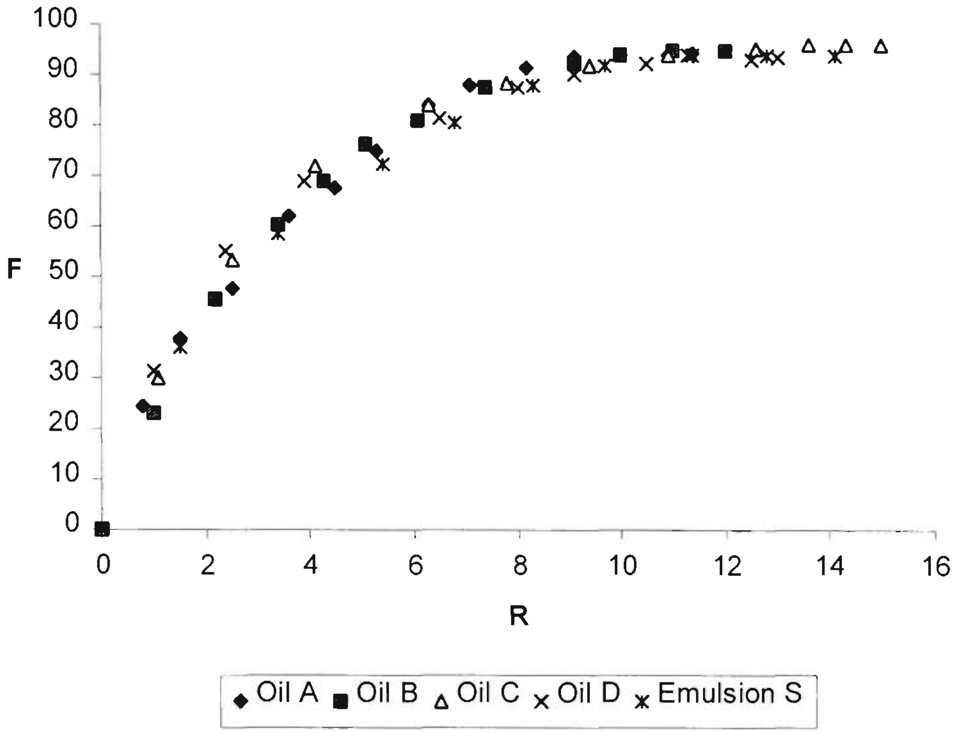

Figure 3.2 : Average percentage by mass of contaminants removed from virgin duck breast feathers, F, versus iron powder-to-oil ratio, R. Individual profiles are documented in Appendix 3.2.

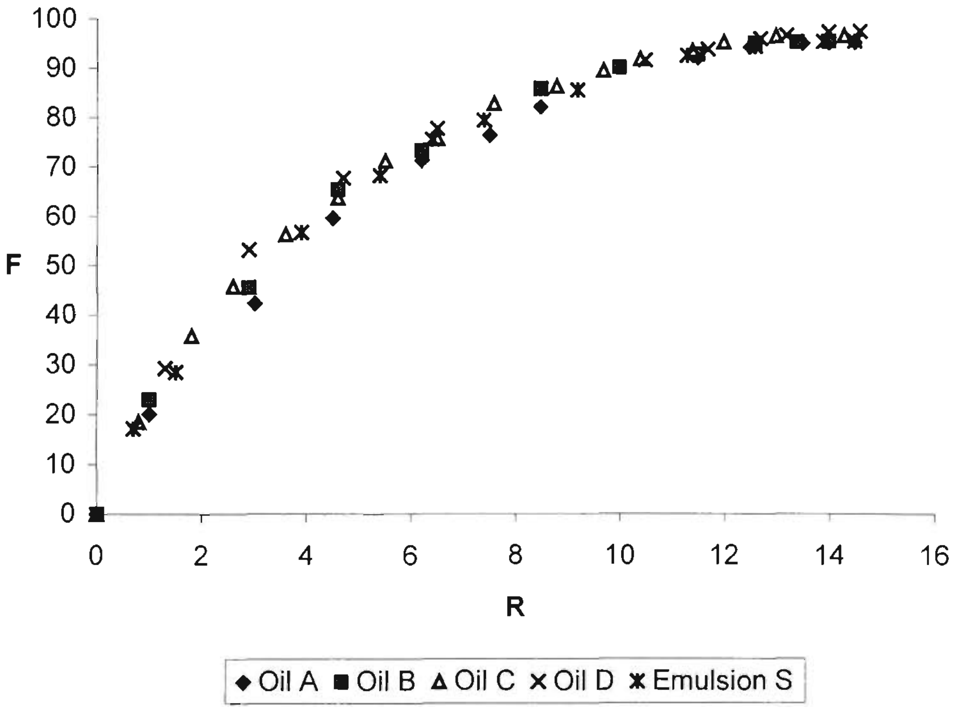

Figure 3.3 : Average percentage by mass of contaminants removed from virgin duck back feathers, F, versus iron powder-to-oil ratio, R. Individual profiles are documented in Appendix 3.3.

3.3.1 Measuring the Removal Efficiency

The method for measuring the efficiency of removal of contaminants from feathers using iron powder is analogous to that previously discussed for determining the pick-up of oil contained in petri dishes. The efficiency parameter $E_1 = P_c/R_c$ for the oil pick-up from petri dishes using iron powder is expressed in the case of feathers as $E_2 = F_c/R_c$ where F_c is the critical value of F, which, for oil removed from feathers is analogous to the critical parameter P_c discussed in Section 2.3.2.

The efficiency of removal (E_2) of the five different contaminants from duck breast feathers using iron powder was found to have values between 8.7 and 8.8 at R = 11.0. In the case of duck back feathers, the efficiency of removal (E_2) of five different contaminants using iron powder was found lie between 7.2 and 7.4 at R = 13.0. Thus the removal of contaminants from breast feathers is more efficient than their removal from the back feathers as reflected by their E_2 values. Individual profiles are presented in Appendices 3.2 and 3.3. However, for each type of feather, there is little difference in the maximum pick-up for the viscous and light oils and emulsion S. Nonetheless, the initial pick-up for the light Oils C and D for $R < 8.0$ (breast feathers) and for $R < 10.0$ (back feathers) are slightly higher than those of the heavy oils. In order to gain a better insight into any differences that may exist between these systems, it was decided to use the initial gradients, as reflected by the α_o values to measure the efficiency of oil pick-up in each case.

3.3.2 Fitting Experimental Data to the Model

The data presented in Appendices 3.2 and 3.3 were used to test the applicability of the mathematical model for the removal of each of the oil systems from both duck breast and back feathers. Figure 3.4 shows a plot of the percentage removal of: (i) Oil C from duck breast feathers, and (ii) Oil A from duck back feathers. These profiles have been fitted using the computer program. Similar plots for the other oils are presented in Appendices 3.4 and 3.5. The α_o values were subsequently determined from the computer fitting and are listed in Table 3.2.

Recalling that α_o is proportional to the initial gradient ("take off" slope) of the pick-up plot (equation 2.16), Table 3.2 shows that the less viscous Oils C and D are removed with slightly greater efficiency as indicated by their higher α_o values compared to the more viscous Oils A and B. These results are in contrast to those obtained for the removal of the same oils from petri dishes (see Section 2.5.1). In particular, the order of efficiency of pick-up is reversed when the oils are removed from glass rather from the feather substrates. This may be due to the greater affinity of the higher molecular weight, more viscous oils for organic substrates such as feathers compared with an inorganic substrate such as glass. However, the precise reason for this is beyond the scope of the current investigation.

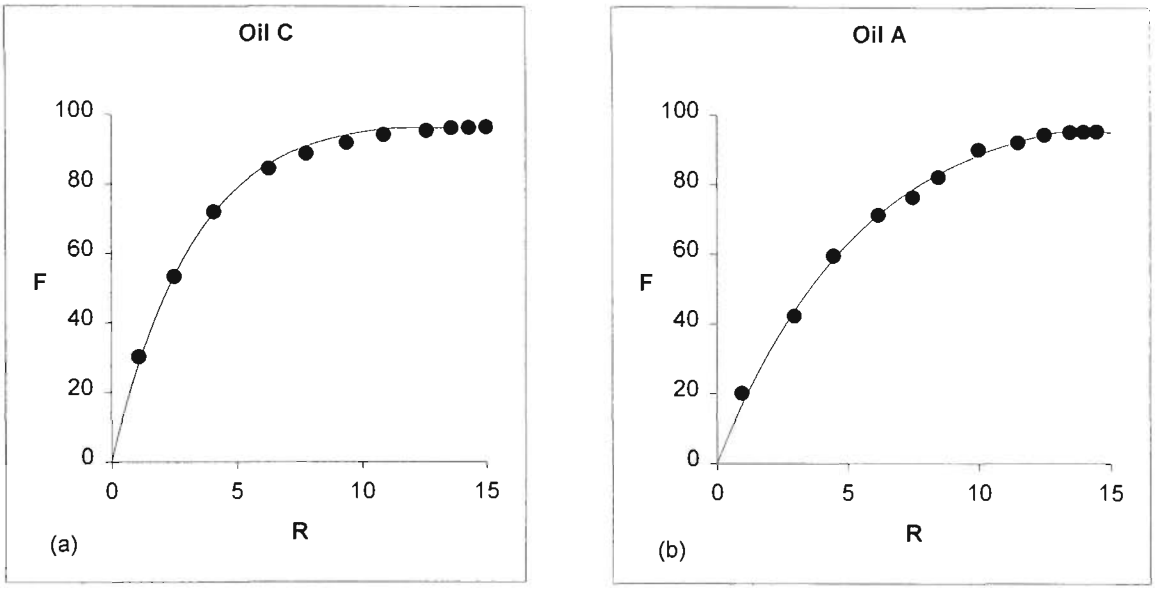

Figure 3.4 : Computer-generated fit for the removal of: (a) Oil C (α_o= 3.40) from duck breast feathers and (b) Oil A (α_o= 2.41) from duck back feathers.

Table 3.2 : Values of α_o for a variety of contaminants.

Contaminants	**Viscosity /cp**	**α_o(breast feathers)**	**α_o(back feathers)**
Oil A	425.5	2.64	2.41
Oil B	115.5	2.85	2.70
Oil C	11.4	3.40	2.92
Oil D	13.0	3.61	3.26
Emulsion S	-	3.18	2.82

3.4 Removal of Contaminants Using Excess Iron Powder

The results for the removal of contaminants from feathers using iron powder are very encouraging and show that a high removal of approximately 96% is possible. The results also suggest that the ultimate value of F for a wide range of oil systems is independent of the type of oil.

Another approach to the removal of contamination from feathers, which is more relevant to a field situation, is to add an excess of iron powder in a series of oil removal applications. Before adapting this approach to a field trial, *in vitro* laboratory studies were carried out on different species of bird feathers with excess iron powder.

A gravimetric method was used to determine the mass of contaminants removed from oil-laden feathers and from treated feathers where oil is removed using a harvesting technique involving excess iron powder. The following experiments were carried out using the application of iron powder to feathers contaminated with each of the oil systems. The procedures were carried out with 5 replicates in each case.

Five feathers were tied together at the base and weighed (f_1), Figure 3.1(d). The feathers were immersed into an oil to achieve saturation, Figure 3.1(a). They were removed and allowed to drain for 10 min before being re-weighed (f_2) on a tared petri dish. The mass of the oil remaining on the petri dish (r) was also recorded. The mass of the oil-laden feathers, f_3, for further experiments was calculated as described previously in Section 3.3 using equation (3.1).

The oiled feathers were then placed in a beaker containing iron powder. The beaker was lightly shaken to ensure that the feathers were covered with excess iron powder, which was immediately taken up on the surface, Figure 3.1(b). The oil-laden iron powder was magnetically harvested from the feathers using the magnetic tester. The feathers were re-weighed, (f_4), and the percentage removal of the contaminant was calculated as previously described in Section 3.3 in accordance with equation (3.4).

For each experiment, the application of iron powder and the magnetic stripping procedure was repeated nine times until a maximum removal of oil from the feathers was achieved, Figure 3.5.

3.4.1 Duck Feathers

The histograms in Figures 3.5 and 3.6 show the results for the *in vitro* cleansing of five different contaminants from duck breast and back feathers respectively using iron powder. In the case of the breast feathers, the more viscous oils A and B are initially removed with a pick-up of approximately 66% and 73% respectively. However, for the less viscous, lighter crude oils C and D, one treatment alone results in approximately 88% removal of oil from the feathers. A high initial removal of approximately 81% is also observed in the case of emulsion S. For each contaminant, a total of nine treatments cleanse the feathers to a maximum value of approximately 97%.

The initial removal of all four oils and emulsion S from back feathers appears to be less efficient than for breast feathers. The first treatment results in the removal of approximately: (i) 47% and 56% of the more viscous Oils A and B respectively, (ii) 61% and 67% of the light Oils C and D respectively, and (iii) 67% of emulsion S, Figure 3.6. However, after nine treatments a maximum value of approximately 95-96% removal of contaminants is achieved, which is comparable to the maximum percentage removal obtained using breast feathers.

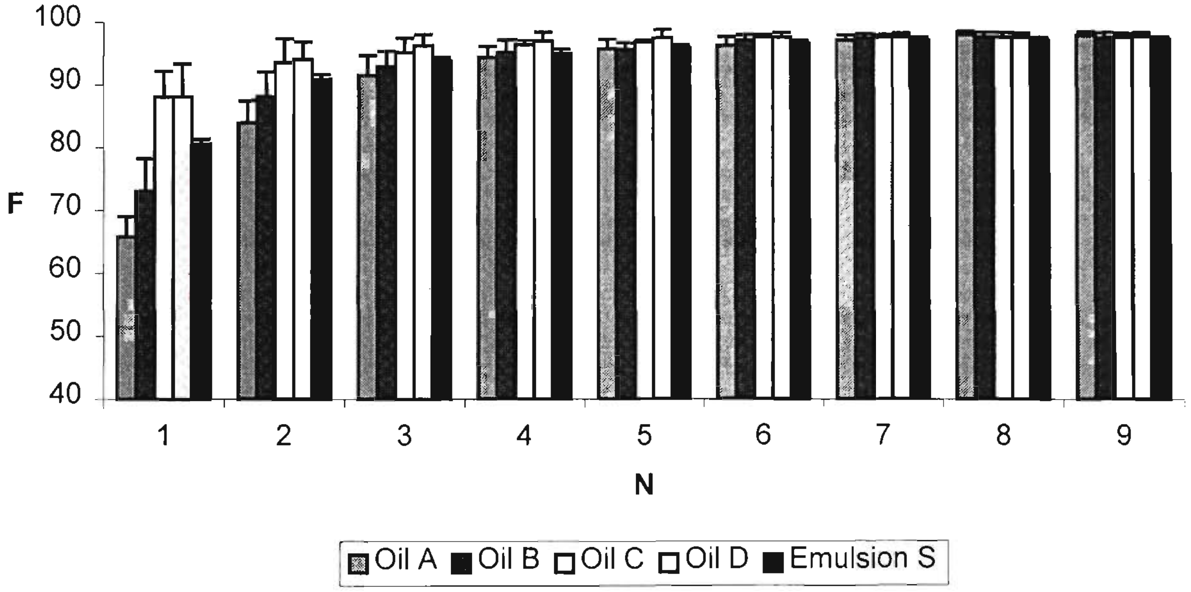

Figure 3.5 : Average percentage by mass of contaminants removed *in vitro* from duck breast feathers, F, after N successive treatments with iron powder and subsequent magnetic harvesting. Error bars represent 95% confidence intervals for 5 replicates. Individual profiles are documented in Appendix 3.6.

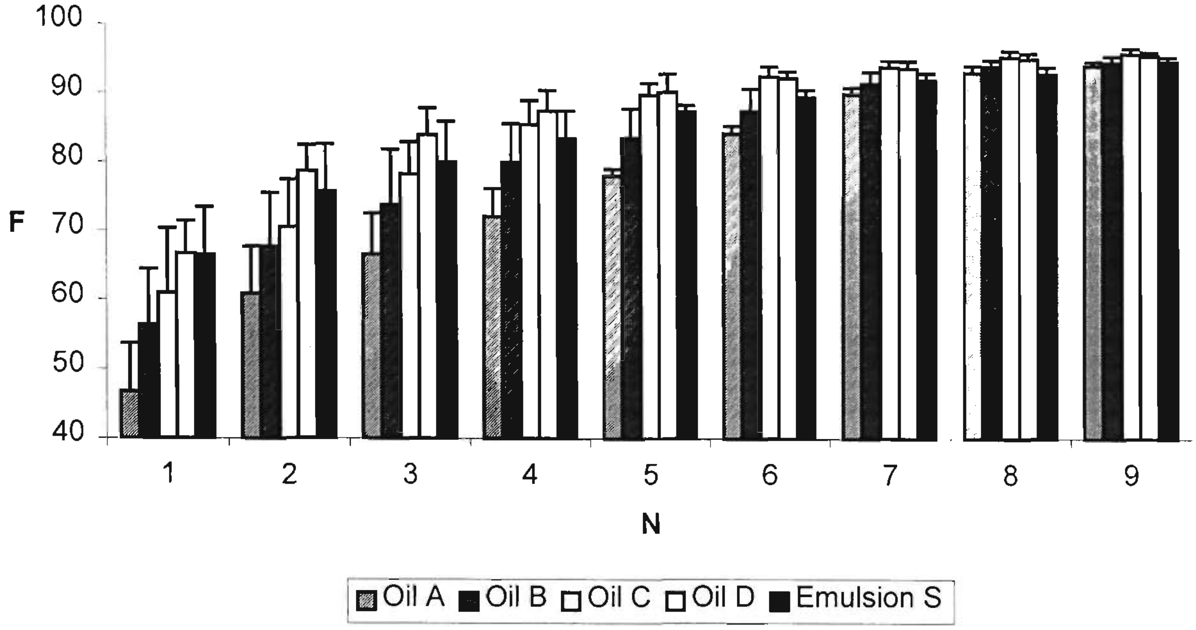

Figure 3.6 : Average percentage by mass of contaminants removed *in vitro* from duck back feathers, F, after N successive treatments with iron powder and subsequent magnetic harvesting. Error bars represent 95% confidence intervals for 5 replicates. Individual profiles are documented in Appendix 3.7.

3.4.2 Penguin Feathers

In the case of penguin breast feathers, the first treatment results in the removal of approximately: (i) 78% and 85% of the more viscous Oils A and B respectively, (ii) 90% of the light Oils C and D, and (iii) 76% of emulsion S, Figure 3.7. In the case of penguin back feathers, approximately: (i) 66% and 71% of Oils A and B, (ii) 87% and 90% of Oils C and D, and (iii) 65% of emulsion S were removed respectively, Figures 3.8.

For all contaminants, subsequent treatments cleansed the feathers with a maximum removal of between 96 and 99% for the two types of feathers. Thus the results suggest that, although in the initial treatments the removal of contaminants from breast feathers is more efficient than that from back feathers, there is little difference in the maximum removal of oil from either breast or back feathers if sufficient treatments are administered.

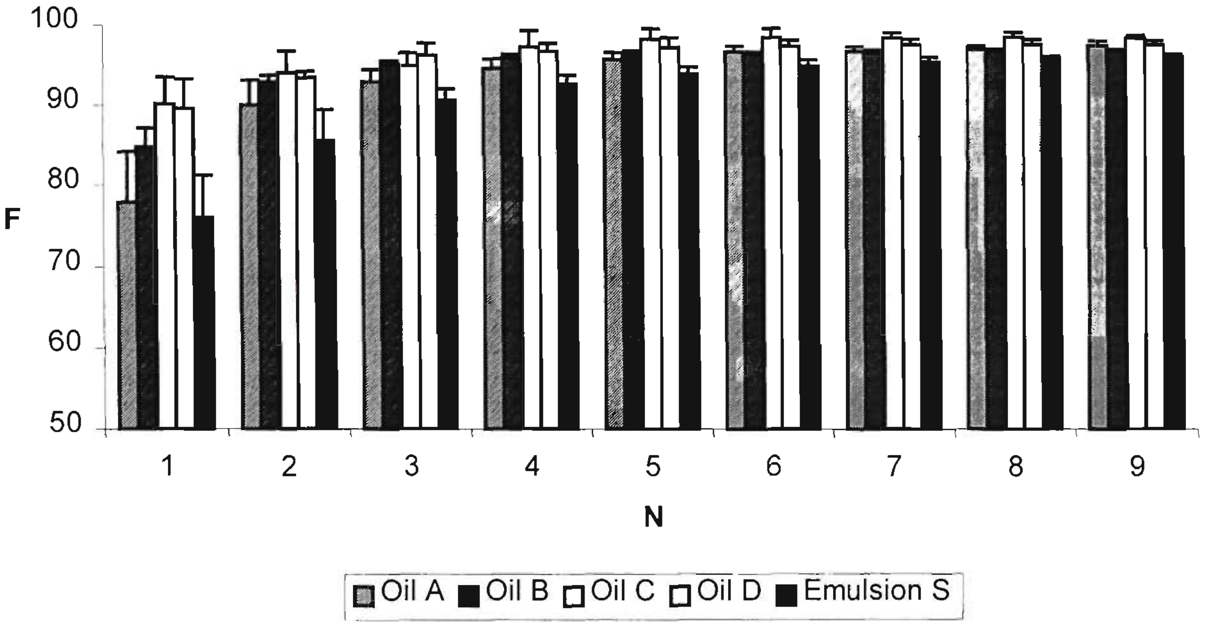

Figure 3.7 : Average percentage by mass of contaminants removed *in vitro* from penguin breast feathers, F, after N successive treatments with iron powder and subsequent magnetic harvesting. Error bars represent 95% confidence intervals for 5 replicates. Individual profiles are documented in Appendix 3.8.

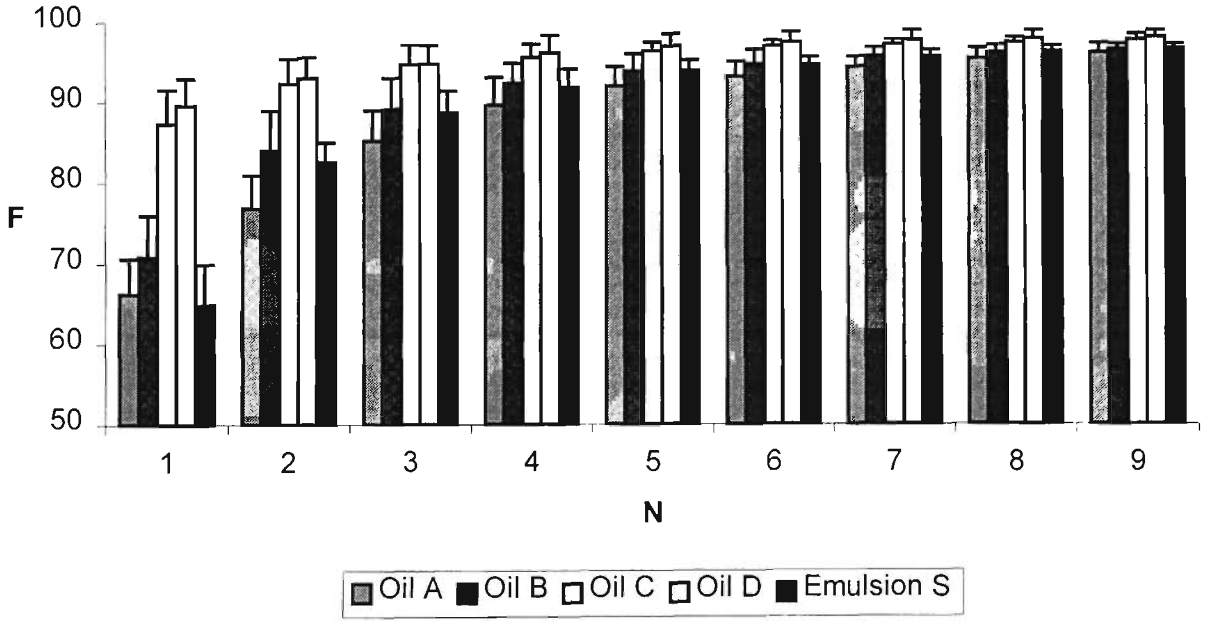

Figure 3.8 : Average percentage by mass of contaminants removed *in vitro* from penguin back feathers, F, after N successive treatments with iron powder and subsequent magnetic harvesting. Error bars represent 95% confidence intervals for 5 replicates. Individual profiles are documented in Appendix 3.9.

3.4.3 Seagull Feathers

In the case of seagull breast feathers, the first treatment results in the removal of approximately: (i) 74% and 76% of the more viscous Oils A and B respectively, (ii) 83% and 84% of the light Oils C and D respectively, and (iii) 72% of emulsion S, Figure 3.9. In the case of seagull back feathers, approximately 65% of Oil A, 72% of Oil B, 77% of Oil C, 83% of Oil D and 76% of emulsion S were removed respectively, Figure 3.10. Again, nine treatments cleanse both breast and back feathers to produce a maximum removal of approximately 98%.

The results suggest that the initial removal of contaminants from the back feathers is slightly less than that of breast feathers. However, after nine treatments there is little difference in the cleansing for both types of feathers.

After nine treatments the percentage removal of contaminants from each feather type is comparable. The comparison of the removal efficiencies between duck, penguin and seagull feathers is discussed in Section 3.6.3.

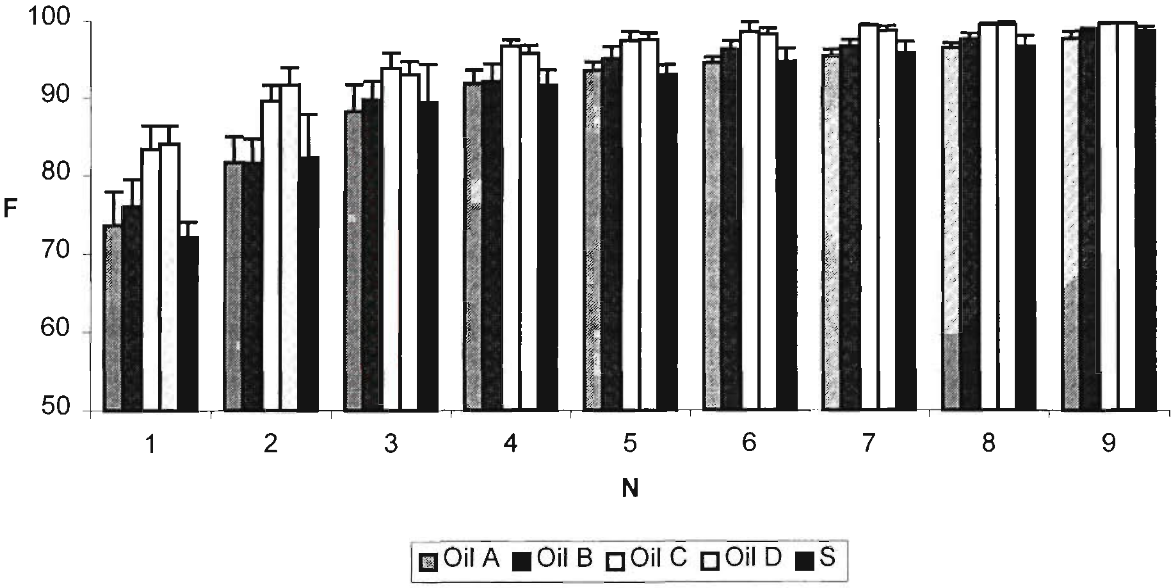

Figure 3.9 : Average percentage by mass of contaminants removed in vitro from seagull breast feathers, F, after N successive treatments with iron powder and subsequent magnetic harvesting. Error bars represent 95% confidence intervals for 5 replicates. Individual profiles are documented in Appendix 3.10.

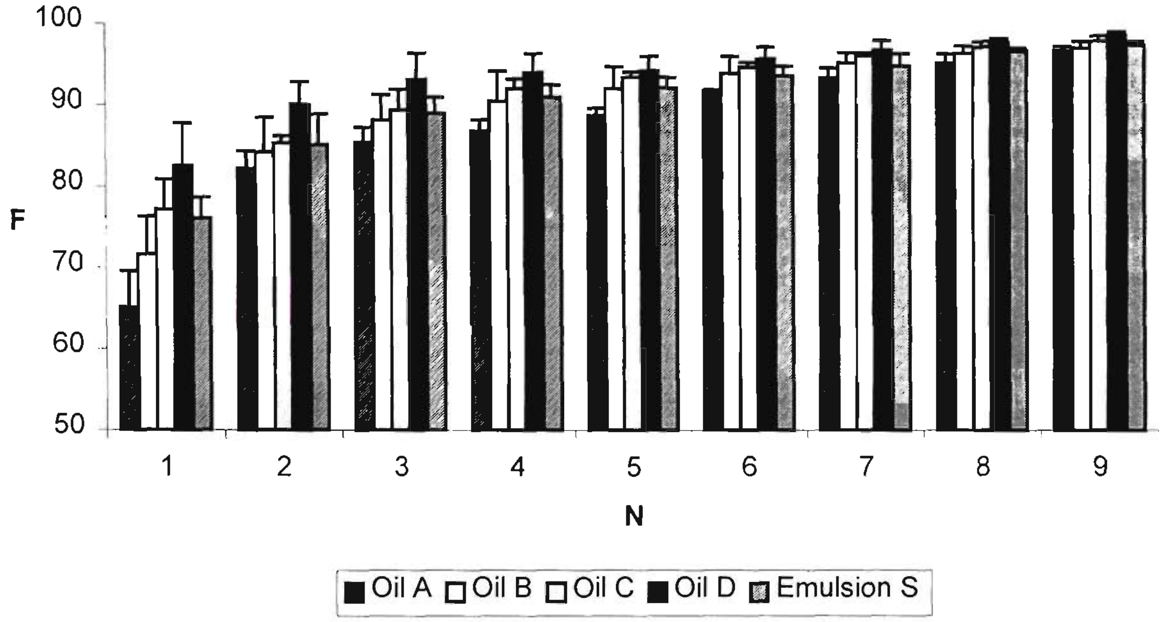

Figure 3.10 : Average percentage by mass of contaminants removed *in vitro* from seagull back feathers after N successive treatments with iron powder and subsequent magnetic harvesting. Error bars represent 95% confidence intervals for 5 replicates. Individual profiles are documented in Appendix 3.11.

3.5 Magnetite as an Alternative Cleansing Agent

An investigation using magnetite as an alternative cleansing agent for feathers was initiated. Magnetite (Fe_3O_4), a natural rock-forming mineral, is a common oxide of iron. It is magnetic and has a specific gravity of 5.2. The mineral is characterised by its black, opaque colour and is generally found near iron deposits. However, alluvial deposits are common throughout Western Australia and Tasmania (Chalmers, 1868). During the natural weathering process, most of the reactive mineral salts are leached out from mineral magnetite thus making it chemically stable and inert under most climatic conditions (Gilluly *et al.*, 1957). The adsorbing and magnetic properties of magnetite have been applied to sewage treatment (Priestley, 1990; Booker *et al.*, 1991), and to the removal of colour and turbidity from water (Anderson & Priestley, 1983). This suggests the use of magnetite as an alternative to iron powder for cleansing oiled feathers.

The histogram in Figure 3.11 shows the percentage by mass of the pick-up of Oils A and C using magnetite. The data show a low initial removal of approximately 16% of Oil A from the oiled feathers, whereas approximately 70% of Oil C is removed. It appears that magnetite is not as effective as iron powder and the data indicate that for the removal of each oil using magnetite, a maximum removal of approximately 93% is achievable compared to approximately 98% for iron powder. Although it is not as effective as iron powder, magnetite still cannot be ruled out as an alternative.

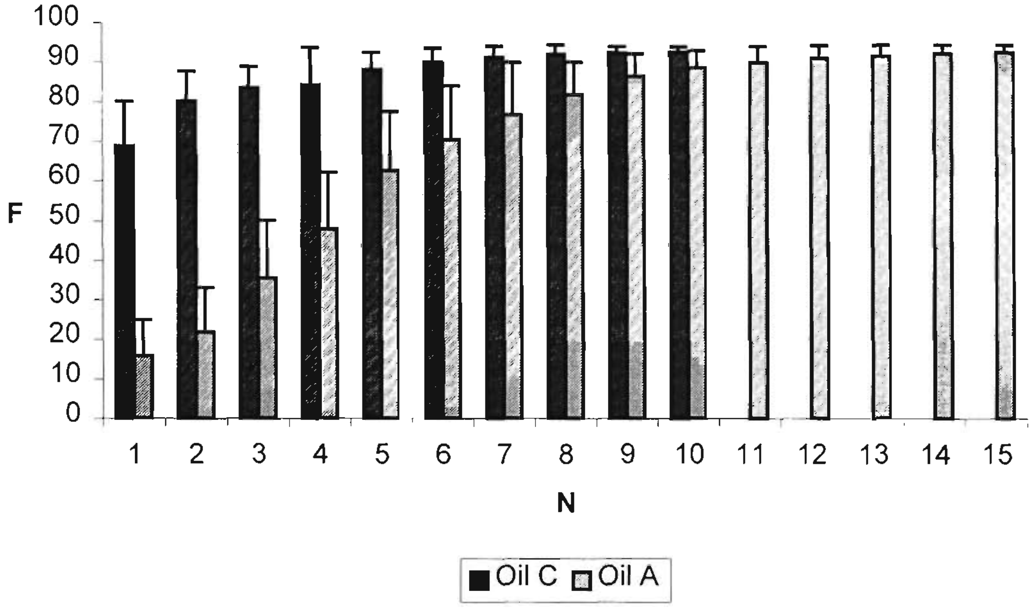

Figure 3.11 : Average percentage by mass of Oils A and C removed from duck breast feathers, F, after N successive treatments with powdered magnetite. Error bars represent 95% confidence intervals for 5 replicates. Individual profiles for powdered magnetite are documented in Appendix 3.12.

3.6 Measuring the Removal Efficiency for the Excess Iron Powder Studies

The efficiency of removal of contaminants from feathers may be determined by considering the plot of F versus N, where F is the percentage by mass of contaminants removed from feathers *in vitro*, and N is the number of treatments. An efficiency parameter, E_3, for *in vitro* removal may be defined by:

$$E_3 = F_o / N_o \tag{3.5}$$

where F_o is the maximum value of F, and N_o is the number of treatments at which this value is attained. This situation is analogous to that previously discussed in Section 3.3.1 where $E_2 = F_c/R_c$ was defined. Ideally, it is desirable to maximize F_o and minimize N_o. Experimentally, for all studies, N = 9 was found to be the number of treatments above which no further significant increase in the value of F was observed. Thus, N = 9 was taken as the number of treatments required to produce a maximum uptake of contaminant.

On the basis of the efficiency parameter E_3 alone, the data in Table 3.3 show that there is little difference in the maximum efficiency for the pick-up for all of the oil systems investigated within each feather type.

Table 3.3 : Efficiency parameter ranges of all oil systems investigated for each feather type.

Feather types		**E_3 values (all oil systems)**
Duck	Breast	10.8-10.9
	Back	10.5-10.7
Penguin	Breast	10.7-10.9
	Back	10.7-10.9
Seagull	Breast	10.8-11.1
	Back	10.8-11.0

However, Figures 3.5-3.10 suggest that there are differences in the *initial* pick-up of contaminants for Oils A, B, C, D and emulsion S for each feather type. Likewise, it is evident that there are differences in the efficiencies of oil pick-up for these oils and emulsion S when $N < 9$.

The mathematical model used previously pertains to the amount of contaminant removed as a function of particle-to-oil ratio, R. However, for *in vitro* studies it was necessary to remove as much oil from feathers as possible and so it was desirable to use excess iron powder to smother the oiled feathers. Thus, in the absence of a theoretical model that relates the amount of contaminant removed to the number of treatments, it was decided to adopt an empirical approach to model the adsorption isotherms. This would give an indication of the relative overall efficiency of oil pick-up for feathers. An empirical equation (3.6) that can be used to fit the typical contaminant uptake curve shown in Figure 3.12 is:

$$F = F_o(1 - e^{-kN}) \qquad (3.6)$$

where k is a constant that determines how effectively the asymptote value F_o is approached.

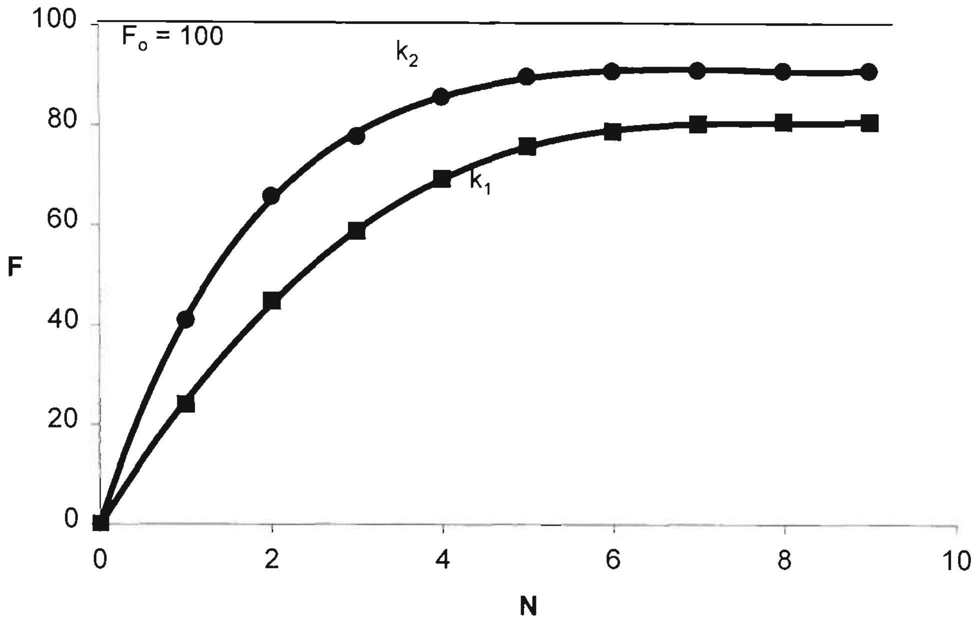

Figure 3.12 : Theoretical plots of F versus N for $F_o = 100$, where: $k_1 = 0.4$ and $k_2 = 0.9$.

Equation (3.6) can be rearranged to give:

$$-\ln (1 - F/F_o) = kN \tag{3.7}$$

Clearly, the greater the value of k, the greater is the efficiency for the oil pick-up. Equation (3.6) can be differentiated to give equations (3.8) and (3.9):

$$dF/dN = F_o k e^{-kN} \tag{3.8}$$

$$(dF/dN)_{N=0} = F_o k \tag{3.9}$$

As with k itself, the product $F_o k$ is indicative of the efficiency of contaminant removal and may be used to establish the relative order of removal efficiencies of the different oils. This empirical model was also used to determine the efficiency of oil pick-up for *in vitro* duck, penguin and seagull breast and back feathers.

The data presented in Appendices 3.13 and 3.14 were used to plot the removal of each oil for both duck breast and back feathers respectively. Plots of $-\ln(1 - F/F_o)$ versus N for the respective removal of Oil A from breast feathers and Oil C from back feathers using iron powder are shown in Figure 3.13. Similar plots for the removal of other oils are presented in

Appendices 3.15 and 3.16. Values of the gradient, k, calculated from linear regression analyses, and the product kF_o for five different contaminants are listed in Table 3.4. For the light Oils C and D, higher values of k and kF_o were obtained, reflecting a greater efficiency of oil pick-up compared to the more viscous Oils A and B and emulsion S.

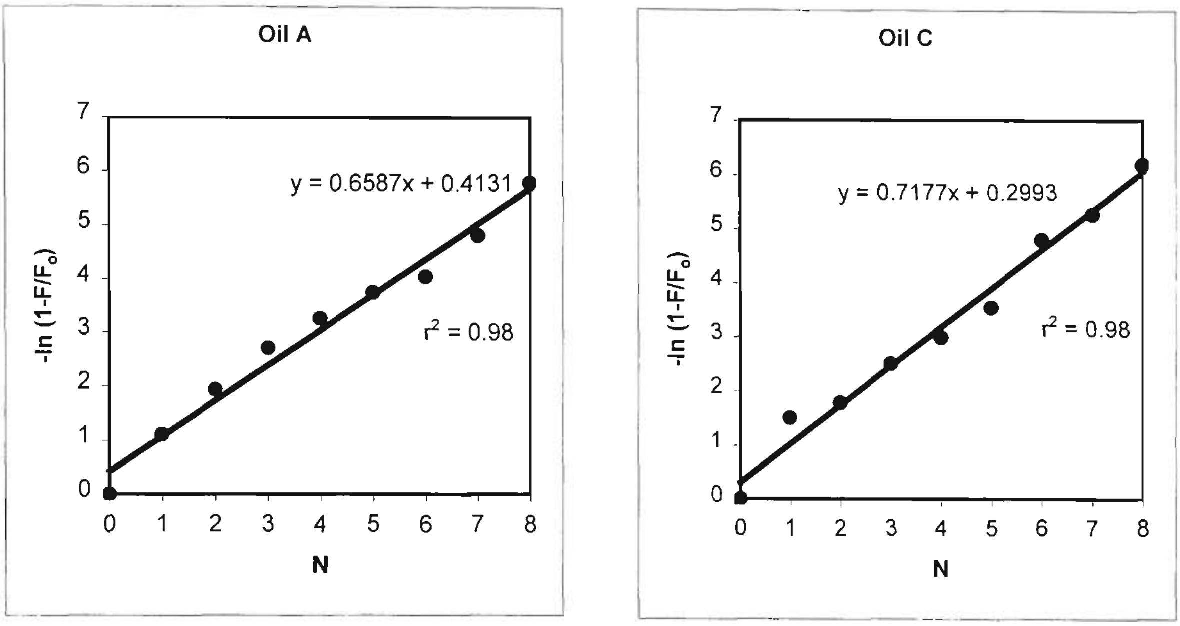

Figure 3.13 : Plots of $-\ln(1 - F/F_o)$ versus the number of treatments, N, for *in vitro* duck breast and back feathers, contaminated with Oil A, and Oil C respectively.

Table 3.4 : Values of kF_o for *in vitro* duck feathers.

	Oil A	Oil B	Oil C	Oil D	Emulsion S
Viscosity/cp	425.5	115.5	11.4	13.0	-
k (breast)	0.66	0.68	0.87	0.90	0.74
k (back)	0.59	0.62	0.72	0.76	0.63
kF_o(breast)	64.42	66.30	84.74	87.84	71.93
kF_o (back)	56.10	58.90	69.40	73.11	60.00

3.6.1 Relationship between Efficiency Parameters

A relationship between the empirical and mathematical models was investigated. The values of α_o and kF_o for both duck breast and back feathers are listed in Table 3.5.

Table 3.5 : The relationship between α_0 and kF_0 for duck breast and back feathers.

Contaminants	α_0(breast)	k (breast)	kF_0 (breast)	α_0(back)	k (back)	kF_0 (back)
A	2.64	0.66	64.55	2.41	0.59	56.05
B	2.85	0.68	66.30	2.70	0.62	59.02
C	3.40	0.87	84.83	2.92	0.72	69.41
D	3.61	0.90	87.84	3.26	0.76	73.11
Emulsion S	3.18	0.74	71.93	2.82	0.63	60.00

A plot of kF_0 against α_0 for all of these systems is presented in Figure 3.14. The linear relationship between kF_0 and α_0 suggests that the empirical model is a reliable indicator of the efficiency of oil pick-up.

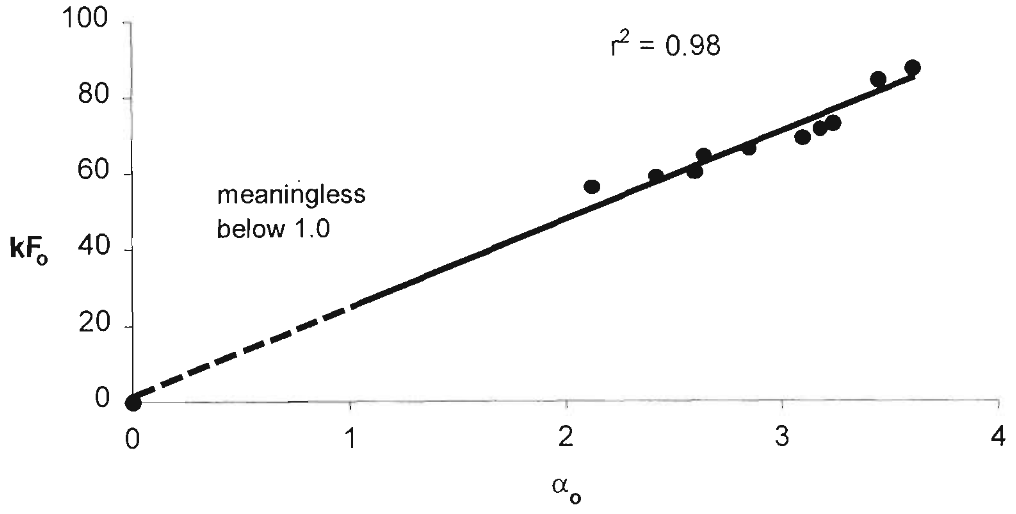

Figure 3.14 : A plot of kF_0 versus α_0 for *in vitro* duck breast and back feathers.

The empirical model was then applied further to assess the efficiency of oil pick-up for both *in vitro* penguin and seagull feathers. A similar trend to that shown by duck breast and back feathers was observed for penguin and seagull breast and back feathers. For the more viscous Oils A and B, lower values of k and kF_0 were obtained, reflecting a lower efficiency of oil pick-up compared to the less viscous Oils C and D and emulsion S. Values of the product kF_0 calculated from linear regression analyses of plots of $-\ln(1 - F/F_0)$ versus N for five different contaminants are shown in Table 3.6. The data from which these values were derived, are presented in Appendices 3.17-3.20.

Table 3.6 : Values of kF_0 for *in vitro* penguin and seagull feathers.

		Oil A	**Oil B**	**Oil C**	**Oil D**	**Emulsion S**
	Viscosity/cp	425.5	115.5	11.4	13.0	-
Penguin	k(breast)	0.57	0.67	0.80	0.83	0.63
	k(back)	0.53	0.64	0.70	0.72	0.62
	kF_0(breast)	55.80	65.12	79.12	80.36	60.86
	kF_0 (back)	50.93	61.70	68.39	70.56	59.89
Seagull	k(breast)	0.48	0.51	0.70	0.63	0.52
	k(back)	0.42	0.51	0.60	0.57	0.52
	kF_0(breast)	46.90	50.29	69.79	62.81	51.32
	kF_0 (back)	40.82	49.73	59.04	56.49	50.91

3.6.2 Further Discussion on the Empirical Model

Both the parameters k and the product kF_0 provide an indication of the efficiency of oil pick-up. The relationship between k and kF_0 was investigated by plotting values of kF_0 against k for duck, penguin, and seagull breast and back feathers, Figure 3.15. The observed linearity between k and kF_0 arises by virtue of the fact that the value of the variable F_0 remains consistent across all of the systems investigated and confirms that either of k or kF_0 can be used as a reliable indicator of efficiency.

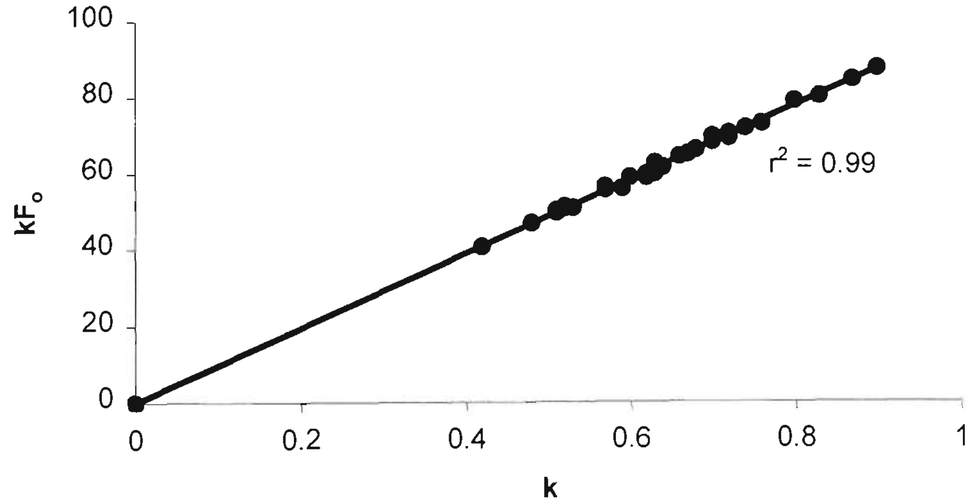

Figure 3.15 : A plot of kF_0 versus k for *in vitro* feathers. The data are documented in Appendix 3.21.

3.6.3 Using the Empirical Model to Compare Removal Efficiencies

3.6.3.1 Terminology Used in This Study

Prior to the comparison of the percentage by mass of contaminant *in vitro* removed from feathers, it is necessary to define the abbreviations used in these studies. These are listed in Table 3.7.

Table 3.7 : Terminology used for feather types.

Abbreviation	Feather types
Fbs (Pn)	breast Feathers (Penguin)
Fbk (Pn)	back Feathers (Penguin)
Fbs (Du)	breast Feathers (Duck)
Fbk (Du)	back Feathers (Duck)
Fbs (Sg)	breast Feathers (Seagull)
Fbk (Sg)	back Feathers (Seagull)

The empirical model was used to compare the efficiency of the *in vitro* removal of contaminants from: (i) different feather types from the same bird (i.e. breast and back) and (ii) the same feather type from different birds (i.e. breast of duck, penguin and seagull).

3.6.3.2 Different Feather Types on Same Birds

A novel method for comparing parameters on x and y axes in the present work has been adapted from that developed by Bigger *et al.*, (2001), for comparing the effects of additives in polymers. A plot of kF_0 (breast) versus kF_0 (back) is shown in Figure 3.16. In this plot the oblique line where kF_0 (breast) = kF_0 (back), represents a data pair where there is no difference in the efficiency of oil pick-up between breast and back feathers. The regions above and below this line are regions where the efficiency is greater for breast or back feathers respectively. The perpendicular distance of a given point from the oblique line indicates the magnitude of the difference and this, when used in conjunction with coordinates of the point, enables a comparison of the relative efficiencies to be made. Furthermore, the method enables systems of high and/or low efficiencies to be readily identified. Clearly, the points that lie furthest from the origin correspond to systems of highest efficiencies.

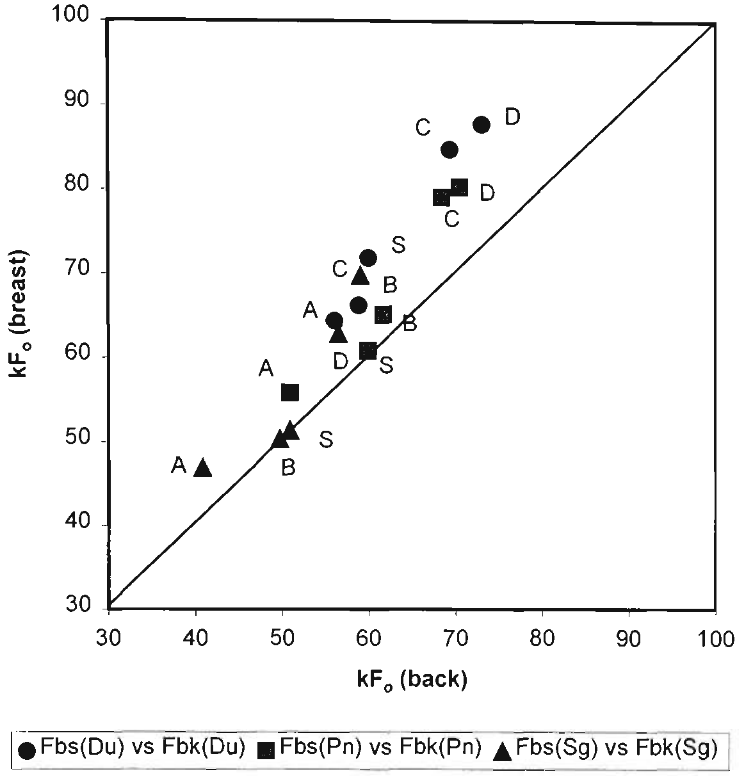

Figure 3.16 : A comparison of contaminant removal between *in vitro* duck, penguin and seagull breast and back feathers. The letters A, B, C, D, and S denote Oils A, B, C, D, and emulsion S respectively.

For most systems, the removal of oil from duck, penguin and seagull breast feathers is, in general, more efficient than the removal from back feathers. However, for Oil B and emulsion S there is little difference in the removal efficiency of contaminants from seagull breast and back feathers. Likewise, there is little difference in removal of emulsion S from penguin breast and back feathers. The kF$_0$ values for duck feathers are furthest from the origin indicating that for the system studied the removal of oil from duck feathers is the most efficient, followed by penguin and seagull feathers.

3.6.3.3 Same Feather Type on Different Birds

The empirical model has been extended to compare the *in vitro* removal of oil from the same feather type on different birds (e.g. breast feathers of duck, penguin and seagull; back feathers of duck, penguin and seagull). Figure 3.17 shows that, for all oils, the removal of oil from duck breast feathers is more efficient than its removal from penguin and seagull breast feathers. Similarly, for all oils, the removal of oil from penguin breast feathers is more efficient than its removal from seagull breast feathers. The kF_0 values for duck feathers are furthest from the origin indicating that the overall removal of oil from duck feathers is the most efficient, followed by penguin and seagull feathers. The kF_0 values associated with the less viscous Oils C and D are furthest from the origin, indicating that the overall removal of these oils from feathers is the more efficient than the other oils.

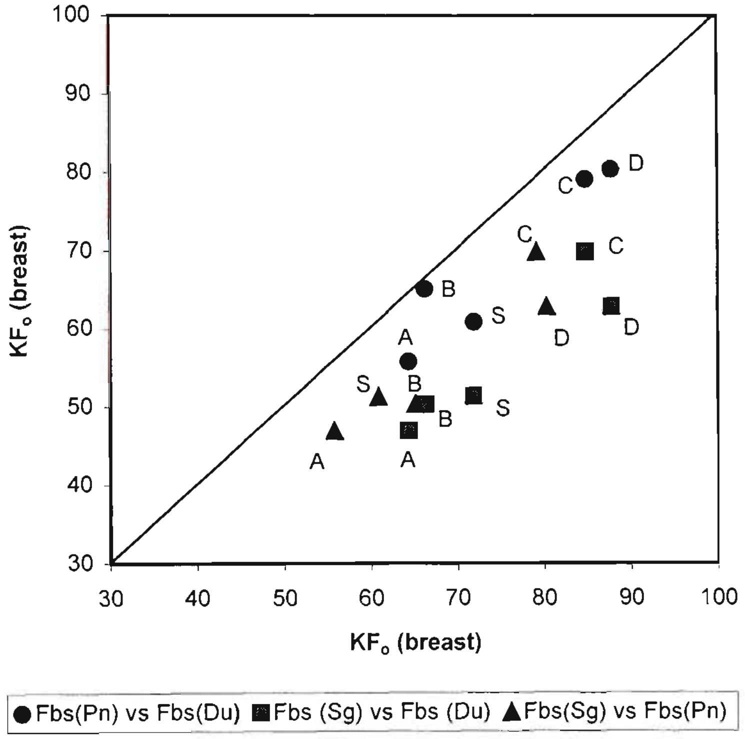

Figure 3.17 : A comparison of the efficiency of oil pick-up by iron powder for *in vitro* duck, penguin and seagull breast feathers. The letters A, B, C, D, and S denote Oils A, B, C, D, and emulsion S respectively.

Figure 3.18 shows that for Oil C and emulsion S there is little difference in the removal of oil from the back feathers of duck and penguin. For Oils A and D, the removal of oil from duck back feathers is more efficient than its removal from penguin back feathers. However, for Oil B its removal from penguin back feathers is slightly more efficient than its removal from duck back feathers. For all systems, the removal of oil from duck back feathers is, in general, more efficient than its removal from seagull back feathers. Likewise, for all systems, the removal of oil from penguin back feathers is more efficient than its removal from seagull back feathers.

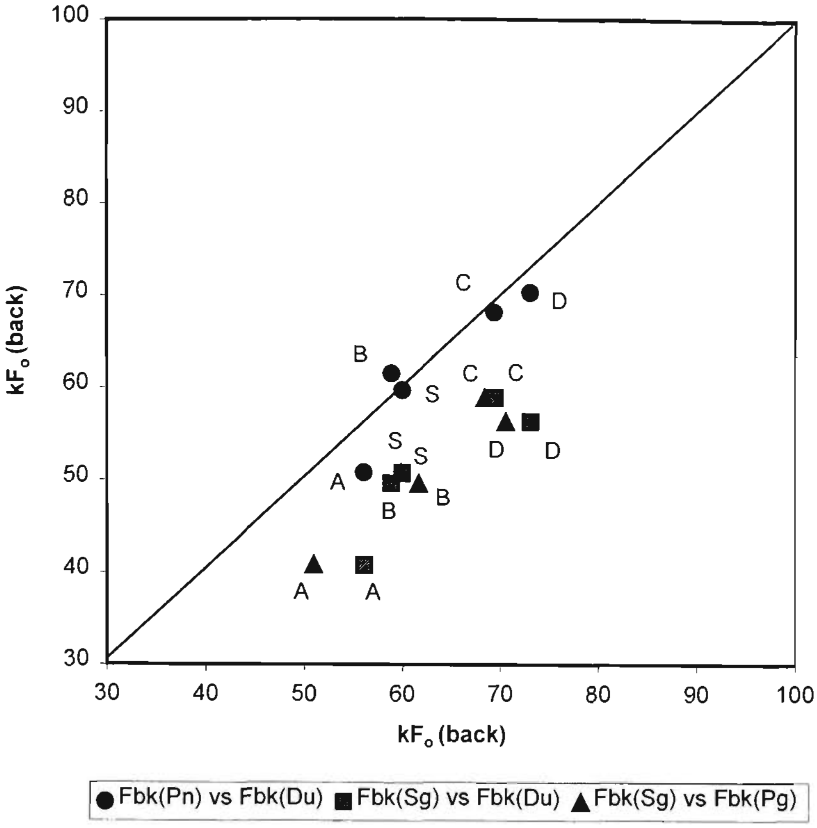

Figure 3.18 : A comparison of the efficiency of oil pick-up by iron powder for *in vitro* duck, penguin and seagull back feathers. The letters A, B, C, D, and S denote Oils A, B, C, D, and emulsion S respectively.

3.6.4 The Relationship between Removal Efficiency and Viscosity

Figure 3.18 shows that the removal of oil from the duck feathers is more efficient for the less viscous oils than for the more viscous oils. To investigate further the effect of viscosity on efficiency of oil removed, it was decided to test whether a correlation exists between these two parameters. A plot of the kF$_0$ for duck feathers versus the reciprocal of the viscosity of the oils is shown in Figure 3.19. The data for the gradient, intercepts and linear regression coefficient (r^2) for duck, penguin and seagull feathers are listed in Table 3.8. The viscosity measurement for emulsion S, could not be determined because of the difficulties in sustaining its stability for a time sufficient to perform the viscosity measurement.

The data from Table 3.8 suggest that the efficiency of the removal of oil from breast feathers is more sensitive to changes in oil viscosity than back feather for each of the three types of bird tested. The intercept values correspond to the theoretical situation where the viscosity is infinite. Thus, the intercepts can be used to indicate the relative order of efficiency of removal of highly viscous oils from the feathers of the three types of birds. The efficiency of removal of oil from duck feathers is greater than that found for penguin feathers, which in turn, is greater than that found for seagull feathers. The gradient values reflect how sensitive the efficiency of oil pick-up is to changes in the viscosity of the oil. In the extreme cases the seagull back feathers show the least sensitivity to changes in viscosity whereas duck breast feathers show the greatest sensitivity. The linearity between kF_o and $1/\eta$ indicates that, in general, the efficiency of oil pick-up increases as the viscosity decreases for *in vitro* duck, penguin and seagull feathers.

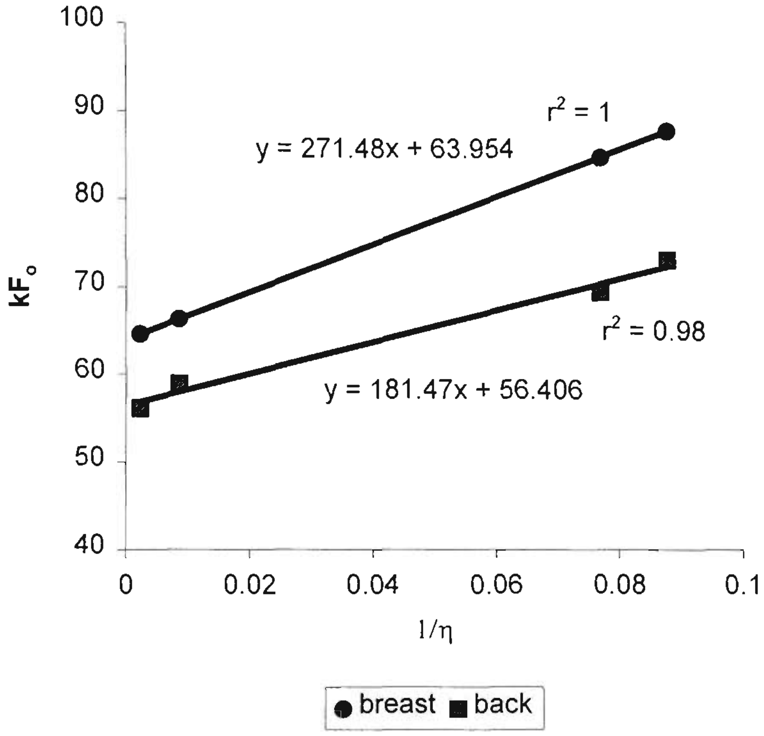

Figure 3.19 : The efficiency of oil pick-up versus reciprocal of the viscosity, $1/\eta$ for *in vitro* duck feathers

Table 3.8 : Effects of viscosity on oil pick-up for duck, penguin, and seagull feathers.

Feather types		Gradient, $d(kF_o)/d(1/\eta)$	Intercept, $(kF_o)_{\eta=\infty}$	r^2
Duck	breast	271.5	64.0	1.00
	back	181.5	56.4	0.99
Penguin	breast	251.5	59.1	0.91
	back	176.7	55.1	0.80
Seagull	breast	235.6	47.1	0.97
	back	167.5	44.2	0.84

3.7 Conclusions

Iron powder was applied to the removal of contaminants from *in vitro* duck, penguin and seagull feathers. The high removal of five different contaminants from these feathers demonstrates the potential of using iron powder as a cleansing agent. It was found that there is little difference in the maximum pick-up for the viscous and light oils and the sea water/oil emulsion. However, there are differences between these contaminants with regard to the initial pick-up. The less viscous oils are initially removed with slightly higher efficiency compared to the more viscous oils and the emulsion. Interestingly, the order of the efficiency of pick-up is reversed when the contaminants are removed from feathers as compared with a glass substrate (petri dish).

Another approach, more relevant to the field situation, is to use excess iron powder to remove contaminants from feathers. The initial removal of the light oils and the emulsion is higher than that of the more viscous oils. However, for all contaminants there is little difference in the maximum oil removal after nine treatments. Thus the ultimate removal of contaminants from oiled feathers appears to be independent of the oil type. Furthermore, the method appears to be equally effective in the presence of seawater. In the absence of a purely theoretical model that relates the amount of contaminant removed to the number of treatments, an empirical model was adopted. A linear relationship between the efficiency parameter kF_0 derived from this model and α_0 suggests that the empirical model is a reliable indicator of the efficiency of oil pick-up. Using the efficiency parameter kF_0, it was found that: (i) the light oils are more efficiently removed than the more viscous oils and the emulsion, and (ii) the breast feathers are more efficiently cleansed than the back feathers.

A graphical method was adapted to compare the efficiency of the removal of contaminants from: (i) different feather types from the same bird and (ii) the same feather type from different birds. The results indicate that, for most oils, the removal of contaminants from duck, penguin and seagull breast feathers is more efficient than their removal from back feathers. Moreover, for all oils, the removal of contaminants from duck breast feathers is more efficient than their removal from penguin and seagull breast feathers. The relationship between efficiency and the viscosities of contaminants was also investigated. It was found that, in general, the efficiency of oil pick-up increases as the viscosity decreases for *in vitro* duck, penguin and seagull feathers.

3.8 References

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Chapter 4 Testing on Duck and Penguin Carcasses

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4.1 Introduction

In order to extend the *in vitro* studies to the field, the next logical step was deemed to be the testing of the protocol on the plumage of carcass models. An association was formed with the Phillip Island Nature Park (PINP), Victoria, Australia, in order to pursue this further. Phillip Island is internationally known for the 'Fairy Penguin Parade', and is a major nesting ground for the Little Penguin (*Eudyptula minor*). Currently there are approximately 26,000 Little Penguin in the vicinity of Phillip Island (Healy, personal communication).

The mortality of Little Penguin on Phillip Island has been well-documented (Obendorf & McColl, 1980; Harrigan, 1992). The primary cause is due to road accidents and predation. A relatively small number are the victims of chemical contamination and the PINP personnel have developed highly effective methods and facilities for dealing with these casualties. Other animals are also treated at the PINP animal rehabilitation facility including wallabies, koalas, possums, shearwaters, seals, albatross, gannets, and seagulls. At PINP, the method used for the removal of oil and chemical contamination from feathers is based on conventional detergent techniques (Jessop & Healy, 1997). From 1994 to 2000 the number of Little Penguin treated for oil contamination and the number of Little Penguin treated for fox bites, starvation and heat stress at the PINP animal rehabilitation facility is presented in Table 4.1.

Table 4.1 : The number of Little Penguin treated annually at the animal rehabilitation facility of PINP from 1994 to 2000.

Year	Little Penguin treated for oil contamination / annually	Little Penguin treated for other conditions / annually
1994-1995	118	106
1995-1996	301[1]	205
1996-1997	24	128
1997-1998	36	142
1998-1999	23	92
1999-2000	236	110

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[1] Includes 270 Little Penguin from the "Iron Baron" oil spill incident (Hull *et al.*, 1998). Data supplied by Margaret Healy, Technical Officer (Rehabilitation), PINP.

4.1.1 Effects of Oil on Wildlife

One of the environmental consequences of an oil spill is the contamination of marine animals and birds (Michael, 1977). The effects of such contamination on birds include the obvious matting of plumage and consequent loss of heat, causing hypothermia (Clark & Gregory, 1971; Jenssen & Ekker, 1989). In many instances, ingestion of oil by preening can prove fatal (Hartung & Hunt, 1966). The problem is compounded when the petroleum products are toxic, such as diesel oil, which contains a number of harmful aromatic components (Hartung & Hunt, 1966; Peakall, *et al.*, 1982). Some toxic components can also be absorbed through the skin (Perry, *et al.*, 1978). It has been reported that a patch of oil about one inch in diameter is sufficient to break down the insulation of the plumage and expose the bird to hypothermia (Dennis, 1959). These considerations argue for a rigorous initial clean-up (stabilization) of the bird, which should ideally involve removal of the bulk of the contaminant. The removal of the bulk of the contaminant is currently reserved for later treatment since it is not practical to transport the conventional detergent-based cleansing equipment to the site. In a minority of cases (including PINP) the treatment centre is close enough to the site of an incident that the distinction between initial stabilisation and later treatment is not such an important consideration. However, there remains a real need for technology which can be used in the field to remove the bulk of the contamination upon first encountering the bird.

4.1.2 Current Stabilisation Protocols for Oiled Birds

Current practices in stabilisation procedures may vary according to the nature of the incident. Established wildlife rescue organisations have existing protocols, which vary to some degree. Some of these organisations have developed standard protocols for stabilising or cleansing oiled birds (Gilbert, 1999; Miller, 1999). Washing and rinsing protocols used by various rehabilitation organizations are described in an Addendum at the end of this thesis. There are a number of factors which influence whether the stabilisation protocols are carried out on site or primarily at a treatment centre. The factors include: (i) distance to a treatment centre, (ii) manpower requirements, and (iii) availability of equipment on the site.

General guidelines currently adopted for stabilising oiled birds are: (i) physical examination, (ii) removing excess oil, (iii) administrating rehydration fluid, (iv) administrating an activated charcoal suspension, (v) keeping the bird warm, and (vi) transporting it to a treatment centre.

Stabilisation of an oiled bird should ideally commence within 8-24 hours of when oil has come into contact with the bird (Miller, 1999). Physical examination is performed on all oiled birds.

Severely contaminated birds are given first aid which includes cleaning their eyes and mouth. Excess oil is removed from the body with an absorbent cloth (Miller, 1999). If the birds are severely dehydrated, rehydration solutions are administered. A rehydration solution essentially consists of glucose, salts and other mineral ingredients. This is followed by administering an activated charcoal suspension to coagulate and absorb oil in the stomach (Holcomb & Russell, 1999). Certain organizations use paper or woollen ponchos to keep the contaminated birds warm and to prevent further poisoning by preening (Harris & Smith, 1977; Stocker, 2000). But this is not the standard care procedures for most wildlife care organizations. The birds are then transported in cardboard boxes, containing no more than three birds, to the treatment facility for further treatment. If the journey is longer than one hour, hot water bottles may be used to prevent hypothermia (Stocker, 2000).

Upon arrival at the treatment centre all birds are moved to warm surroundings. They are again inspected for signs of stress and hypothermia. Most birds remain dehydrated upon arrival at the treatment facility and are usually re-administrated a rehydration solution, followed by an activated charcoal suspension (Schmidt, 1997; Stocker, 2000).

The cleansing of live, oiled birds by conventional methods typically involves the use of detergents and a large amount of warm water (35 to 40°C). If a detergent is unavailable, dishwashing liquid has been found to be a suitable alternative.

Detergent solution 1% (v/v) is prepared in warm water just before the cleansing of the oiled bird. Usually, two persons only are involved in the cleansing process. A wet sponge containing the warm solution is gently pressed onto the oiled feathers and the feathers are gently rubbed or pushed downward. This cleansing process is repeated until there is no visible evidence of oil on the bird. This can be inspected by lifting the feathers from the most contaminated area to ensure that the oil has been cleansed right throughout the plumage. In some treatment facilities, a machine can be used for washing oiled birds without unnecessary handling (Stocker, 2000). Here, a bird in a standing position is placed in a cage with opened wings while the head is kept outside. The cage is then placed into a tank in which cleansing and rinsing process can proceed. The cleansing solution and rinsing water are programmed to suit particular birds. This process is similar to hand-washing an oiled bird but the entire cleansing process only takes 10 min, a fraction of the time normally taken. However, some limitations associated with this bird washing machine include cost, and transportation problems due to the bulkiness of the machine. Moreover, the sponge and bird washing machines are not the techniques used in most places around the world and they are not the techniques being incorporated into the international standards.

The initial cleansing process does not exceed 15 min to avoid causing stress to the bird. Any remaining oil can be removed at subsequent washing sessions. The bird is then rinsed in a container of warm water. It is important to rinse the bird thoroughly to prevent any detergent residue being left on the bird. The detergent residue may cause wetting of the feathers and thus contribute to the mortality rate when the birds are released (Clark & Gregory, 1971; Perry *et al.*, 1978). Furthermore, the detergent dissolves the bird's natural oils subsequently hindering its rehabilitation (Bryndza, *et al.*, 1991).

A follow-up program of waterproof testing for the bird is required. At regular intervals, the cleansed bird is placed in a swimming pool filled with water to observe its water buoyancy and reactions. The outer feathers are lifted to check the down feathers. If the down feathers are dry and the bird can stay in water for more than 2 h without sign of panic, the feathers are considered to be waterproof and it is ready for release.

Despite some success in treating contaminated birds, it has been suggested in Germany that oiled wildlife be euthanized rather than rescue and rehabilitation (Klinkhart, personal communication). Euthanasia may be considered a more humane option to prevent the prolonged suffering of contaminated wildlife.

4.1.3 Stabilization and Treatment Protocols Used at PINP

The treatment facility of PINP is so close to the site of many incidents that initial stabilisation is mainly carried out at the animal rehabilitation facility. Its close proximity to the foreshore of Phillip Island enables the oil-contaminated birds, especially penguins, to be transported to the treatment facility for stabilisation and washing without delay. Cardboard boxes are used for transporting penguins to the facility. The stabilisation and treatment of oiled penguins are similar to the existing standard stabilisation and treatment protocols described previously, but vary to some degree. The procedure is summarised as follows: When oiled penguins are rescued around their nestling place, they are placed with no more than three birds in a carton. The birds are then transported to the treatment facility. Upon arrival at the treatment facility the birds are moved to warm surroundings. They are inspected for signs of stress and hypothermia and heaters are used to warm up chilled birds. The very weak and stressed penguins are dressed with woollen ponchos (Figure 4.1) prior to the stabilization and cleansing. It is recommended that protective gloves be worn at all times during handling of birds.

All penguins are administrated a rehydration solution prepared from Vy'trate^{TM} concentrate (Dover, Jurox Pty. Ltd., Silverwater, NSW 2128, Australia). The solution is prepared by diluting 5 mL of Vy'trate concentrate with 45 mL of luke-warm water. A flexible plastic tube is gently fed down the bird's throat, close to the stomach. A 50 mL syringe is connected to the tube and is used to administer the Vy'trate™ solution, Figure 4.2. The Vy'trate™ solution is administered twice per day until the penguin is eating 150-250 g of fish per day, mainly pilchard.

Figure 4.1 : Oil-contaminated penguin "dressed" in a woollen poncho.

Figure 4.2 : Administering the rehydration solution to an oil-contaminated penguin.

Each bird is also fed with a Tympanyl™ formulation, (Internet Australia Pty. Limited, Castle Hill, NSW 2154). Tympanyl™ is a vegetable oil which emulsifies the ingested oil (Healy, personal communication). Following this treatment the bird is then fed with four fish, twice a day. When the penguin is not under-weight and appears calm, washing may then commence. The method of washing contaminated penguins at PINP is similar to the method described previously. Here, DivoPlusV2^{TM} detergent (supplied by Diversey (A/Asia) Pty. Ltd., Cambellfield, Victoria, Australia) has been selected after a process of trial and error, as the optimum cleansing agent. If DivoPlusV2^{TM} is unavailable, Sunlight^{TM} (Lever Rexona, Australia) dishwashing liquid has been found to be a suitable alternative. Two persons are required to wash each bird. Normally 20 min is the maximum time permitted to carry out a washing session of the bird. However, if the penguin shows signs of stress, washing is immediately terminated.

The cleansing process is repeated until all traces of oil are removed from the penguin. In general, the washing sessions range from a few days to a few weeks depending on the condition of the bird and the severity of the contamination. No attempt is made to replenish the preening oils of the penguin. According to Naviaux & Pittman, (1973) the totally cleansed feathers are water-repellent, and the natural oils appear to return to the feathers, mostly through the preening process. The time taken to regain waterproofing depends on the extent of oil contamination and efficiency in washing process. The detailed stabilisation and treatment methods used at PINP are documented elsewhere (Jessop & Healy, 1997).

4.1.4 Bird Rescue Logistics

The logistics of bird rescue at PINP represents close to a "best case" scenario. Here, initial treatment and stabilisation can effectively be carried out at the treatment centre itself. However, many oil spills occur in remote areas (Piatt *et al.*, 1990). During the rescue of contaminated wildlife, it may take hours or even days to transport these to treatment centres. Because of the long delay, many contaminated animals and birds perish between initial stabilisation and treatment at a rehabilitation facility (Bishop, 1990; Mignucci-Giannoni, 1999). For example, an oil spillage from the "Sea Empress" occurred in February 1996, resulting in the discharge of approximately 72,000 tonnes of crude oil into the seas around the coast of South-West Wales, United Kingdom. Most of the birds died because of the delay in transporting them to other parts of United Kingdom for treatment.

Often many birds have to endure a significant loading of contaminant until arrival at a treatment facility. For example, in 1988, a 231,000-gallon oil spill on the shores of Washington State killed more than 4,000 seabirds. About 3,700 birds were admitted to the Neah Bay treatment centre. When the birds arrived at the treatment centre, many of them were coated with oil a quarter to a half inch thick (Bishop, 1990).

Therefore, in general, time is of the essence when rescuing birds, with a rapid, initial removal of contaminant being an important consideration. It may be argued that initial stabilisation of contaminated birds is crucial to achieving high survival rates. The conventional detergent-washing technique requires an abundant supply of clean running water and produces an equal amount of soapy, oily wastewater. This is not practical as part of the initial stabilisation process as the birds have to be transported to the treatment facility where all the necessary equipment is in place. The delay in the treatment process could be critical in the survival of victims especially where the contaminant is toxic. Thus in developing new protocols, the criteria mentioned in Section 3.1.1 need to be considered.

4.2 Application of Magnetic Particle Technology to the Cleansing of Oiled Birds

4.2.1 Preliminary Tests on Penguin Carcasses

All experiments conducted so far were done *in vitro* on feather clusters. A carcass model study in collaboration with the PINP was initiated. Preliminary tests on the plumage of bird carcasses were carried out to serve as a guide for the development of a methodology in this regard.

Little Penguin (*Eudyptula minor*) which had been killed by cars or predation were found to have their plumage in good condition. Both breast and back feathers suffered little damage and were ideal for field model studies. Such carcasses were stored in a freezer at -20 °C prior to being studied. The animal carcasses being investigated were thawed birds having masses between 0.42 kg to 1.88 kg. Both breast and back feathers were examined.

A thawed penguin was weighed (w_1) on a top-loading balance. A quantity of oil was carefully poured on the breast/back feathers of the whole-penguin, Figure 4.3, and the bird was re-weighed (w_2). Iron powder was applied to the oiled feathers and rubbed in. The feathers were immediately stroked and stripped with a magnetic device, Figure 4.4. The penguin was re-weighed (w_3). The application of iron powder and the magnetic stripping procedure were repeated up to 9 times until the feathers appeared to be cleansed. Less time was required during each subsequent cleansing process as less oil remained on the feathers. The entire cleansing process took about 20 min in this prototype operation. We were not seeking to optimize the time at this stage, rather the emphasis was on method testing and development. The percentage of oil removed from the penguin feathers, C, was determined according to equation (4.1):

$$C = [(w_3 - w_2)/(w_3 - w_1)] \times 100 \qquad (4.1)$$

[Note: C also applies to the percentage by weight of contaminants removed from other carcass feathers (e.g. domestic duck)].

Figure 4.3 : An oiled penguin carcass.

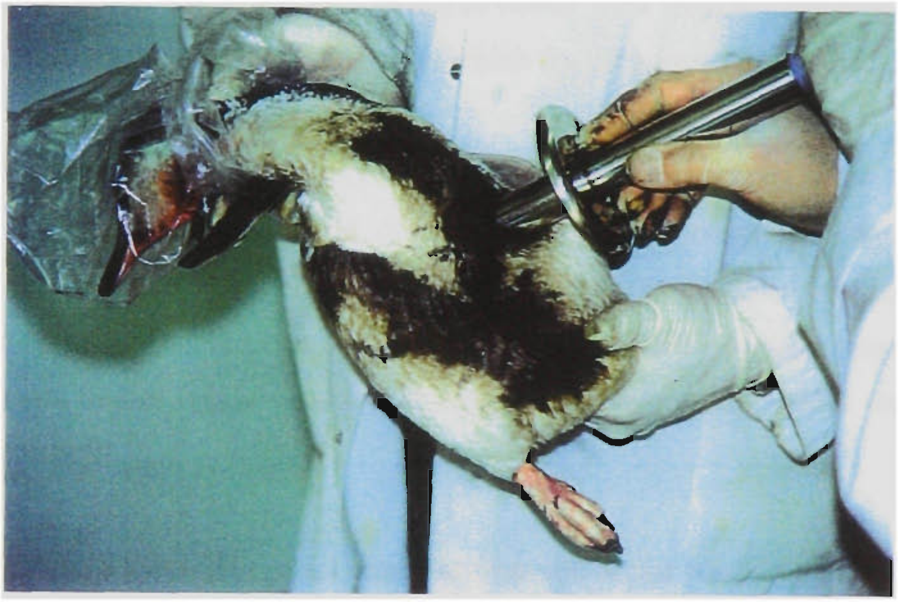

Figure 4.4 : Removal of oil from penguin feathers using a magnetic tester.

4.2.2 Preliminary Results

In the first preliminary test, the initial results for the removal of fresh oil from both the breast and back feathers of the whole oiled penguin feathers were very encouraging, showing a high removal of oil ranging from 87.0% to 100.3% for three types of oils after 7 applications of iron powder, Figure 4.5. Thus, the preliminary results for oil removal for the penguin carcass could be said to reflect the *in vitro* studies.

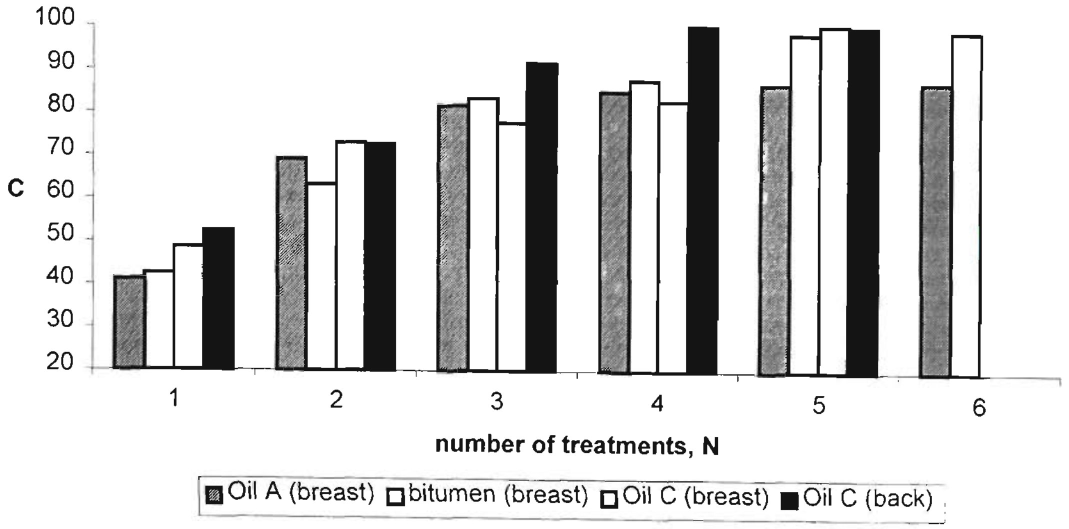

Figure 4.5: Percentage by weight of contaminants removed from the feathers of the Little Penguin (*Eudyptula minor*) after N successive treatments with iron powder and subsequent magnetic harvesting. The raw data are tabulated in Appendix 4.1. Error estimations were not made at this stage.

From the preliminary tests, a number of problems associated with conducting tests on penguin carcasses were identified. These are: (i) leakage of bodily fluid from the penguin's orifices, (ii) moisture on thawed feathers, and (iii) degree to which the oil penetrates the feathers.

It was observed during the preliminary tests that bodily fluid leaked from the penguin's orifices. This affected the gravimetric determinations of oil removed from the penguin plumage, resulting in exaggerated values, sometimes greater than 100% removal, Table 4.2. In one of the trials it was observed that the soiled material from the penguins was also removed from the magnetic device, again resulting in exaggerated values, e.g. 107% removal after 5 treatments, Table 4.2.

Table 4.2: Percentage by weight of oil removed from the breast feathers of the Little Penguin (*Eudyptula minor*) after five treatments with iron powder and subsequent magnetic harvesting.

N	% Oil B removed	% Oil C removed
1	55.9	48.6
2	85.2	72.7
3	88.9	77.3
4	106.8	82.4
5	107.1	100.3

The thawed penguins that were tested always contained a certain amount of moisture within their feathers, resulting in extra weight being added to the bird. This problem does lead to inaccuracies due to the water being shed with handling and being removed with the oil. To overcome this problem each penguin carcass was dabbed with tissue to remove excess water prior to experiments, Section 4.3.1.

In one of the preliminary tests, the first application of iron powder on the back feathers of a penguin contaminated with emulsion S resulted in an extremely high initial removal of 85.2%. Table 4.3 shows in general a removal of oil which is perhaps unexpectedly high. This high pick-up was attributed to the oil not being allowed to sufficiently penetrate the feathers. It was observed that in the initial treatment an unusually large amount of oil was removed, suggesting that most of the oil was still on the surface of the plumage. This brought attention to the need for allowing a controlled penetration of contaminants into the plumage. Measures for overcoming the above problems are discussed in a later section, Section 4.3.1.

Table 4.3: Percentage by weight of emulsion S removed from the back feathers of the Little Penguin (*Eudyptula minor*) after N treatments with iron powder and subsequent magnetic harvesting.

N	% emulsion S removed
1	85.2
2	92.1
3	93.3
4	96.7
5	96.7
6	99.3
7	99.6

4.2.3 Error Estimation and Reproducibility of Oil Removal

Unlike the *in vitro* studies, the removal of contaminants from a section of the plumage of a carcass could not be carried out in replicate because of the limited number of carcasses available. However, as much contaminant as practical was used on each carcass so as to minimise weighing errors. Typically an amount of contaminant covering around 20% of the breast and back feathers of the carcass was used for both penguins and ducks. An attempt was made to estimate the error and the reproducibility of the removal of an oil patch from the plumage of a bird carcass by performing replicate experiments on the same bird.

Specifically, five patches of oil were successively applied to the breast feathers of a carcass of penguin and duck and four patches of oil were successively applied to the back feathers. The carcass was initially weighed. A known weight of oil was applied to the first test patch and the carcass was left for 15 min for the oil to penetrate the feathers completely. Iron powder was applied to the oiled feathers and rubbed in. The feathers were then magnetically stripped. The carcass was then reweighed and the difference in mass calculated to obtain the quantity of oil removed. The application of iron powder and the magnetic stripping procedure was repeated eight more times. The cleansing procedure was then repeated successively another four times on a different section of breast feathers and three times on a different section of back feathers to obtain the average oil removal and a reproducible measure of the reliability of the treatment. Oils B and C were chosen because the former represents an oil of higher viscosity whereas the latter represents an oil of lower viscosity. The removal of each test patch followed the standard protocol of 9 applications as described above.

The error estimation may be presented by the two-tailed student t-distribution for 95% confidence limits, $\bar{x} \pm t_c \sigma_{\bar{x}}$, and the percentage error (% error), $(t_c \sigma_{\bar{x}} / \bar{x}) \times 100$, Appendix 4.2.

The reproducibility may be presented by the percentage coefficient of variance, %CV, Figures 4.6 and 4.7. The %CV is defined by (equation 4.1):

$$\%CV = 100s / \bar{x} \tag{4.1}$$

The smaller the %CV, the more precise is a set of measurements. A more detailed discussion of %CV is presented in Appendix 4.2.

The data for these experiments, presented in Appendices 4.3 and 4.4 show that the reproducibility, as reflected in the decreasing magnitude of %CV, increases with the number of treatments. For both crude oils, the %CV decreases with the number of treatments for both the breast and back penguin and duck feathers. The %CV for both the breast and back feathers of penguin and duck is comparable using Oil C. However, the %CV for the moderately viscous Oil B is higher than the less viscous Oil C in the early stages of treatments. In the later stages of treatments the %CV for both crude oils are comparable.

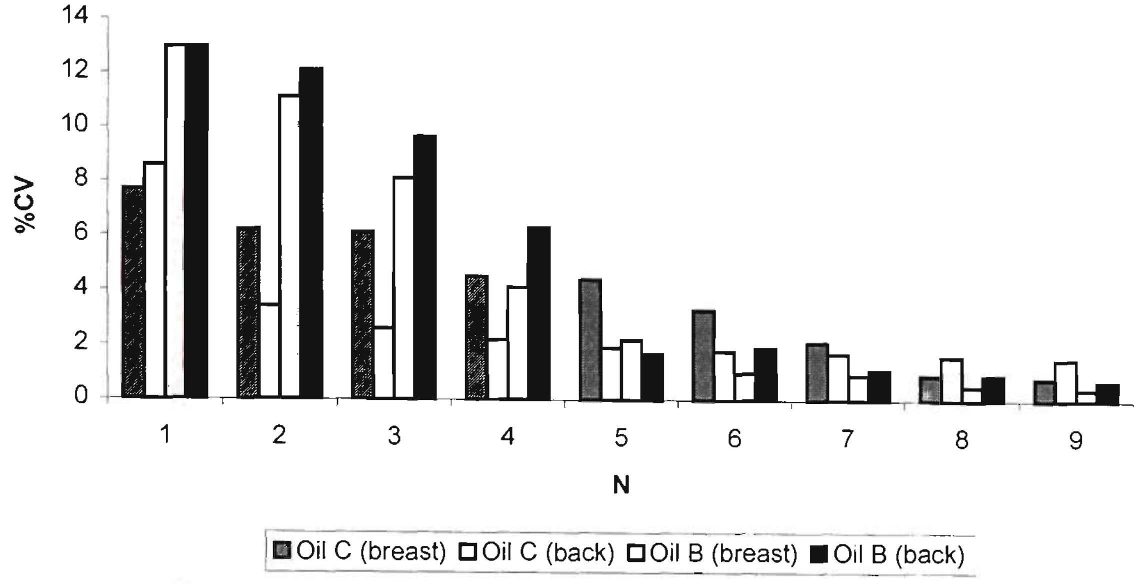

Figure 4.6: %CV of Oils B and C removed from the feathers of the Little Penguin (*Eudyptula minor*) after N treatments with iron powder and subsequent magnetic stripping. Individual profiles are documented in Appendix 4.3.

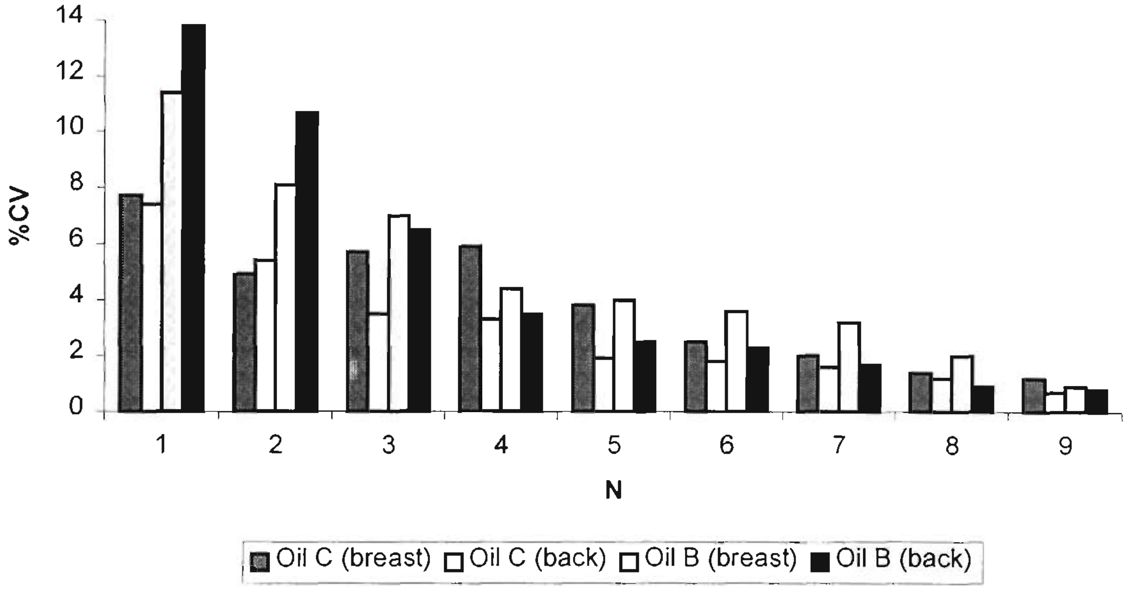

Figure 4.7 : %CV of Oils B and C removed from the feathers of the domestic duck (*Anas platyrhynchos*) after N treatments with iron powder and subsequent magnetic stripping. Individual profiles are documented in Appendix 4.4.

Thus using the %CV values obtained from the two crude oils of different viscosities, it is possible to estimate the reproducibility of the removal of other contaminants such as Oils A, B, C, D, and emulsion S from the plumage of a carcass. The %CV for these oils are expected to decrease with the number of treatments. Moreover, it is anticipated that the %CV for these oils in the later stages of treatments are comparable.

4.2.4 Comparison of Reproducibility between *in vitro* and Carcass Studies

The reproducibility for the *in vitro* studies on a cluster of penguin and duck feathers (see Appendices 3.6 - 3.9) for Oils B and C also suggest that the %CV decreases with the number of treatments. For the first treatment with iron powder the %CV for both the *in vitro* breast and back feathers ranged from 2% to 13% compared to the carcass feathers of between 7% to 14%, After 9 treatments, the %CV is between 0.3 - 0.7% for the *in vitro* penguin and duck feathers, and between 0.4-1.5% for the respective bird carcasses, Appendices 4.3 and 4.4. Thus the %CV for both *in vitro* and carcass model are comparable after 9 treatments.

4.3 Methodology for Cleansing Oiled Bird Carcasses

Having conducted preliminary tests on the penguin carcass, a full methodology was developed to cleanse oil from the oiled penguin and duck in a systematic manner. For each experiment involving penguin and duck carcasses, the absolute error, ε (Appendix 4.2) was calculated using the % error based on the 5 patch experiments described in Section 4.2.2. In the case of the viscous Oils A and B, the absolute errors associated with the removal of these oils were taken to be equivalent to the percentage error calculated for Oil B in the 5 patch experiment. Likewise, in the case of lighter Oils C, D, and emulsion S, the absolute errors associated with the removal of these oils were taken to be equivalent to the percentage error calculated for Oil C in the 5 patch experiments.

4.3.1 Little Penguin (*Eudyptula minor*)

The following procedures were carried out in order to minimize the problems of handling and treating the carcass. Frozen penguin carcasses weighing between 0.8 kg and 1.4 kg were thawed overnight to room temperature. Experiments were conducted in the research laboratory with a controlled temperature of 21 °C. The orifice and the soiled area of a penguin were fully covered with plastic bags to prevent any mass loss. Each penguin was gently dabbed with tissue to remove any excess water. The carcass was weighed on a top-loading balance and some oil was carefully poured over the breast feathers to cover as wide an area as possible in order to minimise the error in weighing. The oil was carefully patted into the feathers and the carcass was left for 15 min for the oil to penetrate the feathers. The oiled carcass was re-weighed and the oiled-feathers were immediately covered with iron powder which was gently rubbed into the feathers. The iron powder/oiled feathers were magnetically stripped of the oiled iron powder by stroking the plumage with the magnetic probe. The entire cleansing process took approximately 20 min (including repeats).

The probe was able to achieve considerable penetration during this process. The penguin was then re-weighed. The application of iron powder and magnetic stripping procedure was repeated up to 9 times until visual inspection revealed the feathers to be cleansed. Figure 4.8 shows the different stages of cleansing process in the removal of oil from the breast feathers of Little Penguin carcasses. The same type of oil was then applied on the back feathers for each carcass. The whole cleansing process of the back feathers using iron powder was again repeated.

For oil systems A, B, C, D and emulsion S, the histograms in Figures 4.9 and 4.10 display the removal of contaminants from penguin breast and back feathers using iron powder. In the case of breast feathers, the light Oils C and D have initial removal of approximately 73% and 74%. However, for the two oils of greater viscosities Oils A and B, the initial removal are lower at approximately 53% and 57% respectively. An initial removal of approximately 46% is observed in the case of the emulsion S. For all systems, a total of 8 more treatments cleanse the feathers to a maximum value of approximately 97% to 99% in all cases.

In the case of back feathers, the initial removal was 69% and 62% for Oils C and D respectively. However, for Oils A and B, an initial treatment results in 46% and 45% removal of these oil from back feathers respectively. A removal of approximately 50% is observed in the case of the emulsion S. Subsequently eight more treatments achieved a maximum removal of 97% and 99% for all oil systems.

4.3.2 Domestic duck (*Anas platyrhynchos*)

Adult domestic ducks (*Anas platyrhynchos*) were obtained from the Victoria Market, Melbourne, and weighed between 2.2 kg to 2.6 kg. The breast and back feathers were in good conditions and were ideal for model studies. The carcasses were stored in a freezer at -20 °C. The designed methodology for the Little Penguin was adopted for the studies involving thawed duck carcasses. Each removal of contaminants from the plumage followed the standard protocol of nine applications as described previously, Section 4.3.1. Figure 4.11 shows the different stages of cleansing process in the removal of oil from the breast feathers of the domestic duck carcass. The same type of oil was then applied on the back feathers for each carcass and the cleansing process using iron powder was again repeated. Experiments for the removal of oil from the whole carcasses were not carried out because of the unavailability of seagull carcasses.

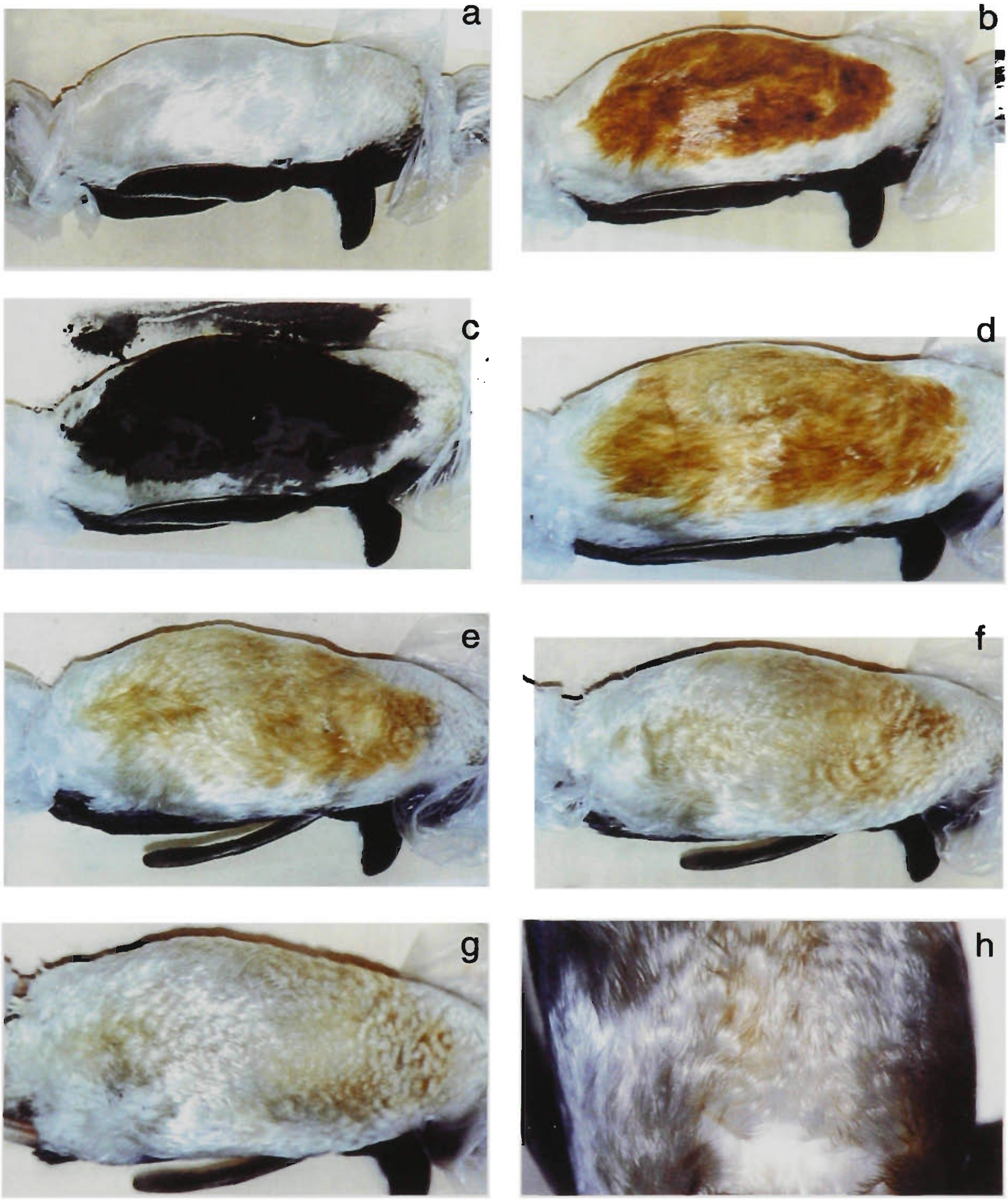

Figure 4.8 : Stages of cleansing oil from the feathers of a penguin carcass: (a) uncontaminated carcass, (b) oiled carcass, (c) oiled carcass covered with iron powder, (d) 2 treatments with iron powder and magnetic harvesting, (e) 4 treatments with iron powder and magnetic harvesting, (f) 6 treatments with iron powder and magnetic harvesting, (g) 9 treatments with iron powder and magnetic harvesting, and (h) a closer examination of feathers after 9 treatments.

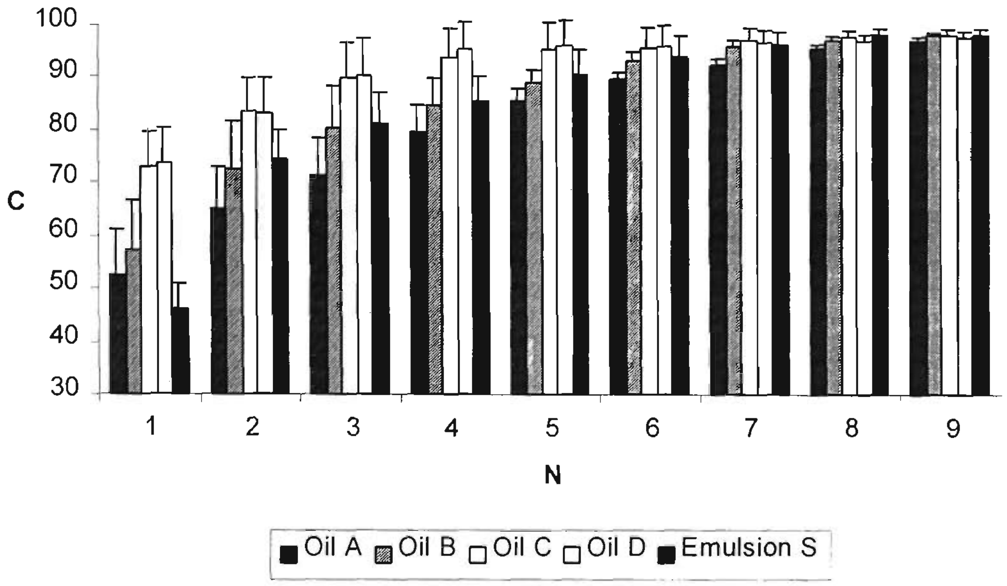

Figure 4.9 : Percentage by weight of contaminants removed from the breast feathers of the Little Penguin (*Eudyptula minor*) carcass, after N successive treatments with iron powder and subsequent magnetic harvesting. Error bars represent the absolute errors based on 5 patch experiments. Individual profiles are documented in Appendix 4.5.

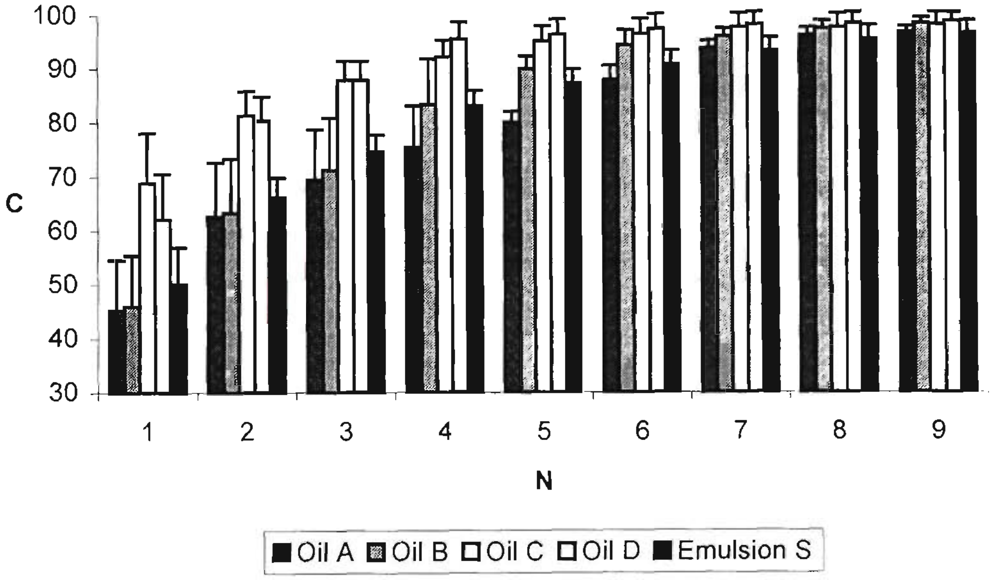

Figure 4.10 : Percentage by weight of contaminants removed from the back feathers of the Little Penguin (*Eudyptula minor*) carcasses, after N successive treatments with iron powder and subsequent magnetic harvesting. Error bars represent the absolute errors based on 4 patch experiments. Individual profiles are documented in Appendix 4.5.

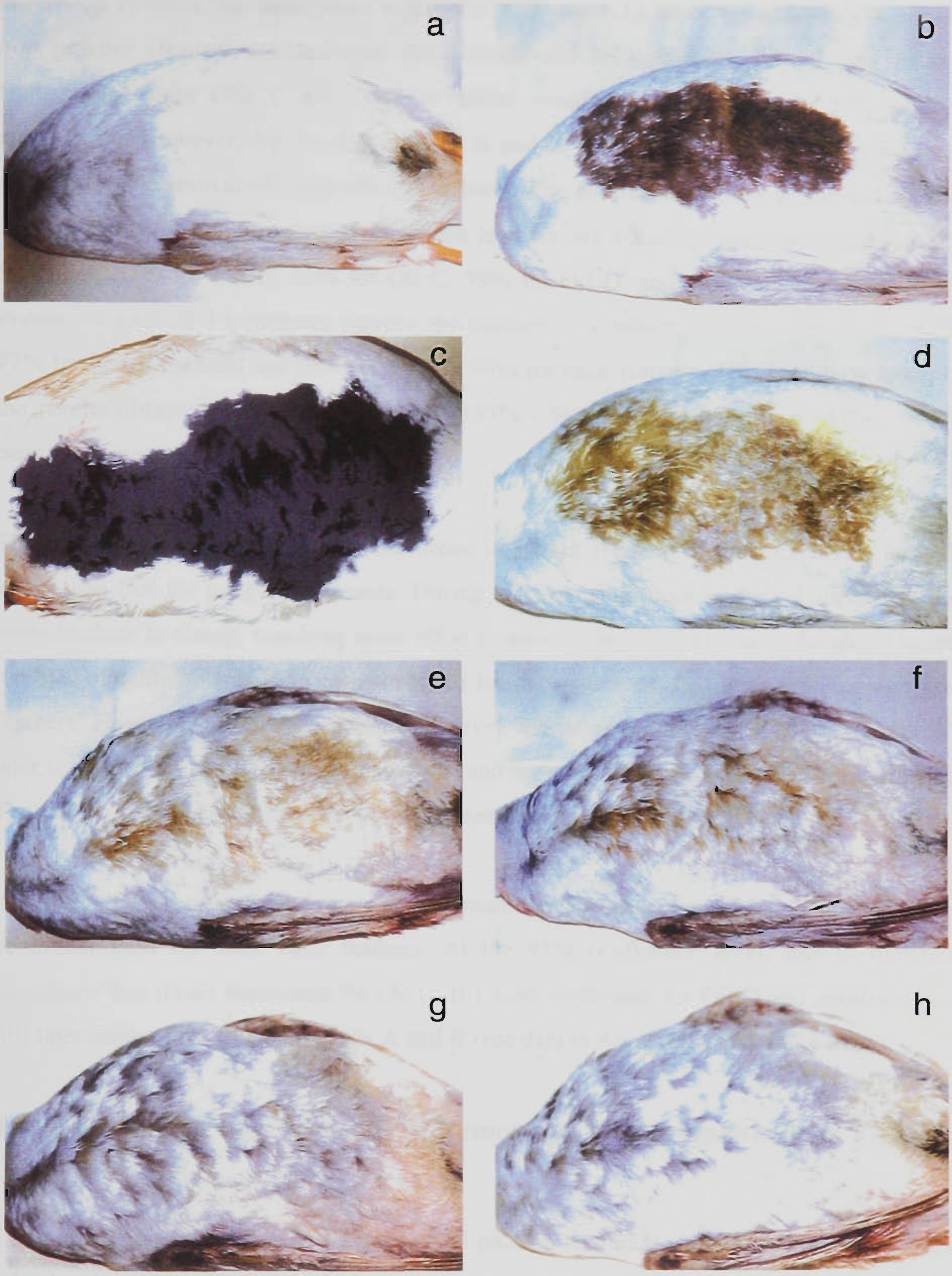

Figure 4.11 : Stages of cleansing oil from the feathers of a duck carcass: (a) uncontaminated carcass, (b) oiled carcass, (c) oiled carcass covered with iron powder, (d) 2 treatments with iron powder and magnetic harvesting, (e) 4 treatments with iron powder and magnetic harvesting, (f) 6 treatments with iron powder and magnetic harvesting, (g) 9 treatments with iron powder and magnetic harvesting, (h) a closer examination of feathers after 9 treatments.

For all oil systems, the histograms in Figures 4.12 and 4.13 show the efficiency with which iron powder cleanses contaminated duck breast and back feathers. In the case of breast feathers, the light Oils C and D show initial removal of approximately 53% and 67% respectively. However, for the viscous Oils A and B, one treatment results in approximately 40% and 56% removal of these oils respectively. The emulsion S shows an initial removal of approximately 52%. In the case of duck back feathers, the initial removal was found to be 32% for Oil A, 51% for Oil B, 55% for Oil C, 59% for Oil D, and 47% for emulsion S. For all systems, a total of 9 treatments cleanse the feathers to a maximum value of between 92% to 97% for breast feathers and between 90% to 95% for back feathers. This is slightly lower than the results obtained for the breast feathers (97% - 99%) and back feathers (97% - 99%) of penguin carcasses.

The removal of all oils from both the breast and back feathers of duck carcasses is slightly lower than that for penguin carcasses. During the cleansing process, the oil appears to cause some feathers to clump, requiring more effort to remove the oils. In general, for all oil systems, removal of contaminants from penguin breast feathers appears to be higher than for duck breast feathers. However, at the 95% confidence level, this is only statistically significant (i) at the later stage of treatments for Oil A and Oil B, and for most treatments for Oil C and emulsion S. There is no statistically difference for Oil D (see data in Appendices 4.5 and 4.6).

In general, for all oil systems, removal of contaminants from penguin back feathers appears to be higher than for duck back feathers. At the 95% confidence level, this is statistically significant for: (i) all treatments for Oil C, (ii) most treatments for Oil D and emulsion S, and (iii) later stage of treatments for Oils A and B (see data in Appendices 4.5 and 4.6).

4.4 Measuring the Efficiency of Removal of Contaminants from Feathers

The method for assessing the efficiency of oil pick-up for the *in vitro* experiments (see Section 3.13) has been adapted to the carcass experiments. An efficiency parameter, E_4, for the carcass is given in equation (4.2):

$$E_4 = C_o / N_o \qquad (4.2)$$

where C_0 is the maximum value of C, which, in turn, is the percentage by weight of contaminants removed from the carcass feathers and N_o is the number of treatments at which this value is attained. This situation is analogous to that previously discussed in Section 3.13 where an efficiency parameter E_3 was defined as $E_3 = F_o / N_o$. For all experiments, N = 9 was found to be the minimum number of treatments sufficient to remove almost all of contaminants from the feathers.

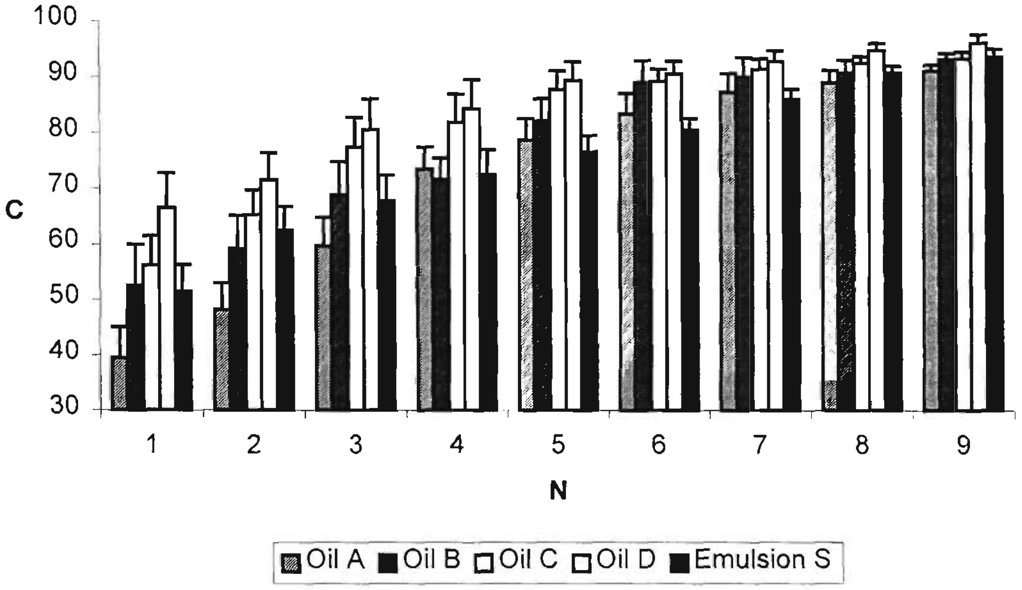

Figure 4.12 : Percentage by weight of contaminants removed from the breast feathers of the domestic duck (*Anas platyrhynchos*) carcasses, after N successive treatments with iron powder and subsequent magnetic harvesting. Error bars represent the absolute errors based on 5 patch experiments. Individual profiles are documented in Appendix 4.6.

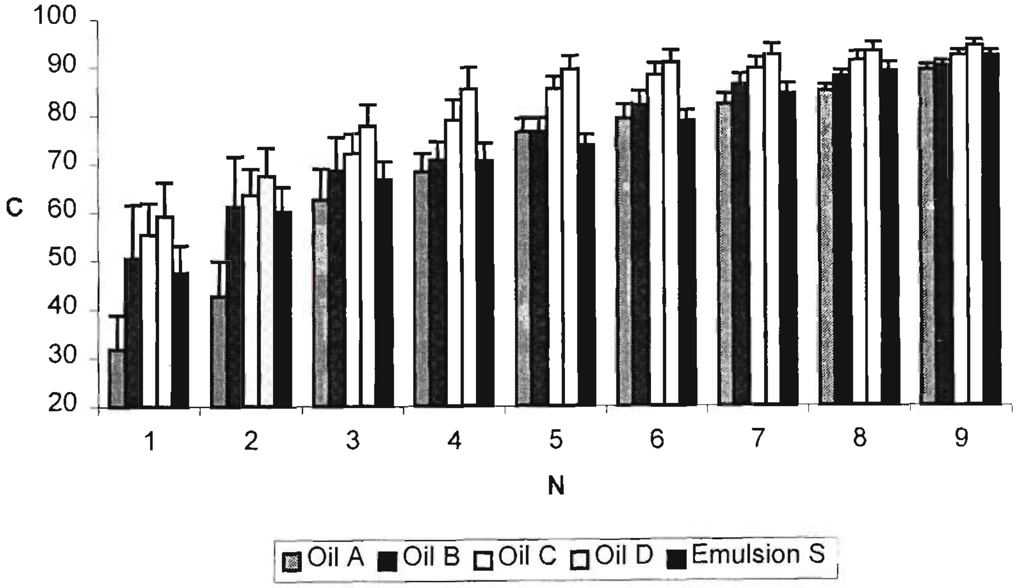

Figure 4.13 : Percentage by weight of contaminants removed from the back feathers of the domestic duck (*Anas platyrhynchos*) carcasses, after N successive treatments with iron powder and subsequent magnetic harvesting. Error bars represent the absolute errors based on 4 patch experiments. Individual profiles are documented in Appendix 4.6.

On the basis of the efficiency parameter E_4, the data in Table 4.4 show that for all oil systems there is little difference in the maximum efficiency for the pick-up within each feather type.

Table 4.4 : Efficiency parameter ranges of all oil systems for each feather type.

Feather types		**E_4 values (all oil systems)**
Duck	breast	10.2-10.8
	back	10.0-10.5
Penguin	breast	10.7-10.9
	back	10.8-11.0

However, there are differences in the *initial* pick-up of all oils for each feather type (see Figures 4.9, 4.10, 4.12, and 4.13). Moreover, it is evident that there are differences in the efficiencies of oil pick-up for these oils where $N < 9$.

An empirical approach analogous to that applied in Section 3.6 to measure the efficiency of oil pick-up for *in vitro* studies was also used to model the adsorption isotherm derived from experiments on bird carcasses. In the case of the latter, equation (4.3) was used:

$$- \ln (1 - C/C_o) = kN \qquad (4.3)$$

where C and C_o have been defined in relation to equation (4.2), and k and N have their usual meanings previously defined in relation to equation (3.6).

A plot of $-\ln(1 - C/C_o)$ versus N for Oil B and Oil C enables the relative overall efficiency of oil pick-up for breast and back feathers of penguin carcasses to be determined respectively (see Figures 4.14). The plots for other oils are presented in Appendices 4.7 and 4.8. Values of the gradient k, calculated via a linear regression analysis, and the product kC_o for five different contaminants are listed in Table 4.5. The lighter Oils C and D show higher values of k and kC_o, reflecting a greater efficiency for the oil pick-up compared to the more viscous Oils A, B and the emulsion S. A similar trend was observed for duck breast and back feathers. Individual values of $-\ln(1 - C/C_o)$ for these feathers are documented in Appendices 4.9 - 4.12.

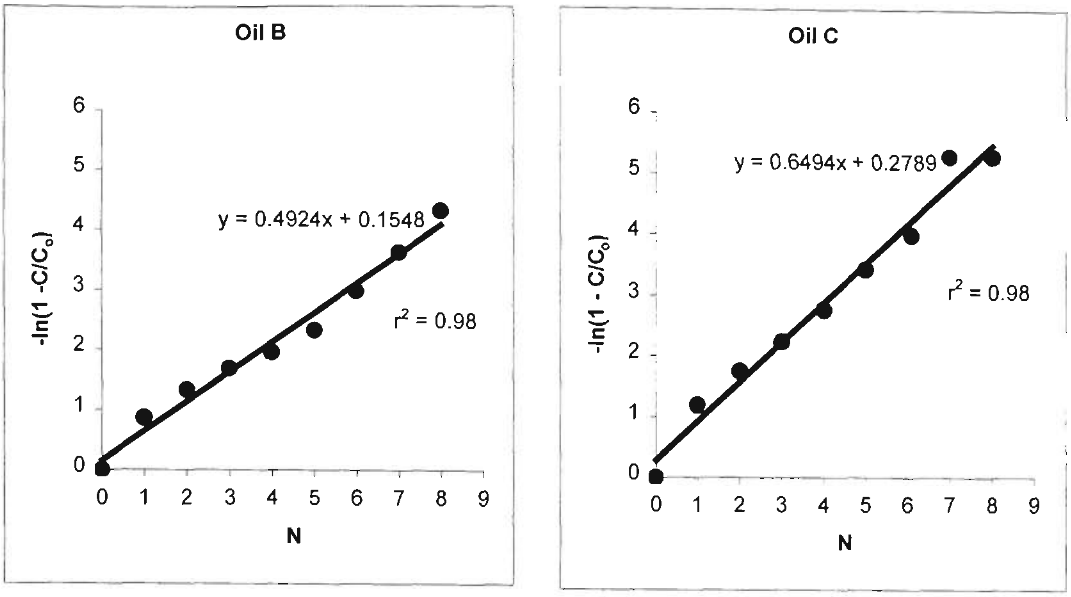

Figure 4.14 : Plots of $-\ln(1 - C/C_o)$ versus N for breast and back feathers of penguin carcasses contaminated with Oil B and Oil C respectively.

Table 4.5 : Values of k and kC_o for feathers on carcass duck and penguin.

Oil/Emulsion	**A**		**B**		**C**		**D**		**Emulsion S**	
Viscosity/cp	425.5		115.5		11.4		13.0		-	
Efficiency parameter	k	kC_o	k	kC_o	k	kC_o	k	kC_o	k	kC_o
Duck breast	0.41	37.52	0.45	42.12	0.54	50.65	0.54	52.91	0.35	32.97
Duck back	0.37	33.11	0.42	37.93	0.51	47.23	0.52	49.19	0.35	32.37
Penguin breast	0.45	43.83	0.49	48.27	0.58	57.13	0.56	54.99	0.51	50.18
Penguin back	0.52	50.54	0.54	53.35	0.65	64.03	0.65	64.55	0.49	47.53

4.4.1 Relationship between Efficiency Parameters

As mentioned in Section 3.62 the product kF_o is directly proportional to initial efficiency k, and since C_o might be expected to vary across different systems, it was necessary to investigate the relationship between k and kC_o. Values of kC_o were plotted against k for whole-carcass duck and penguin breast and back feathers, Figure 4.15. The linear relationship between k and kC_o shows that the value of C_o is indeed consistent across all of the systems investigated. Thus either of these indicators can be used as a reliable indicator of the efficiency of pick-up.

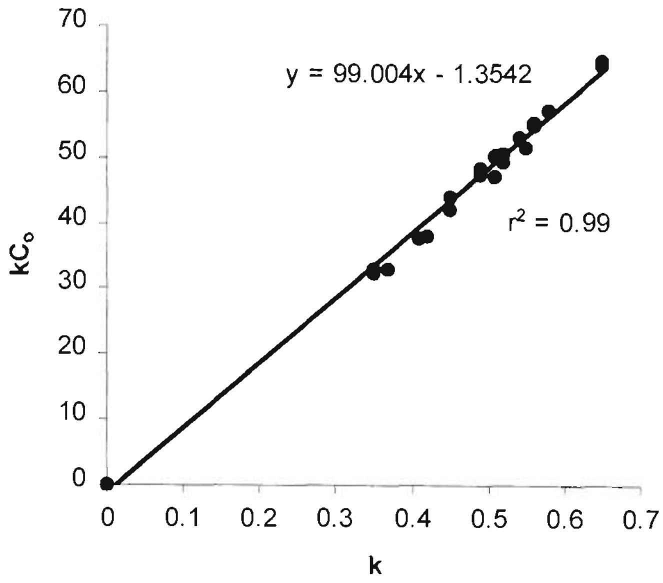

Figure 4.15 : A plot of kC$_o$ versus k for carcass feathers.

4.4.2 Using the Empirical Model to Compare Removal Efficiencies

Before comparing the percentage by weight of contaminant removed from the feathers of the bird carcass, it was necessary to define the terms used in these studies. Firstly, C is the percentage by weight of contaminants removed from carcass feathers. Other abbreviations are listed in Table 4.6.

Table 4.6 : Symbols used in whole-bird carcass studies.

Abbreviation	Feather types
Cbs (Pn)	Carcass breast Feathers(Penguin)
Cbk (Pn)	Carcass back Feathers (Penguin)
Cbs (Du)	Carcass breast Feathers (Duck)
Cbk (Du)	Carcass back Feathers (Duck)

The empirical model was used to compare the efficiency of removal of contaminants from: (i) carcass, different feather types on the same bird, (ii) carcass, same feather type on different birds, and (iii) *in vitro* versus carcass for the same feather types on the same bird.

4.4.2.1 Different Feather Types on Same Species

A comparison between the efficiency of oil removal from the breast and back feathers from the carcass duck and penguin is shown in Figure 4.16. The removal of all oils, except emulsion S, from duck breast feathers is more efficient than its removal from duck back feathers. For all oil systems, except emulsion S, removal of oil from penguin back feathers is more efficient than its removal from penguin breast feathers. The greater kC_0 values for the light Oils C and D (furthest from the origin) indicating that the removal of these oils from feathers is more efficient than the other oils.

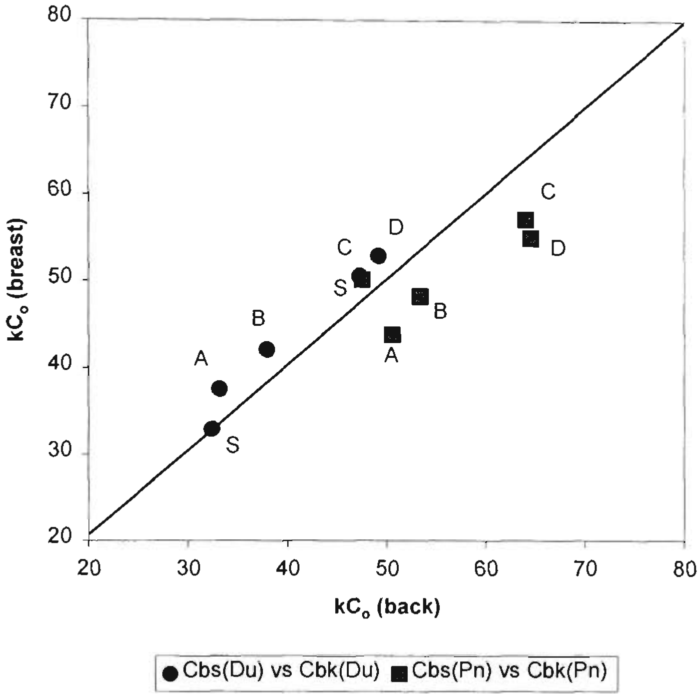

Figure 4.16 : A comparison of the efficiency of oil pick-up by iron powder for carcass duck and penguin feathers. The letters A, B, C, D, and S denote Oils A, B, C, D, and emulsion S respectively.

4.4.2.2 Same Feather Type on Different Species

A comparison between the removal of oil from the same feather type on carcasses of different species is shown in Figures 4.17 and 4.18 respectively. For Oils A, B, C and emulsion S, the removal of oil from penguin breast feathers is more efficient than its removal from duck breast feathers. The removal of Oil D from penguin breast feathers is only slightly more efficient than its removal from duck breast feathers. For all oil systems, the removal of each oil from penguin back feathers is more efficient than its removal from duck back feathers. The greater kC_0 values associated with the less viscous Oils C and D are furthest from the origin indicating that the removal of these oils from feathers is more efficient than the other oils.

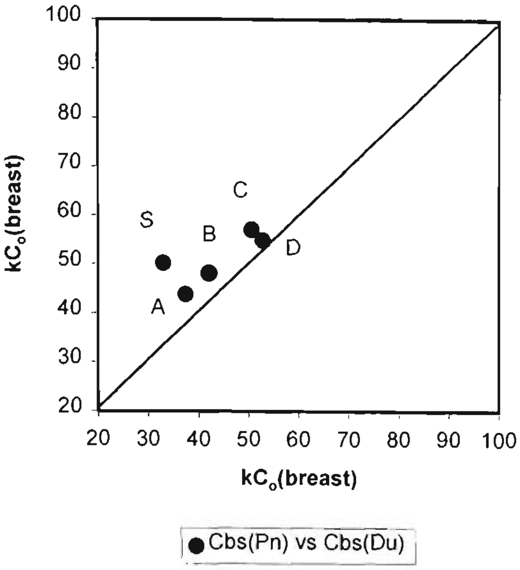

Figure 4.17 : A comparison of the efficiency of oil pick-up by iron powder for carcass penguin and carcass duck breast feathers. The letters A, B, C, D, and S denote Oils A, B, C, D, and emulsion S respectively.

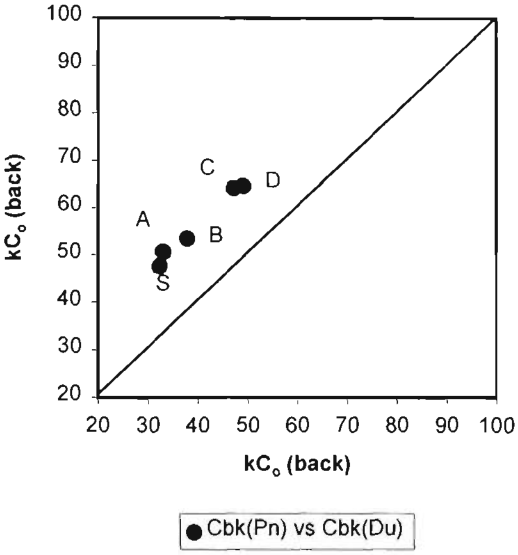

Figure 4.18 : A comparison of the efficiency of oil pick-up by iron powder for whole- carcass penguin and carcass duck back feathers. The letters A, B, C, D, and S denote Oils A, B, C, D, and emulsion S respectively.

4.4.2.3 *In vitro* Versus Carcass for Same Feather Type on Same Bird

Figure 4.19 shows that, the *in vitro* removal of each oil from duck breast feathers is more efficient than its removal from the carcass duck breast feathers. This trend is also observed for penguin feathers, where the *in vitro* removal of oil from the breast feathers is more efficient than its removal from the carcass penguin breast feathers.

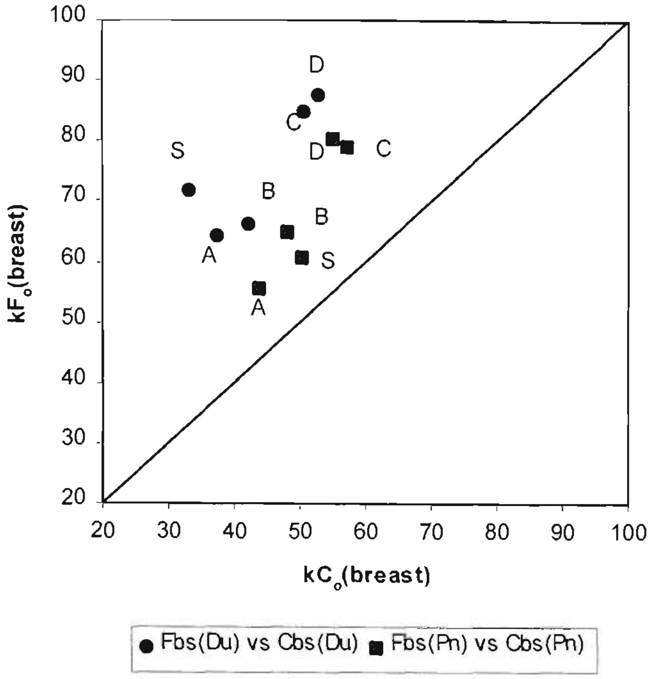

Figure 4.19 : A comparison of the efficiency of oil pick-up by iron powder between *in vitro* and carcass duck and penguin breast feathers.

Figure 4.20 suggests that the removal of all oils from *in vitro* duck back feathers is more efficient than its removal from the carcass duck back feathers. Likewise, the *in vitro* removal of all oils except Oil A from penguin back feathers is more efficient than their removal from

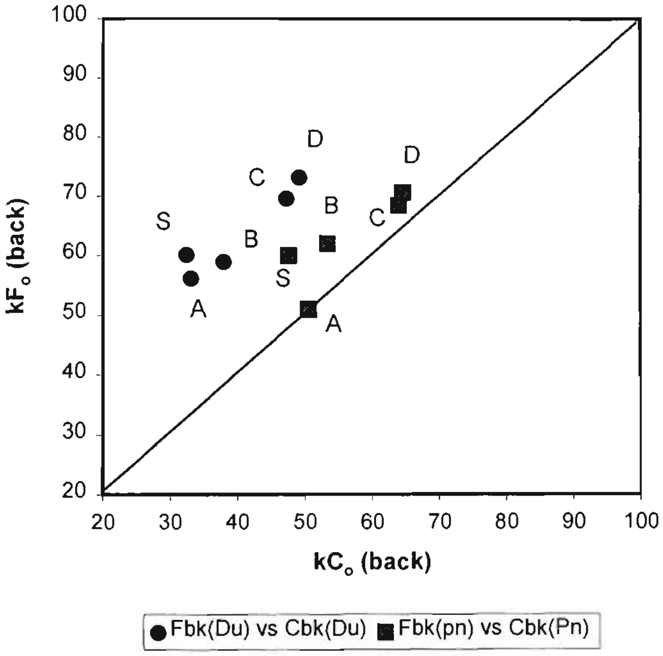

Figure 4.20 : A comparison of the efficiency of oil pick-up by iron powder between *in vitro* and carcass duck and penguin back feathers.

the carcass penguin back feathers. When dealing with a cluster of 5 or 6 feathers, it is easier to remove oil from the feathers than removing oil from the feathers of a carcass. This is not surprising, as carcass feathers are more mutually shielded than feather clusters. Both Figures 4.19 and 4.20 show that the removal of contaminants from the feathers is more efficient for the less viscous oils than for the more viscous oils.

4.4.3 Relationship between Efficiency Parameters and Viscosity

A plot of the kF_0 values for penguin feathers versus the reciprocal of the viscosity of four oils is shown in Figure 4.21. The data for the gradients, intercepts, and linear regression coefficient (r^2) for duck and penguin feathers that were obtained from similar plots are listed in Table 4.7.

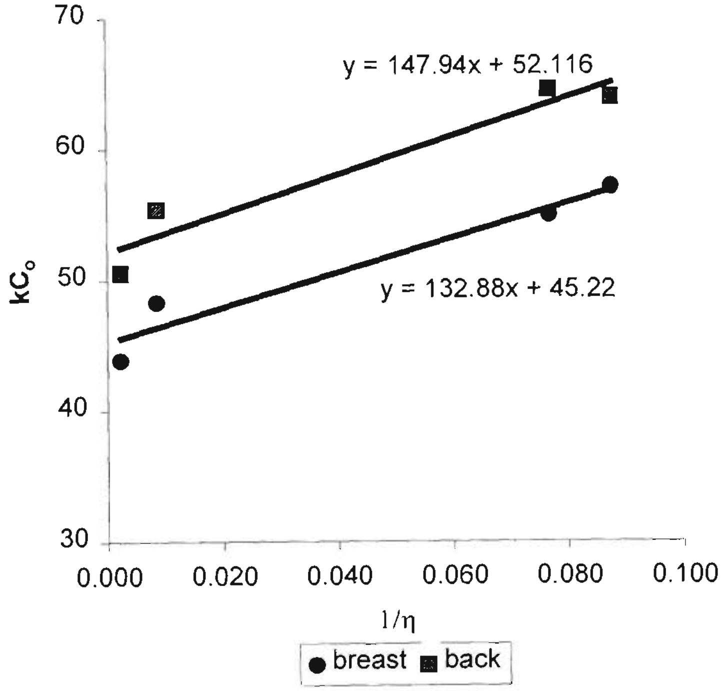

Figure 4.21 : The efficiency of oil pick-up, kC_0, versus the reciprocal of the viscosity, $1/\eta$, for carcass penguin feathers.

The data suggest that: (i) the efficiency of the removal of oil from back feathers is more sensitive to changes in oil viscosity than breast feathers for the two types of carcasses studied, (ii) the efficiency of the removal of oil from penguin back feathers is slightly more sensitive to changes in oil viscosity than penguin breast feathers, and (iii) the efficiency of removal of oil from duck breast feathers is slightly greater than that found for duck back feathers as revealed by the respective values of the intercepts. However, the efficiency of removal of oil from penguin back feathers is slightly greater than that found for duck breast feathers. The data also show that the efficiency of oil pick-up, in general, increases as the viscosity decreases, for both carcass duck and penguin feathers.

Table 4.7 : Effects of viscosity on oil pick-up from feathers on the carcasses of duck and penguin.

Feather types		Gradient, $d(kC_o)/d(1/\eta)$	Intercept, $(kC_o)_{\eta=\infty}$	r^2
Duck	breast	158.4	38.8	0.96
	back	177.4	34.5	0.95
Penguin	breast	132.9	45.2	0.94
	back	147.9	52.1	0.93

4.5 Treating Weathered Oil Contamination

During the rescue of oiled birds it may take hours or even days to transport them to a treatment centre. The oil on the feathers may become dried and tar-like (weathered) because of this delay (Copley, 1999). Indeed, the feathers may be in a weathered condition where the birds are first encountered.

At PINP, despite its close proximity to the sea, it is found that almost all oiled penguins have weathered, oil-contaminated (WOC) feathers, and are frequently coated with a tar-like residue. Some WOC feathers, less seriously contaminated, respond to detergents. Others contaminated with thick and tarry oils do not respond as well and require the application of pre-conditioning agents, or multiple washings with a detergent DivoPlusV2^{TM}. One of the aims of this research was to prepare feathers contaminated with weathered oil in a laboratory for further experiments with different pre-conditioning agents and iron powder.

4.5.1 Pre-conditioning Agents for Treating Weathered Oil on Feathers

The use of pre-conditioning agents such as light mineral oil (liquid paraffin) (Randall *et al.*, 1980) or olive oil as used by the Wildlife Health Centre (WHC, 2000) to pretreat the tarry feathers of animals and birds has been documented. For example, the pre-treatment process prior to washing with detergents involves applying warm, light-weight mineral oil or light olive oil on the affected area of the oiled bird. The light oil slowly softens the tar residue and this can be removed with an absorptive pad. Alternatively, after the light oil is applied to its feathers, the oiled bird is wrapped in a towel for 30 min before washing with detergents.

Other potential pre-conditioning agents may also be also considered. Perhaps the most appropriate pre-conditioning agents are chemicals based on the natural preening oils of the birds themselves. The chemical composition of natural preening oils has been investigated (Odham & Stenhagen, 1971). These preening oils are mostly alkyl alcohols and fatty acids. For example, of the total acidic components excreted by the preening gland of Peiping duck, the main ones are 4-D-methylhexanoic acid (40.5%) and 2-D-methylhexanoic acid (33.7%). Furthermore, the dominant alcohol excreted by this gland is octadecanol (34.2%). For the domestic goose, the acidic component is reported to consist of 2,4,6,8-tetramethyl decanoic acid (45.3%) and the alcohol component consists of octadecanol (99.5%) (Weitzel *et al.*, 1952; Murray, 1962).

Surprisingly, squalene, an acrylic triterpene ($C_{30}H_{50}$), which is commonly known as shark liver oil is found as the main component (87%) in the preening gland of Magpie goose (*Anseranas semipalmala*) (Odham & Stenhagen, 1971). Other components are straight chain acids (C_7-C_{12}) and alcohols (C_{10}-C_{16}).

In the preliminary studies, octadecanol and 4-D-methylhexanoic acid were chosen to be trialled on duck feathers since these are the two main components of the preening oil of the Peiping duck. However, 4-D-methylhexanoic acid, is not available, so 2-D-methylhexanoic acid, also a component of the preening oil of the Peiping duck, was used instead. Interestingly, this substance is described as "corrosive" by the manufacturer. It is possible that the corrosive nature of this substance is exploited as an anti-microbial or anti-fungal agent in birds and this is an area for further investigation. Since octadecanol is a solid at 293K it cannot be used as a pre-conditioning agent and octanol was used instead. Squalene, which represents another class of chemical, was also tested since it is the main component of the preening oil of the Magpie goose. Light olive oil and liquid paraffin were also selected because they have been successfully used as pre-conditioning agents to soften "tarry" bird feathers (WHC, 2000). These trials were carried out *in vitro* on clusters of duck breast feathers.

In developing protocols involving pre-conditioning agents for the treatment of oiled birds with iron powder, factors to consider are: (i) toxicity, (ii) pick-up with respect to iron powder, (iii) ability to solubilize significant amounts of weathered oil, (iv) similarity to natural preening oils, and (v) availability.

4.5.2 Preparation of Feathers Contaminated with Weathered Oil

Two clusters of *in vitro* weathered feathers were prepared from 2 oils of different viscosities. Preliminary studies were conducted on the moderately viscous Oil B and the light Oil C. A cluster of pre-weighed duck breast feathers was immersed in a given oil to achieve saturation. The oiled cluster was removed and allowed to drain for up to 15 min before it was re-weighed. The oiled feathers were then suspended for up to 14 days to allow evaporation of any volatile components of oil over time. The oiled feathers were weighed at different time intervals during the 14 days.

The loss of mass of the oiled feathers over time is shown in Figure 4.22. This represents the loss of the more volatile components and the "weathering" of the heavier components onto the feathers.

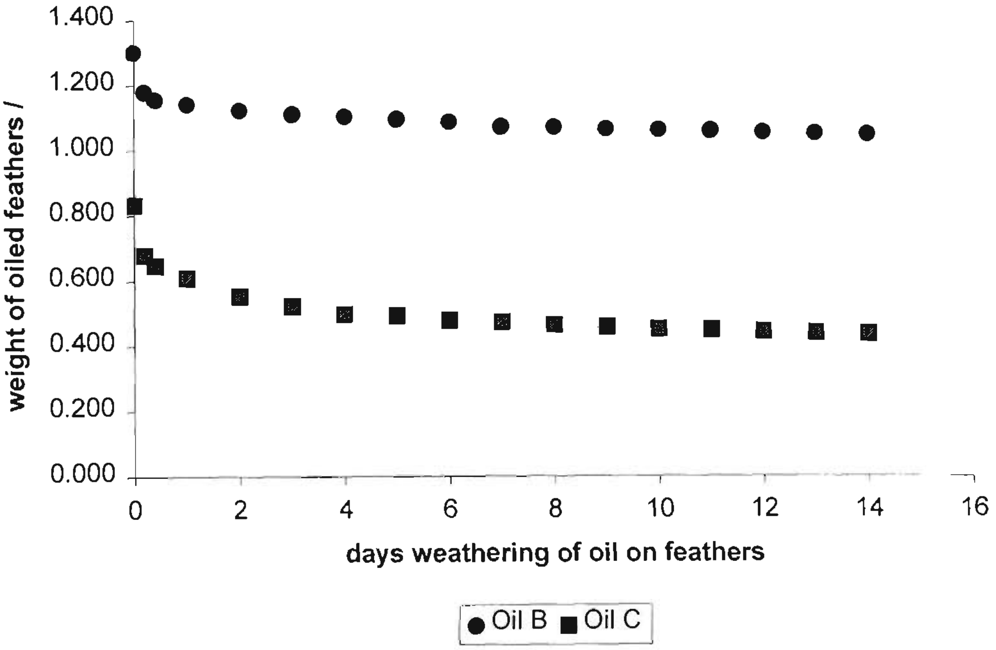

Figure 4.22 : Weight of oiled breast feathers of the domestic duck (*Anas platyrhychos*) over time.

As expected, a higher rate of evaporation is observed for light Oil C compared to the viscous Oil B. After 14 days the percentage by weight of Oil C evaporated is approximately 50% and that of Oil B is approximately 20%. The results show that after 5 days, the rate of evaporation for both oils has slowed down considerably. The feathers are considered to be fully weathered at the time the graph becomes parallel to the time axis.

4.5.3 Application of Iron Powder Alone to Feathers Contaminated by Weathered Oil

Seven clusters of oiled duck feathers were prepared and suspended in air for different time intervals. For each cluster the iron powder application and magnetic stripping procedure was repeated up to 9 times.

The data generated by the above experiment are listed in Table 4.8. The results illustrate the cleansing efficiency of the iron powder for two different oils, namely the moderate viscosity Oil B, and the light Oil C. As the oiled feathers were exposed in air for a longer period of time, the percentage of oil removed decreased, Figure 4.23. The results also show that the removal of lighter Oil C is slightly higher than that of the more viscous Oil B. The data show that for the oiled feathers which had been exposed in air for more than 5 days, between 13% and 20% of oil still remained on the feathers after 9 treatments with iron powder. The feathers appeared light brown indicating that some oil residues were still present.

Table 4.8 : Percentage by weight of oil removed from duck breast WOC feathers after 9 treatments with iron powder and subsequent magnetic harvesting as a function of the number of days of weathering in air.

Days of exposure in air	% Oil B removed	% Oil C removed
0.33	96.5	97.5
1.00	92.3	94.2
2.00	90.3	91.6
5.00	85.9	87.3
7.00	82.2	83.7
11.00	80.6	83.4
14.00	79.6	82.5

The results tabulated in Table 4.8 show that for the oils tested, iron powder is the most effective ($F_o > 90\%$) in cleansing contaminated feathers which are less than 2 days old. Therefore, using iron powder alone is not sufficient to cleanse severely WOC feathers. At PINP pre-conditioning agents (and even degreasers) have been used to soften the residue before washing with detergents. If the pre-conditioning agents are unavailable, multiple washings with detergents such as DivoPlusV2^{TM} are carried out (Jessop & Healy, 1997). However, this might not be appropriate for birds less robust than the Little Penguin.

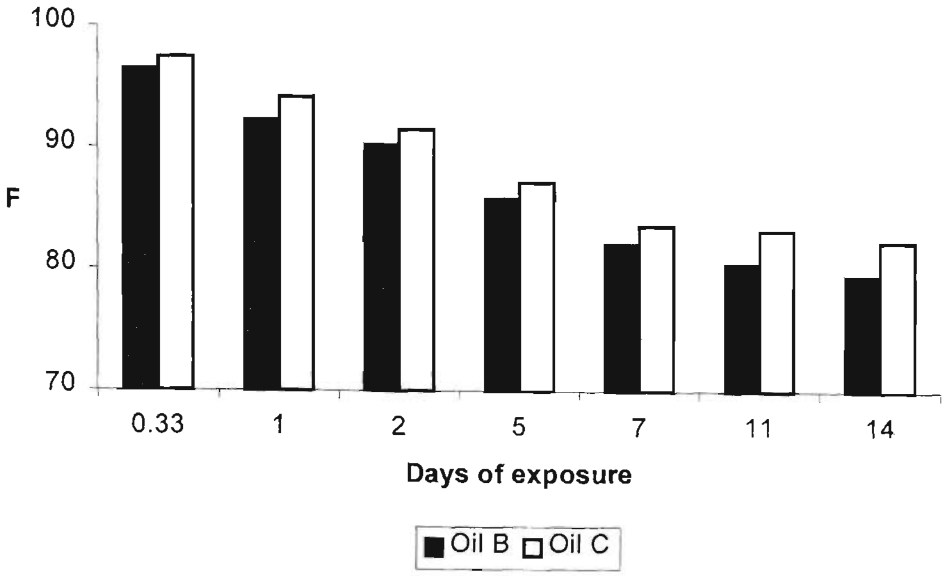

Figure 4.23 : Percentage by weight of oil removed from weathered duck breast feathers after 9 treatments with iron powder and subsequent magnetic harvesting as a function of the number of days of weathering in air.

4.5.4 Control Experiments

4.5.4.1 Affinity of Pre-Conditioning Agents for Iron Powder

Prior to conducting tests on the WOC feathers using pre-conditioning agents, a control experiment was performed to ascertain the degree of affinity between iron powder and the pre-conditioning agents themselves.

The method for ascertaining the affinity of pre-conditioning agents for iron powder is similar to that carried out for determining the pick-up of contaminant (e.g. Oil A) from a petri dish using iron powder, Section 2.5.

The histogram for the affinity of pre-conditioning agents for iron powder is presented in Figure 4.24. A high initial removal of approximately 64% is observed in the case of olive oil. In the case of octanol and liquid paraffin, an initial removal of approximately 35% and 62% respectively is observed. The initial removal of oils based on natural preening oils such as squalene and 2-D-methylhexanoic acid is approximately 59% and 43% respectively. However, a sufficient application of iron powder picks up all of the pre-conditioning agents to an extent of approximately 95-97 %.

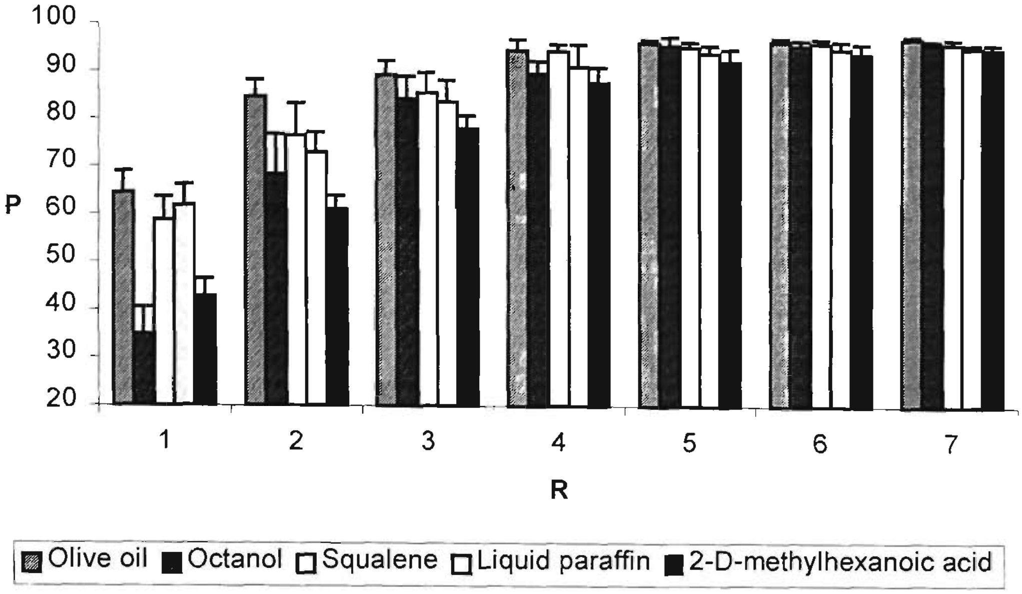

Figure 4.24 : The affinity of the pre-conditioning agents themselves for iron powder. Error bars represent 95% confidence intervals for 5 replicates. Individual profiles are documented in Appendix 4.13.

4.5.4.2 Affinity of Heavy Crude Mixed with a Pre-Conditioning Agent for Iron Powder

Shell HD crude oil is tarry and a solid at room temperature and is therefore an ideal oil for "worse case scenario" investigations. Olive oil was trialed as a solvent for this crude oil since it is the best performing pre-conditioning agent with respect to its pick-up using iron powder.

It was found that 9.6 g of olive oil can solubilise 20 g of Shell HD crude oil completely. The affinity of this solution for iron powder was then investigated and the results are presented in Figure 4.25. The data show that a maximum pick-up of this mixture of approximately 96% may be achieved for a given R.

Having shown that pre-conditioning agents are effective in softening the tarry feathers, the next step is to experiment on feathers contaminated with heavy and tarry oil and to subject these feathers to treatment with a pre-conditioning agent.

4.5.5 The Removal of Pre-Conditioning Agents from Duck Feathers

Having shown that pre-conditioning agents have an affinity for iron powder. An investigation was then carried out to determine the amount of pre-conditioning agents that could be removed from duck breast feathers using iron powder. The method for determining the percentage removal of pre-conditioning agents from duck breast feathers using iron powder is similar to those conducted for the removal of contaminant (e.g. Oil A) from duck feathers using iron powder, Section 3.10.

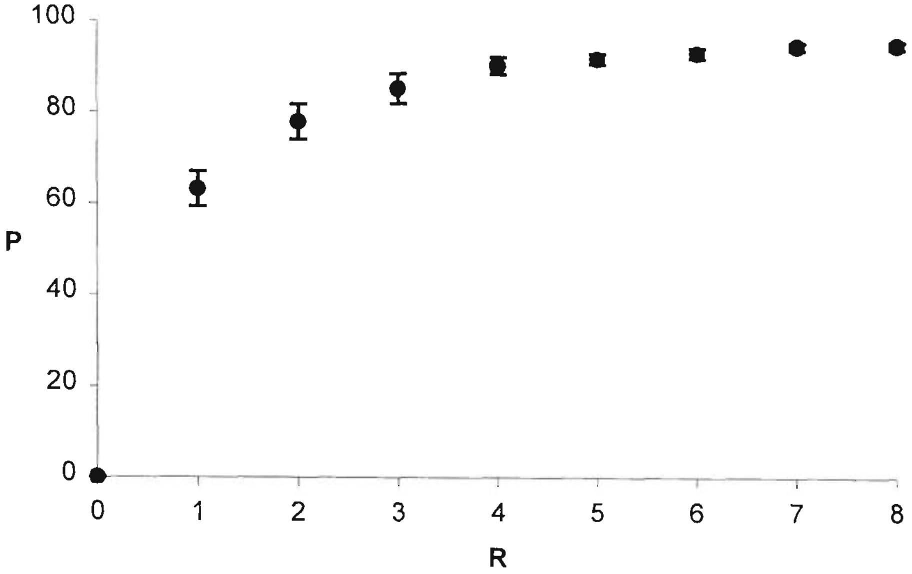

Figure 4.25 : The affinity of Shell HD crude oil for iron powder. The crude oil was "pre-treated" (solubilized) with olive oil. Error bars represent 95% confidence intervals for 5 replicates. The data are documented in Appendix 4.14.

The histograms for the removal of pre-conditioning agents from duck breast feathers are presented in Figure 4.26. A high initial removal of approximately 82% of 2-D-methylhexanoic acid is observed, followed by the initial removal of 74% for squalene, 70% or liquid paraffin, 63% for olive oil and 59% for octanol. Interestingly, olive oil does not show the highest removal from feathers despite the fact that it is the most highly removed from a glass petri dish. After eight more treatments with iron powder and subsequent magnetic harvesting, approximately 93-97% of the pre-conditioning agent was removed.

4.5.6 Experiments on Weathered, Oil-Contaminated (WOC) Feathers

4.5.6.1 WOC (Light Oil)

In order to remove the dried oil residues on the feathers, further treatments of the feathers using pre-conditioning agents were necessary. The treatment procedure was carried out as follows: three clusters of oiled feathers, after being exposed to air for 7, 11 and 14 days, were weighed. They were treated with iron powder and magnetically harvested. The WOC feathers were immersed in a pre-conditioning agent and removed immediately. The feathers were again treated with iron powder which was magnetically harvested. The treatment with a pre-conditioning agent and the iron powder/magnetic harvesting procedure was repeated three more times. At this point, the feathers appeared cleansed.

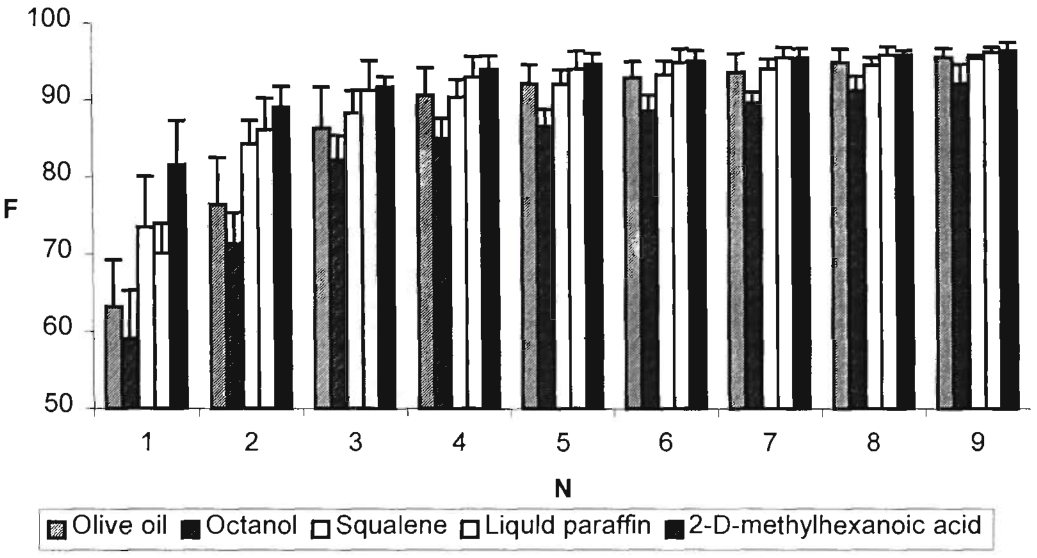

Figure 4.26 : Percentage by weight of pre-conditioning agents removed from the *in vitro* duck breast feathers after N successive treatments with iron powder and subsequent magnetic harvesting. Error bars represent 95% confidence intervals for 5 replicates. Individual profiles are documented in Appendix 4.15.

A comparison of the percentage of oil removed with and without pre-conditioning agents is shown in Figures 4.27 and 4.28. The results show that for Oils B and C, the removal of contaminants from the WOC duck feathers using pre-conditioning agents is higher than without using pre-conditioning agents. The results for the removal of both Oils B and C from the WOC duck feathers using the pre-conditioning agents are very promising, showing a high removal of oil from 94 - 97% after 5-14 days of weathering of feathers, compared with 80 - 87% without using pre-conditioning agents.

4.5.6.2 WOC (Heavy Crude)

Having shown that iron powder has an affinity for Shell HD crude oil in olive oil, investigations were then conducted to explore the oil pick-up phenomenon when this mixture was applied to duck breast feathers. Pre-conditioning agents were used to soften the feathers, followed by iron powder application and magnetic harvesting.

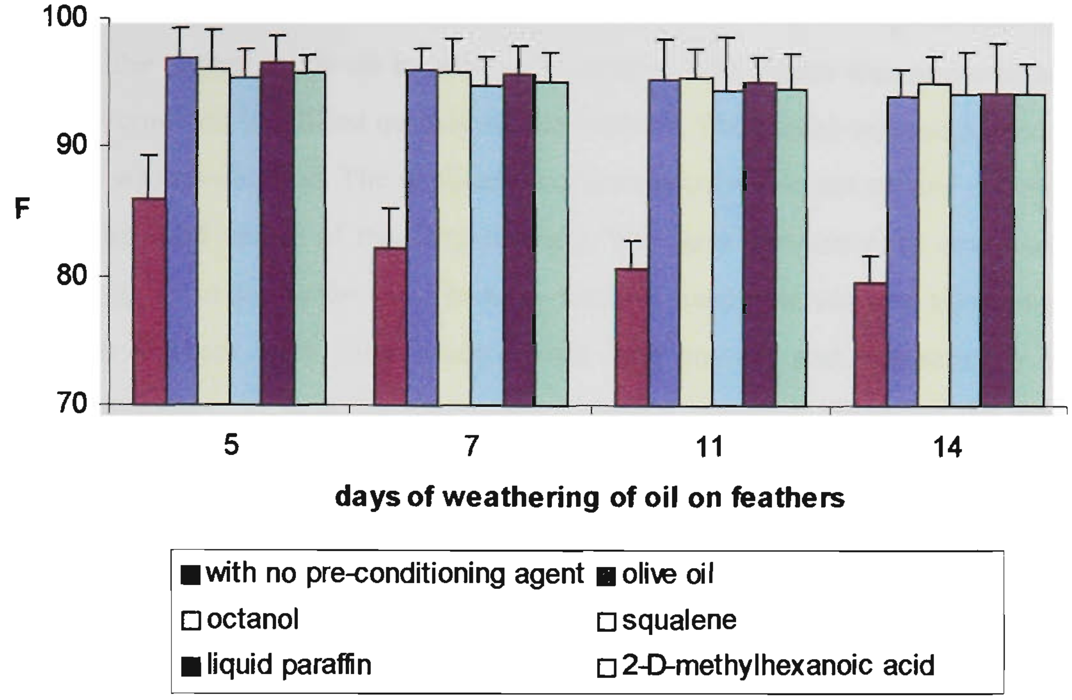

Figure 4.27 : A comparison between the percentage removal of Oil B from the oiled duck breast feathers after four treatments with a pre-conditioning agent followed by 9 treatments with iron powder/magnetic harvesting process. Each procedure was carried out in triplicate. Individual profiles are documented in Appendix 4.16.

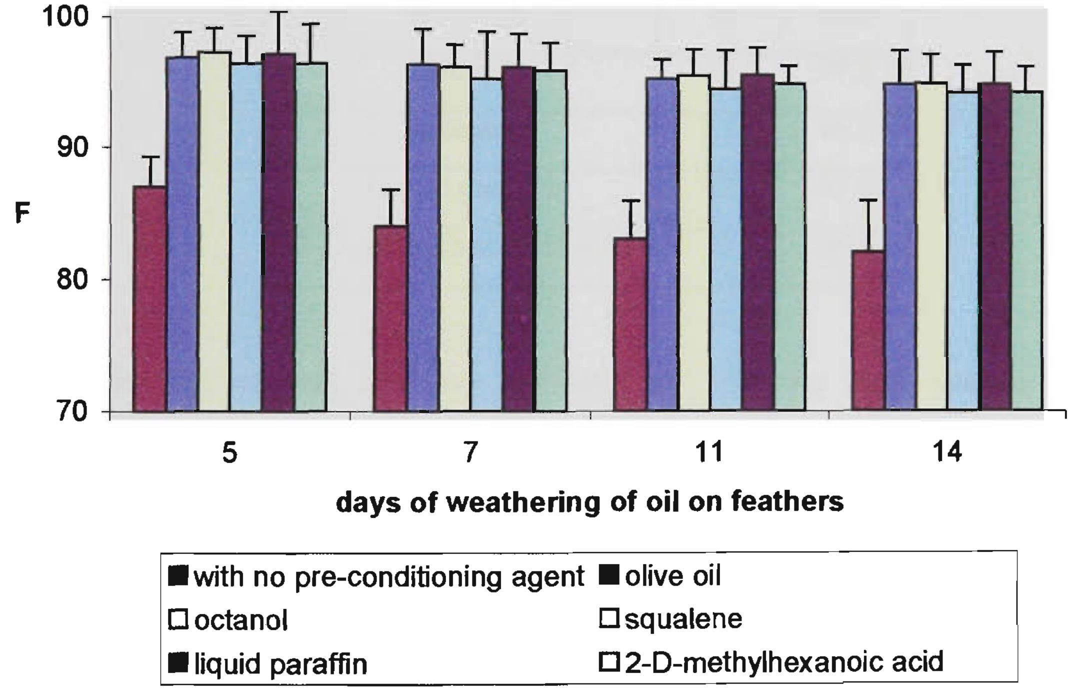

Figure 4.28 : A comparison between the percentage removal of Oil C from the oiled duck breast feathers after four treatments with a pre-conditioning agent followed by nine treatments with iron powder/magnetic harvesting process. Each procedure was carried out in triplicate. Individual profiles are documented in Appendix 4.17.

A beaker containing Shell HD crude oil was placed in a warm water bath for 10 min to melt the oil. The melting point was found to be 29.0 °C. A cluster of pre-weighed duck feathers was immersed in the melted crude oil to achieve saturation. The cluster was removed and allowed to drain. The crude oil solidified quickly on the feathers. The cluster was suspended in air for a day before it was re-weighed. The application of iron powder was not carried out on the cluster because of the solid nature of the tarry feathers. The tarry feathers were immersed in a pre-conditioning agent to soften the oil. The tarry feathers were removed and allowed to stand for 10 min. The feathers were then covered with iron powder and magnetically stripped as described previously. In between every two magnetic stripping processes the feathers were saturated with a pre-conditioning agent. This cleansing process was repeated up to 16 times until the feathers appeared cleansed.

Table 4.9 lists the percentage by weight of oil removed, F, after N treatments with pre-conditioning agents and the application of the iron powder/magnetic harvesting procedure.

Table 4.9 : The F values of oiled duck breast feathers after N successive treatments with pre-conditioning agents, iron powder and subsequent magnetic harvesting. Each procedure was carried out in triplicate.

Pre-conditioning agents	**N**	**F**
Olive oil	16	96.0
Octanol	13	97.1
Squalene	13	96.6
Liquid paraffin	13	97.0
2-D-methylhexanoic acid	12	96.9

The results for the removal of heavy and tarry oil from the duck feathers using pre-conditioning agents and subsequent iron powder/magnetic harvesting are very promising, resulting in the maximum removal of 96 - 97% of oil, Table 4.10. Octadecanol solution (prepared by dissolving 1.0 g of octadecanol in 10.0 mL of 2-D-methylhexanoic acid) and 2-D-methylhexanoic acid appears to be the most effective single pre-conditioning agent tested. However, both octadecanol solution and 2-D-methylhexanoic acid appear to bleach the feathers. Thus neither are ideal for use individually as pre-conditioning agents. Furthermore, both octanol and squalene are expensive. Ultimately, olive oil has been selected as the optimum pre-conditioning agent because it is non-toxic, cheap and effective.

4.5.7 Experiments on Feathers Contaminated with Heavy Crude Mixed with a Pre-Conditioning Agent

Olive oil was thus used for the pre-conditioning of duck, penguin and seagull feathers laden with Shell HD crude oil. This was followed by the application of iron powder and subsequent magnetic harvesting as described previously. Figure 4.29 shows duck breast feathers at different stages of the treatment process. Similar cleansing results were obtained for the other feather types.

The histograms in Figures 4.30, 4.31, and 4.32 show the percentage removal of Shell HD crude oil from the oiled *in vitro* penguin, duck and seagull feathers respectively after pre-conditioning with olive oil, followed by successive treatments with iron powder and subsequent magnetic harvesting.

4.6 Testing on Live-Birds

A discharge of bunker oil from an unknown ship occurred on New Year's day, 2000 near Phillip Island. The oil was washed ashore around the vicinity of the Nobbies, 5 km from the animal rehabilitation facility. As a result of the oil spill, many Little Penguin returning from sea to their nesting habitats were covered with oil. Rangers from PINP and volunteers (including the author) set out to rescue the oiled birds around their nesting place. No more than three oiled birds were placed in a carton at a time and transported back to the animal rehabilitation facility for treatment. The weak and the more severely contaminated birds were placed in a woollen poncho, and all birds were rehydrated with Vytrate^{TM} electrolyte solution as described previously. Within 7 days 236 oiled penguins were rescued, 12 of which subsequently died from severe oil contamination.

The degree of oil contamination on oiled birds is divided into three categories: (i) lightly contaminated feathers, (ii) moderately oiled feathers and (iii) severely oiled feathers. On the third day after the oil spill, the first oil-contaminated penguin investigated had feathers that were moderately contaminated. On inspection, the feathers were dried and tarry. It was deemed necessary to use a pre-conditioning agent. While a volunteer securely held the oiled penguin, olive oil was applied by hand to soften the tarry feathers. The feathers were then covered with iron powder and immediately stroked with a magnetic device in one direction. The application of olive oil, iron powder and the magnetic stripping procedure was repeated 14 times.

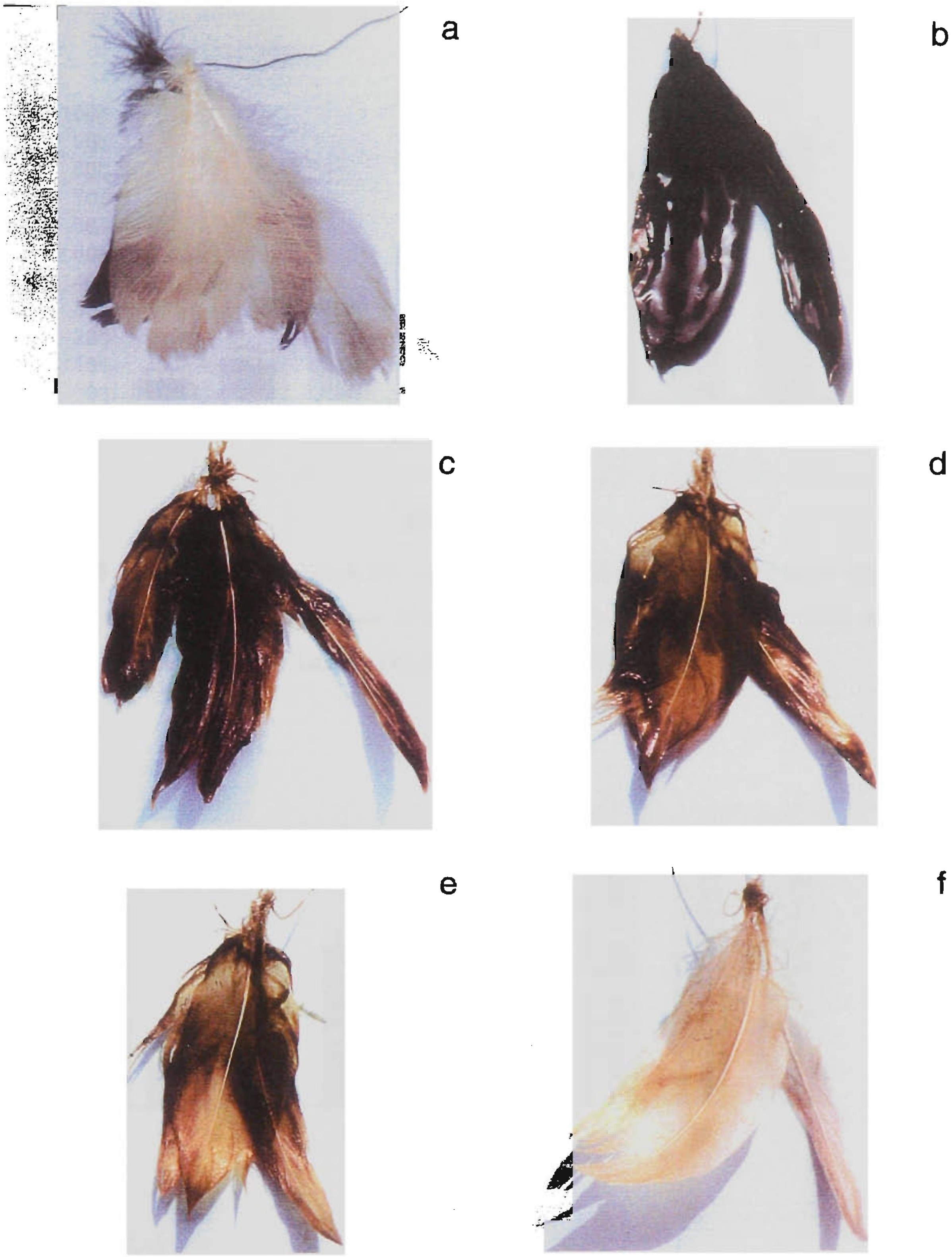

Figure 4.29 : Different stages of the magnetic cleansing process for duck breast feathers contaminated with Shell HD crude oil, which was pre-conditioned with: (a) original feather, (b) oil-laden feather, (c) 4 treatments with olive oil/iron powder and magnetic harvesting, (d) 8 treatments with olive oil/iron powder and magnetic harvesting, (e) 12 treatments with olive oil/iron powder and magnetic harvesting, and (f) 16 treatments with olive oil/iron powder and magnetic harvesting

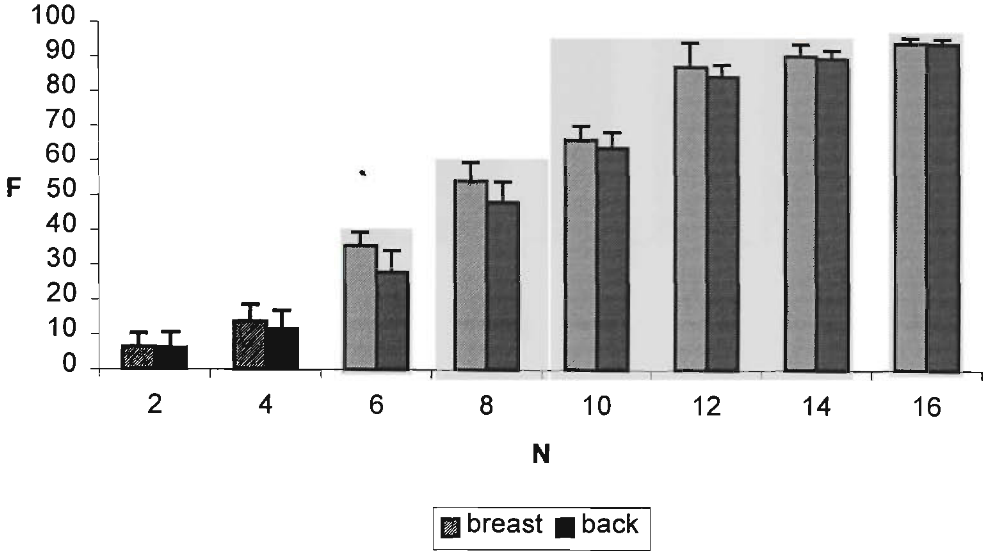

Figure 4.30 : Average percentage by weight of contaminants removed from the *in vitro* feathers of the domestic duck (*Anas platyrhynchos*). Error bars represent 95% confidence intervals for 5 replicates. The data are presented in Appendix 4.18.

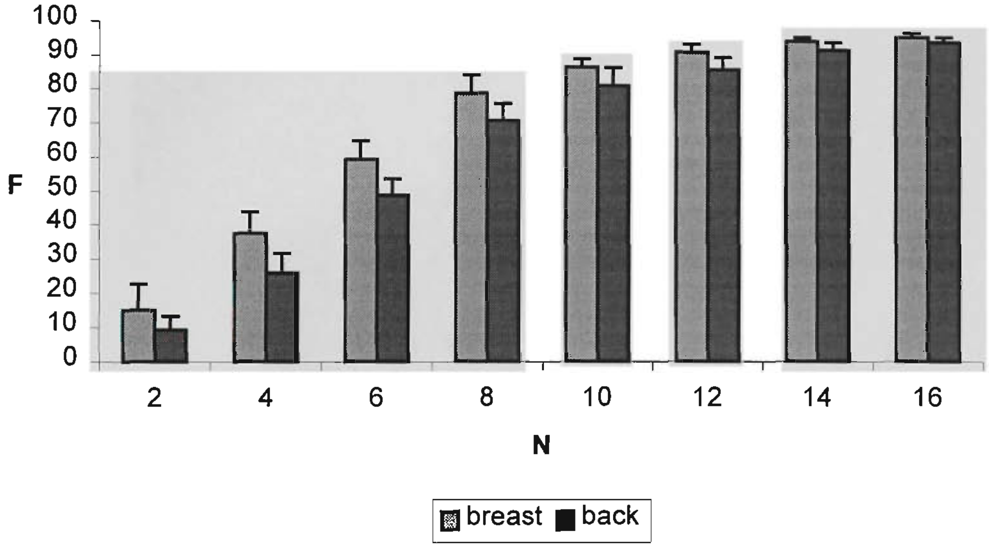

Figure 4.31 : Average percentage by weight of contaminants removed from the *in vitro* feathers of the Little Penguin (*Eudyptula minor*). Error bars represent 95% confidence intervals for 5 replicates. The data are presented in Appendix 4.19.

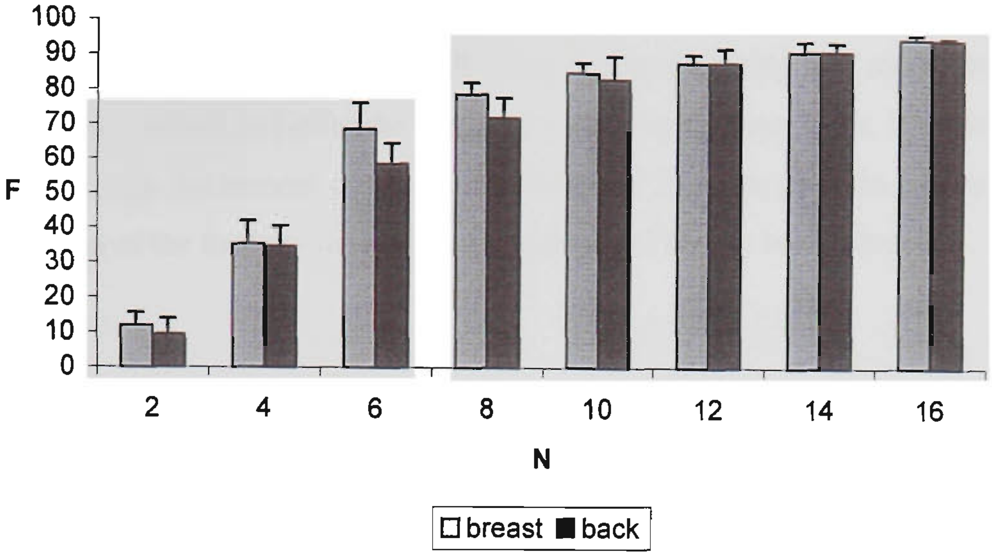

Figure 4.32 : Average percentage by weight of contaminants removed from the *in vitro* feathers of the common seagull (*Larus novaehollandiae*). Error bars represent 95% confidence intervals for 5 replicates. The data are presented in Appendix 4.20.

On the same day, the second penguin that was rescued had feathers that were severely contaminated, Figure 4.33. Again, the above cleansing procedure was repeated 16 times on a section of the breast feathers.

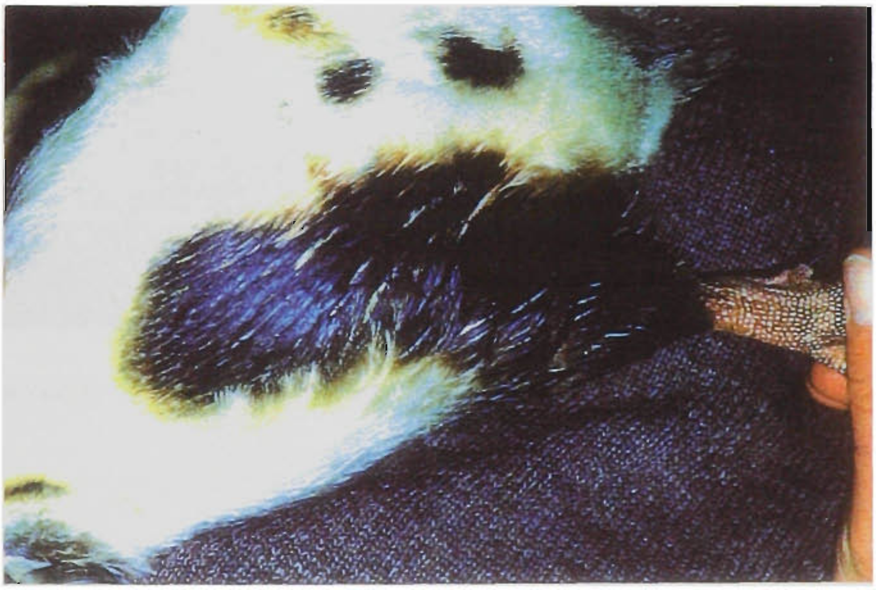

Figure 4.33 : A severely oiled penguin.

On the sixth day after the oil spill, a third rescued penguin was found to be severely contaminated. The above cleansing procedure was repeated up to 10 times. At this stage it was 2 am, the cleansing process had to be stopped for all the cleaning personnel to have a deserved rest. After a break of 8 h, the cleansing procedure was repeated 10 more times.

Penguin 1

It was necessary to hold the penguin at all times during cleansing and so it was difficult to weigh the penguin before and after the magnetic cleansing process. Thus, it is not possible to determine accurately the amount of oil that was removed from the penguin feathers. However, visual inspection of the feathers shows that the majority of oil has been removed.

Penguin 2

Figure 4.34 shows that the bulk of the oil has been removed from a section of the breast feathers of the second penguin after 16 treatments with iron powder. The results are encouraging considering that this was a severely contaminated penguin. The magnetic cleansing procedure was not continued beyond 16 treatments in this case. The entire cleansing process took approximately 30 min.

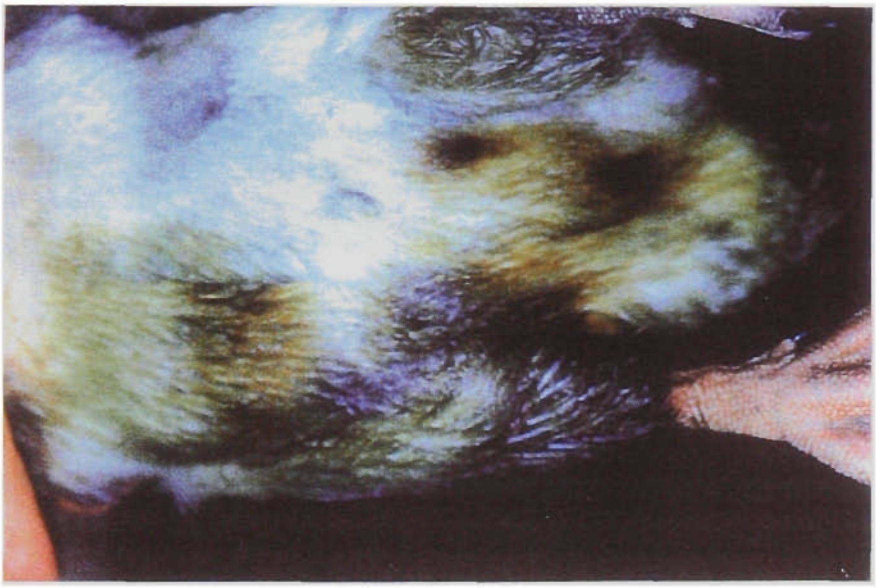

Figure 4.34 : A severely oil-contaminated penguin after being cleansed (same bird as in Figure 4.33).

Penguin 3

For the third oiled penguin, the magnetic cleansing process shows that the majority of oil has been removed after 20 treatments (10 treatments for each interval). The whole operation was carefully carried out, allowing rest period in order not to stress the bird. The entirecleansing process took approximately 40 min. Figure 4.35 shows the different stages of the cleansing process. It appears that the bulk of the oil has been removed. It is anticipated that with further treatments of olive oil and iron powder, most of the oil could be removed.

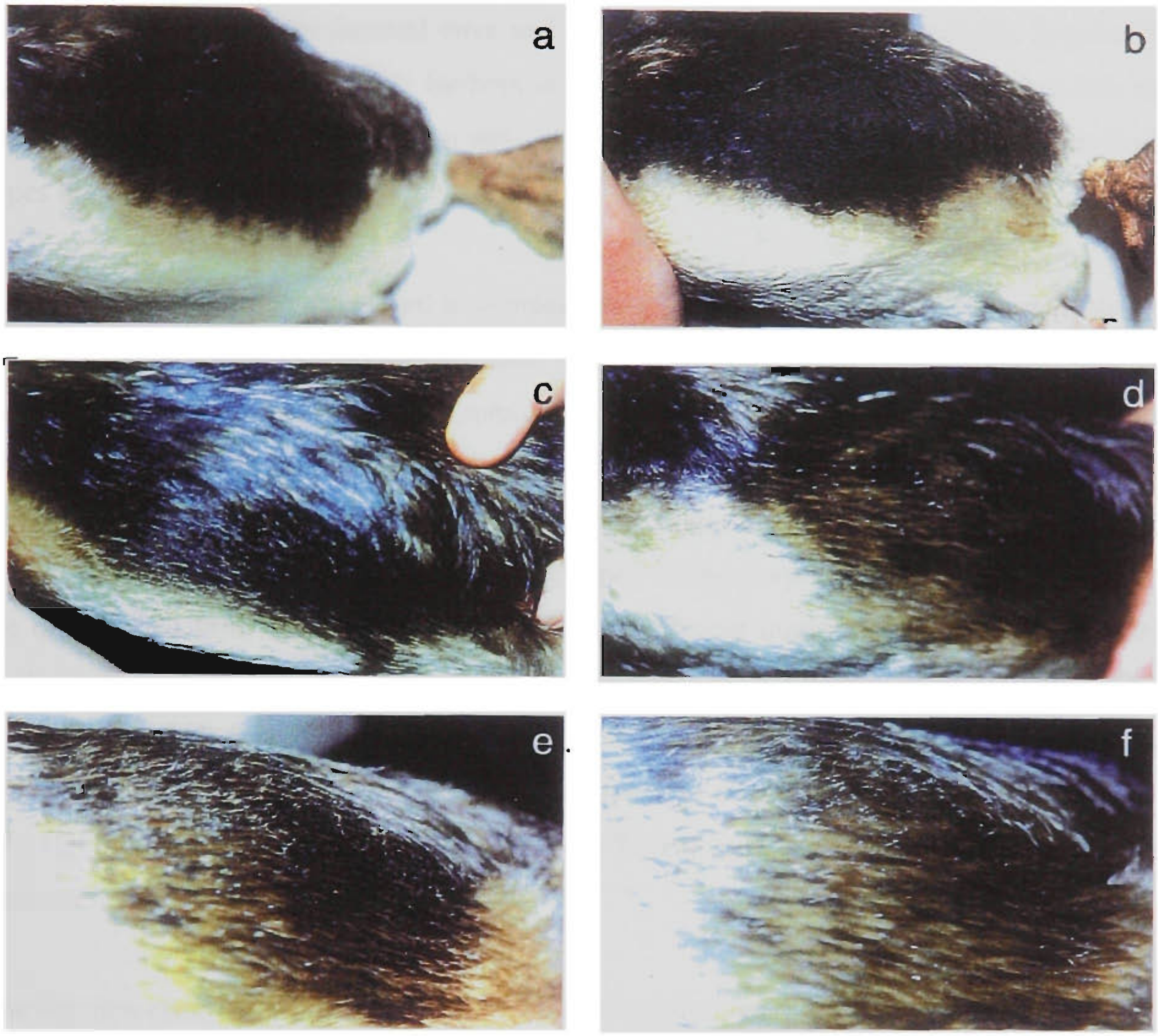

Figure 4.35 : Different stages of cleansing a severely oiled penguin: (a) oiled contaminated live penguin, (b) application of olive oil and iron powder, (c) 5 treatments with olive oil/iron powder and magnetic harvesting, (d) 10 treatments with olive oil/iron powder and magnetic harvesting, (e) 15 treatments with olive oil/iron powder and magnetic harvesting, and (f) 20 treatments with olive oil/iron powder and magnetic harvesting.

4.7 Conclusions

It has been demonstrated that the use of iron powder as a cleansing agent for the removal of contaminants from the plumage of whole birds is feasible. Preliminary studies indicate a high removal of contaminant from the plumage of duck and penguin carcasses. An experimental methodology was developed for quantifying the removal of contaminants from plumage and for the estimation of experimental error and reproducibility. The reproducibility as presented by decreasing magnitude of %CV for both *in vitro* and carcass models is comparable after nine treatments. A removal of greater than 90% of five different contaminants from different feather types has been achieved.

An empirical model was developed to compare the efficiency of removal of contaminants from the plumage of penguin and duck carcasses. It was found that the removal of lighter oils from the feathers is more efficient than the removal of more viscous oils and sea water/oil emulsion. The empirical model was also used to compare the efficiency of removal of contaminants from: (i) different feather types on the same bird, (ii) same feather type on different birds, and (iii) *in vitro* and carcass for the same feather types on the same bird. The removal of each of the oils studied from duck breast feathers is more efficient than the respective removal from duck back feathers. The removal of most of the oils from penguin back feathers is more efficient than their removal from penguin breast feathers. The removal of all oils from penguin breast feathers is more efficient than their removal from duck breast feathers. The removal of all oils from penguin back feathers is more efficient than their removal from duck back feathers.

The *in vitro* removal of all oils from duck and penguin breast feathers is more efficient than their removal from carcass duck and penguin breast feathers respectively. The removal of all oils from *in vitro* duck back feathers is more efficient than their removal from carcass duck back feathers. In general, the *in vitro* removal of all oils from penguin back feathers is more efficient than their removal from carcass penguin back feathers. The relationship between the efficiency parameters and viscosity was also determined. The results suggest that the efficiency of oil pick-up, in general, increases as the viscosity of the oil decreases.

The cleansing of oiled feathers was extended to weathered, oil-contaminated feathers. It was deemed necessary to used pre-conditioning agents to soften the weathered oil on feathers. Different pre-conditioning agents were trialled and olive oil was subsequently selected as the optimum agent for treating weathered feathers. The use of olive oil followed by the application of iron powder and subsequent magnetic harvesting of the oil on both *in vitro* duck feathers and feathers of live penguins has shown promising results.

Preliminary investigations on a limited number of live penguins (with weathered, oil-contaminated feathers) have shown that iron powder has the potential to remove the bulk of the contaminants (and cleansing agent) when birds are first encountered or during the initial stabilisation process. This outcome suggests that a portable magnetic device which can be used at the site of an oil spill to remove the bulk of oil from birds might be feasible. This is currently under consideration at Victoria University and industry participation is being sought.

Factors to be considered in the application of magnetic versus detergent cleansing methods include: efficiency of removal of contaminant, nature of the cleansing agent, stress to the bird, cost, labour intensity, and portability of equipment. It may be argued that even though the current studies result in removals in the high 90% range, even a few percent remaining is sufficient to cause hypothermia. However, it must be emphasized that these studies are prototypical and it may be possible to achieve a removal approaching 100% with improvements in magnetic devices and iron powder. For initial clean-up, it is not necessary to achieve 100% removal of contaminants from feathers. In relation to the nature of the cleansing agent and the cost, iron powder is a non-irritant, non-toxic and relatively cheap whereas detergents are found to remove the preening oils of birds and to damage the surface of the barbule. It should be appreciated that any cleansing protocol will involve stress to the bird. Magnetic particle technology has the potential for refinement which could greatly reduce cleansing time. Although, magnetic cleansing may not be a practical alternative to standard detergent methods at this time, this is highly likely to change in the future where it could become either a substitute or a complementary method.

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Chapter 5 Assessment of Feather Damage and Feather Recovery after Cleansing Procedures

5.1 Introduction

5.2 Feather Microstructure

5.3 Qualitative Assessment of Feather Damage

5.4 Quantitative Assessment of Feather Damage

5.5 Grid Coherency as a Quantitative Indicator of Feather Damage

5.6 The Development of a Practical "Damage" Parameter for Feathers

5.7 Conclusions

5.8 References

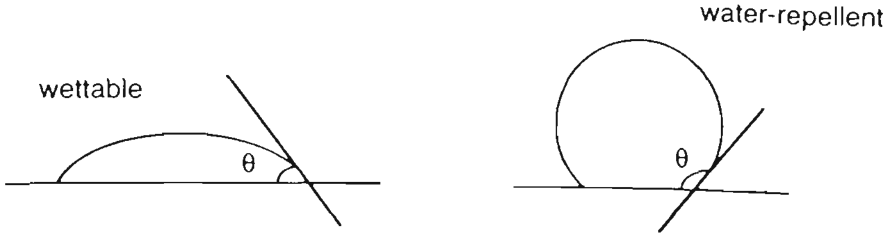
5.1 Introduction

During the 1970's the survival rate for birds contaminated by oil spills was very low (Smail, 1978; Perry *et al.*, 1978). Recovery times were highly variable ranging from days to months (Perry *et al.*, 1978; Mahoney, 1984). With improvement in detergent formulation and methodology (particularly rehabilitation techniques), the survival of oiled birds has now greatly increased (Bassères *et al.*, 1994; Schmidt, 1997). However, the problem of determining when to release the bird back to the wild is still tackled in a relatively complicated manner. In standard international procedures, this is usually ascertained by simply putting the bird into a pool at various stages during the rehabilitation process and observing its behaviour (Jessop & Healy, 1997; Stocker, 2000). This requires a well-equipped rehabilitation facility with a high level of available expertise.

Currently, there is no convenient quantitative way of examining the feathers for information that would suggest that a given bird is ready for release. There are a number of approaches to this problem, some of which have already been investigated whilst others are more hypothetical. One approach, yet to be fully developed, involves the use of the technique of gas chromatography (GC) to monitor the level of preening oils and waxes on sample feathers taken from the rehabilitating bird. The GC methodology for the identification and analysis of preening oils and waxes of various birds has been reported in the literature (Murray, 1962; Odham & Stenhagen, 1971). Elder (1954), Stettenhein (1972) and Elowson (1984) note that preening oils might be an important factor in providing feather water repellency.

The relationship between the water repellency of plumage and the level of preening oils and waxes in selected individual feathers is unclear and remains to be established. According to Gill (1990), a bird regularly applies preening oils and waxes to its plumage in order to provide an insulating and waterproofing layer. The importance of the feather microstructure in conferring water repellency has also been discussed (Elowson, 1987). Smail (1978) claims that it is the structural properties of the feather which are sufficient, in themselves, to provide waterproofing, and that the preening oils and waxes are necessary only to keep the plumage supple.

Rijke (1968, 1970) proposed that the wettabilty of feathers could be explained by a textile model (Cassie & Baxter, 1944). In this model, the water repellency of a surface is determined by whether water "beads up" or "spreads out", Figure 5.1. Thus the fine structure of a feather may be compared to the "criss-cross" pattern of a fabric.



(a) $\theta < 90^\circ$ (b) $\theta > 90^\circ$

Figure 5.1 : Contact angles of water droplets on: (a) wettable and (b) water-repellent surfaces.

Elowson (1984) argues that the "textile model" does not reliably describe water repellency in feathers because feather structure is more complex and variable than textiles. Some species of birds do not conform to the "textile model" and the wettability of feathers is also influenced by the architecture of the feather coats. Thus different species of bird are different in the density, distribution and extent of the overlap of their feathers.

One approach to assess water repellency is to measure the "roll-off" angle of water droplets on individual feathers (Kennedy, 1970). The roll-off angle is the tilt angle of the surface required to roll drops of water (of a known volume) off the surface. In principle, feather recovery during the rehabilitation process could be assessed by exploiting this parameter. A low roll-off angle would suggest a greater water repellency (less damage), whereas a high roll-off angle would suggest greater wettability (higher damage). Such experiments are difficult to set up and conduct and this approach may not be practical.

Gravimetric determination of water repellency of plumage in oiled birds has been reported. For example, it was demonstrated that the amount of water absorbed by the plumage of oiled jackass penguins (*Spheniscus demersus*) was more than that absorbed by non-oiled controls (Kerley *et al.*, 1987). However, since this method is very time and labour intensive, it is unlikely that it could be developed into a routine method for assessing the water repellency of plumage in recovery birds.

In this study, feather damage was initially assessed qualitatively by visualising the feather vane coherency using optical microscopy. It is assumed that less coherency is related to more feather damage. Subsequent scanning electron microscopy (SEM) was also used in order to search for microstructural features which could be exploited as *quantitative* indicators of damage.

5.2 Feather Microstructure

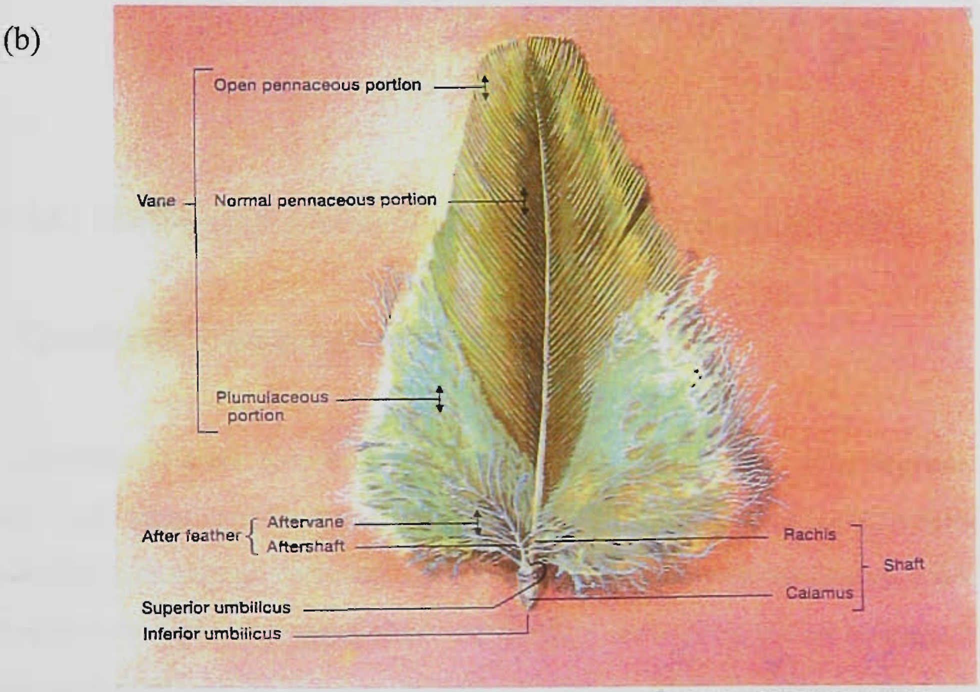
Feathers are divided into six basic categories (Gill, 1990): contour, flight, down, semiplume, filoplume and bristle, Figure 5.2(a). Contour feathers include a shaft which is essentially composed of two parts, the calamus and the rachis, Figure 5.2(b). The calamus is implanted in the feather follicle and the rachis is a solid portion of the shaft above the skin. On each side of the base of the rachis can be seen the plumulaceous (soft and fluffy) texture. The pennaceous (firm and compact) texture appears beside the rachis for a short distance and then spreads outwards at higher levels in the vane. The hooklets (tiny hooks) are located on the distal barbules.

Although the contour feather has been chosen as the subject for this investigation, a brief description of other feather types is appropriate (Bone, 1988; Gill, 1990). Flight feathers are large, stiff, and completely pennaceous. Down feathers are highly plumulaceous and have a greatly reduced or absent rachis. Semiplumes have a well-developed rachis with entirely soft vanes. Filoplumes have a fine shaft that thickens distally, ending in a terminal tuft of one to six short barbs with plumulaceous barbules. Bristle feathers are simplified feathers that consist only of a stiff, tapered rachis with usually only a few barbs clustered around the base.

In the present study, contour feathers were used since they are the primary insulating feathers. Feathers from three species of bird were employed, namely the domestic duck (*Anas platyrhynchos*), Little Penguin (*Eudyptula minor*), and the Silver Gull (*Larus novaehollandiae*). The carcasses used are of birds that have been killed either at abattoirs (ducks) or by accidents (such as road kill - penguins). Every attempt has been made to extract feathers with the utmost care. Certainly, the "undamaged" feathers do not show that the microscopic feather architecture has been disrupted by this process. "Proof of principle" investigations were carried out primarily on the domestic duck contour feathers since this is widely employed as a standard laboratory model (Jenssen & Ekker, 1989; Bassères, 1994). Our microscopic examination of the these feathers suggest that, in non-disrupted feathers, most of the hooklets on the distal barbules do not actually come into contact with the neighbouring proximal barbules and, therefore, cannot be described as being engaged.

It would appear that most of the hooklets project into the space defined by surrounding barbules, although not all are horizontally disposed. However, such engagement might ensue from the barbules moving with respect to each other as a result of disruption. In this way the hooklets would act like "grappling hooks" to limit the extent of disruption to the vane coherency. The hooklets may also act as elastic buffers in this regard without actually becoming engaged.

Feather types: bristle, semiplume, flight, and (bottom row) contour, down, bristle/eyelash, and filoplume



The main parts of a typical contour feather

Figure 5.2: (a) The six basic categories of feathers and (b) a typical contour feather [from Brooke & Birkhead (Eds.), 1991].

The fact that in many textbooks, the hooklets are represented in idealized schematic diagrams as being almost perfectly engaged (see Figure 5.3) can be misleading in representing the subtle role(s) that the hooklets might play. Thus we also advocate a role for the hooklets in *directly* maintaining the waterproofing properties of the feathers. The hooklets may project into the aforementioned space and provide additional support for water droplets which might otherwise pass through and wet the feathers. They may also maintain a high air-to-water contact area resulting in a high contact angle, enabling the droplets to roll off. We suggest that another role for the hooklets (to be discussed later) involves directing the mechanical strain on a feather as it grows.

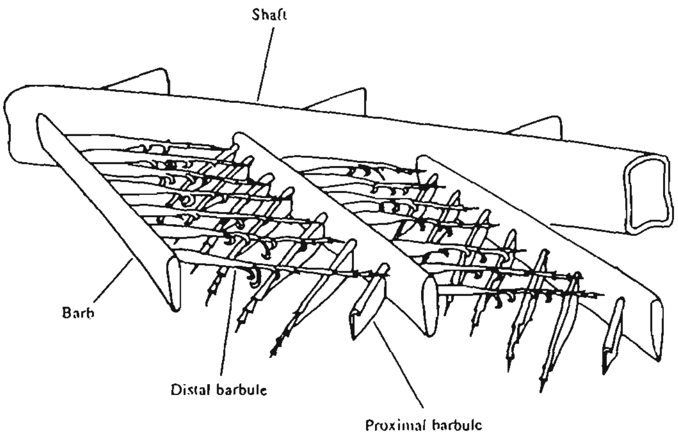


Figure 5.3 : Structure of a primary flight feather (from Ennos *et al.*, 1995).

5.3 Qualitative Assessment of Feather Damage

Initial inspections were carried out using optical microscopy. The contour feathers of the domestic duck were used in these studies and Oil C was used to contaminate these feathers. Virgin feathers, detergent-cleansed oiled feathers and iron powder-cleansed oiled feathers were examined in turn. The detergent-cleansed feathers were prepared as follows. Firstly, 5% (v/v) detergent was prepared by mixing 10 mL of "Decon 90" detergent with 190 mL of distilled water. Sample oiled breast feathers from a domestic duck *(Anas platyrhynchos)* were held by their quills and agitated in the 5% (v/v) detergent for a period of 10 min. The feathers were then rinsed by agitating them in distilled water for 5 min. The feathers were allowed to dry in air for 1 week. Samples of single feathers were placed on a glass plate and clamped down. A Nikon optical microscope (labophot 248625), fitted with a Nikon camera, Model 401 was used to examine the feather structure.

Representative photomicrographs for these investigations are shown in Figure 5.4 (a-c). The virgin feathers display a classic, highly coherent vane. The feathers, after oiling and cleansing with detergent, display noticeable disruption to the vane. However, the feathers cleansed with iron powder show that the coherency of the vane has been essentially restored to its original condition, with the feathers being visually (and texturally) indistinguishable from the virgin feathers. We have since confirmed this quantitatively (see Section 5.5).

It was surmised that an even closer examination of the feathers might provide clues as to potential *quantitative* indicators of feather damage. Therefore, it was decided to examine feather sections under the SEM. Again, contour feathers of the domestic duck were used. In this case, feather sections were carefully dissected so as not to disrupt the existing microstructure. These were mounted on pins, which were then gold-coated for SEM examination. Figure 5.5 (a-c) shows the electron micrographs of an undamaged feather section at different magnifications. Again, a high degree of vane coherency is observed and the hooklets are seen not to be engaged.

Figure 5.6 is a SEM image of a detergent-treated virgin feather which appears to show hooklet elongation. It should be emphasised that these high resolution micrographs should be treated with caution because of the limited field of view. However, the apparent unravelling or extension of hooklets in detergent damaged feathers was considered as a possibility for further investigation as a quantitative indicator for damage.

5.4 Quantitative Assessment of Feather Damage[1]

Building on the information obtained from the SEM study, it was decided to explore the extension of the hooklets in both untreated and detergent-treated feathers by exploiting available digital imaging technology. In this way, the *entire* feather may be explored rather than a limited field of view. Such imaging technology is being increasingly used in industry and education (Ando *et al.*, 1997; Liberatore & Breem, 1997; Shimeld *et al.*, 2000).

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[1] This work was carried out as part of a collaborative project involving members of the Animal Rehabilitation Technology (ART) Group, Victoria University. The members include: John Orbell, Stephen Bigger, Lawrence Ngeh, Leroy Godinho, Kate Broadhurst, Ee Kai Tan, Manfred Zabinskas, Meris Zheng, Merryn Coutts and Oliver Percovich.

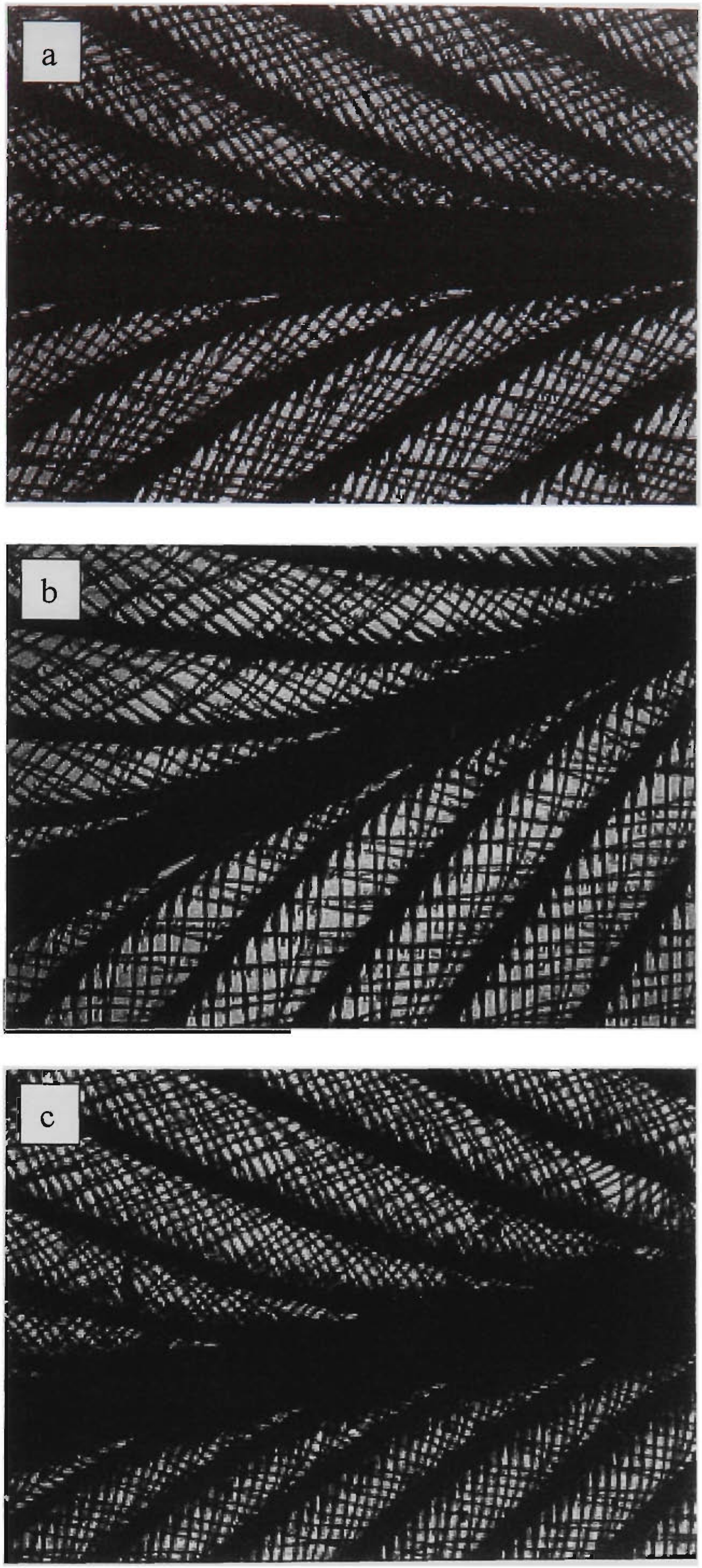


Figure 5.4 : An optical microscopic examination of the coherency of the hydrophobic microstructure of duck breast feathers viewed at 50× magnification: (a) virgin feathers, (b) after oiling and cleansing with detergent, (c) after oiling and cleansing with iron powder.

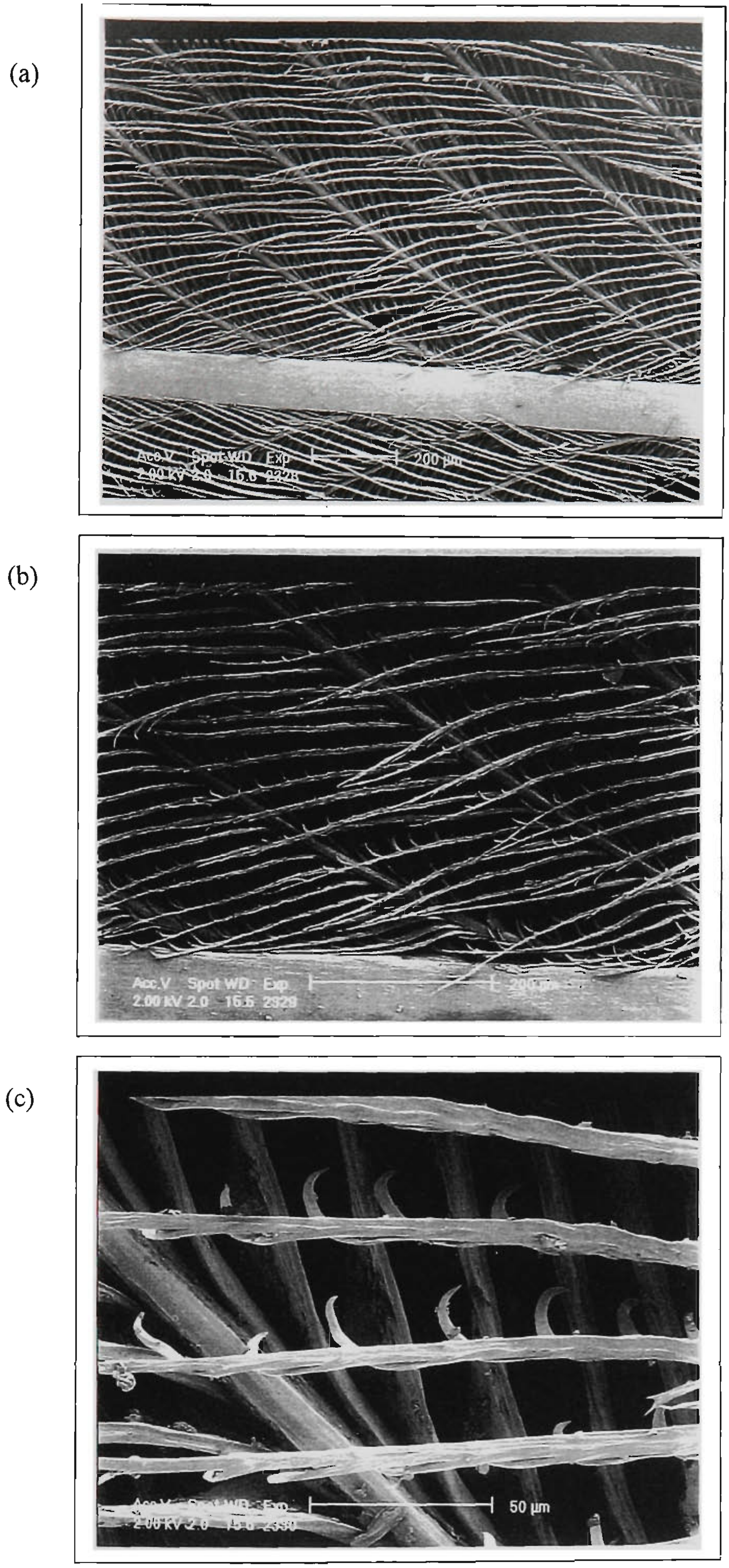


Figure 5.5 : Scanning electron micrographs of untreated duck feathers at : (a) 100×, (b) 200×, and (c) 800× magnification.

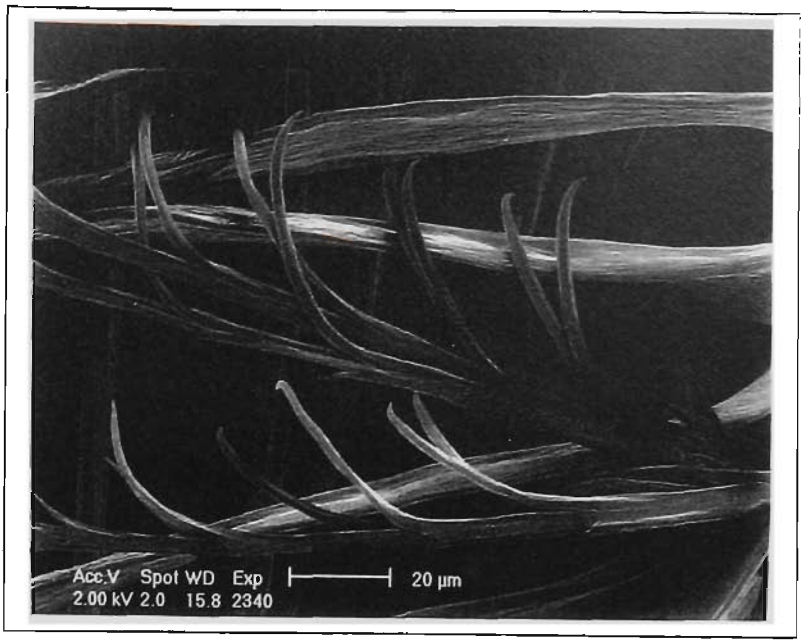


Figure 5.6 : Scanning electron micrograph of a non-oiled feather subjected to 10% (v/v) detergent treatment.

In this study, contour duck feathers from the same location of the breast of the same bird were investigated. Untreated feathers were agitated in 10% (v/v) "Decon 90" detergent for a duration of 5 min (see Section 5.3). A 10% (v/v) detergent solution was used in order to deliberately damage the feathers to a greater extent than the commonly used 5% (v/v) detergent. The feathers were then rinsed thoroughly in distilled water for 5 min and allowed to dry in air for 1 week. A control experiment, 0%(v/v) detergent was also carried out by agitating untreated feathers in distilled water for 5 min and also air-drying for 1 week. It should be emphasized that, at this stage, no attempt is being made to mimic how birds might be normally washed and rinsed. After the damage indicator has been established, this issue can be addressed.

Barbs from the base to the tip of a representative contour feather were carefully selected and dissected from either side of the rachis. Each barb was placed on a 1 mm vernier micrometer slide and covered by a 0.01 mm glass slip. These feathers were then examined under a Zeiss Axioplan 2 light microscope at a 200× magnification. For the purpose of accurate measurement, hooklets lying in the plane of the barb vane were brought into focus. It is reasonably assumed that these hooklets are representative and randomised. The hooklet extension is defined from where the hooklet leaves the barbule stem, to the tip of the hooklet along the contour. This provides adequate quantities of hooklet measurements per captured image.

To measure the hooklet extension, the microscope was linked to a Kontron digital imaging system. The associated software (KS300, version 2, 1995) enables a customised "macro" to be developed for specific imaging tasks. For this research program, a macro was developed so that for a given captured image a visual trace could be made along a hooklet of interest using crosshairs controlled by the "mouse", Figure 5.7. The extension distance is then automatically stored within a database which can be conveniently transferred into a Microsoft Excel^{TM} spreadsheet(s) for subsequent analysis. The macro was calibrated using a micrometer slide: 1mm vernier, 0.01 mm divisions, which correlates with the appropriate magnification of the microscope (200× in this case). This technique allows a large number of accurate measurements to be made in a short period of time.

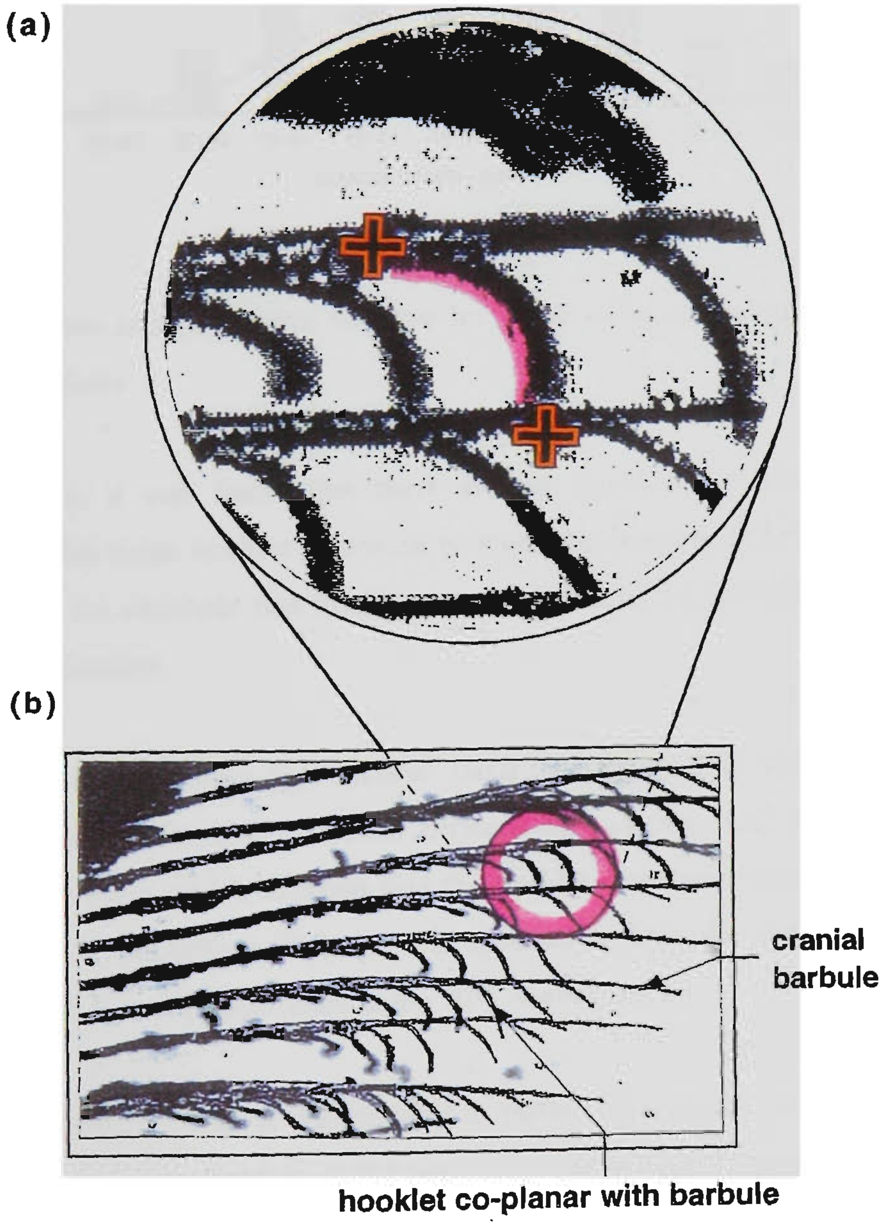


Figure 5.7 : Digital image of hooklets on a barbule at: (a) 800× and (b) 200× magnification showing a focus on hooklets that lie in-plane. Indicated on the enlarged view is how a trace is made with the "mouse" in order to record the hooklet extension.

For convenience, the feather was arbitrarily divided into three sections along its length, namely, the base, the middle and the tip. The following data were collected within each section for untreated and treated feathers. For virgin, untreated feathers, 270 measurements of hooklet extension were recorded from each section, Appendix 5.1, and for treated feathers, 300 measurements of hooklet extension were recorded from each section, Appendix 5.2. For all sets of data, reasonably normal distributions are observed (see for example Figure 5.8).

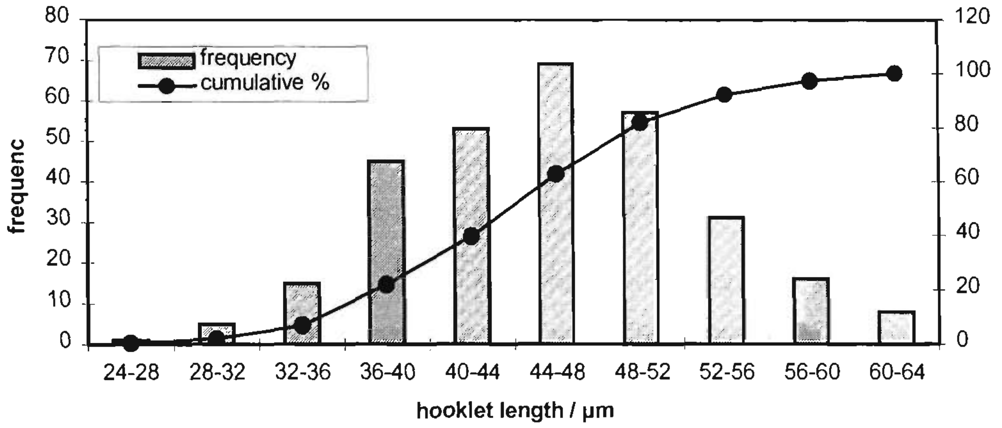


Figure 5.8 : Histogram and cumulative % curve for 300 hooklet measurements made on 10% detergent treated feathers.

Considering all data, it was found that there are no significant differences at the 95% confidence level in the mean hooklet extension between the controls and the detergent-treated feathers. Therefore, we conclude that hooklet extension cannot be considered an appropriate indicator of feather damage.

When the data is considered on a "per section" basis (see Figure 5.9), not surprisingly, there remains no difference in hooklet extension between the controls and the treated feathers. However, a trend emerges which suggests that the hooklet extension increases on going from the tip to the base of the feather. This trend is apparent in both the control and the treated samples (see Table 5.1) and is significant at the 70% confidence level.

In view of this interesting trend, it was decided to further investigate the property of hooklet extension with respect to the location of the hooklet on the feather. In particular, it was earlier surmised (see Section 5.2) that an additional role for the hooklets could be to direct the mechanical strain on a feather as it grows, hence contributing to its curvature. Our approach to this problem involved the measurement of a very large number of hooklet extensions from the base to the tip of a representative contour feather, with a view to analysing the distribution of extensions on either side of the rachis (left and right).

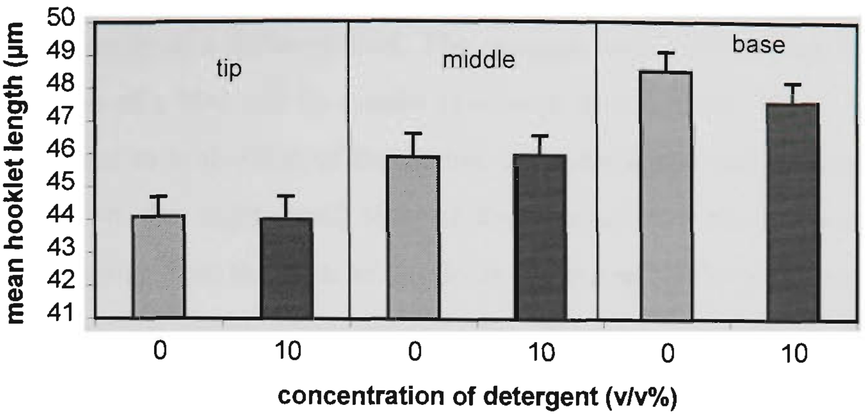


Figure 5.9 : A comparison of the mean hooklet extensions observed in different feather sections for control and detergent-treated feathers. Error bars represent 70% confidence intervals for 100 replicates, Table 5.1.

Table 5.1 : Summary of results for mean hooklet extension (µm) of control (0% (v/v) detergent) versus 10% (v/v) detergent treatment at 70% (1σ) and 95% (2σ) confidence levels for 100 measurements.

Feather section	**Detergent concentration, (v/v)%**	**Mean hooklet length, $\bar{x}$ / µm**	**s**	$\sigma_{\bar{x}}$	**± 1.0** $\sigma_{\bar{x}}$	**± 2.0** $\sigma_{\bar{x}}$
Tip	0 (control)	44.1	5.6	0.6	± 0.6	± 1.1
	10	44.0	7.3	0.7	± 0.7	± 1.4
Middle	0 (control)	45.9	7.1	0.7	± 0.7	± 1.4
	10	46.0	6.7	0.6	± 0.6	± 1.3
Base	0 (control)	48.5	6.0	0.6	± 0.6	± 1.2
	10	47.6	6.4	0.6	± 0.6	± 1.3

A methodology similar to that described previously was used to examine an undamaged virgin feather originating from the breast region of the domestic duck *(Anas platyrhynchos)*. Barbs were dissected individually from both sides of the rachis and were mounted in sets of six adjacent barbs per glass slide, to provide a collection of 31 mountings. Using the imaging procedure described previously a total of 4,545 data were recorded, Appendix 5.3. The data for this frequency is given in Appendix 5.4.

Analysis of these data showed them to be normally distributed (see Figure 5.10) with an average hooklet extension of 35.6 µm. It should be noted that this is different from the average hooklet extension measured previously (46.0 µm, Table 5.1), which is not unexpected since the feather was taken from a different bird. The average hooklet extension is expected to vary according to the age of a bird and its gender (Lucas & Stettenheim, 1972). When the data are analysed with respect to both sides of the rachis, an interesting trend emerges, Figure 5.11. It can be seen that on the right hand side of the feather the hooklet extension decreases monotonically on going from the base to the tip as suggested by the previous study. On the left hand side of the feather, which corresponds to the direction in which the feather curves, the hooklet extension at the tip is significantly less. Therefore it is possible that the variation in hooklet extension on either side of the rachis contributes to the curvature of the growing feather by an asymmetry in mechanical strain.

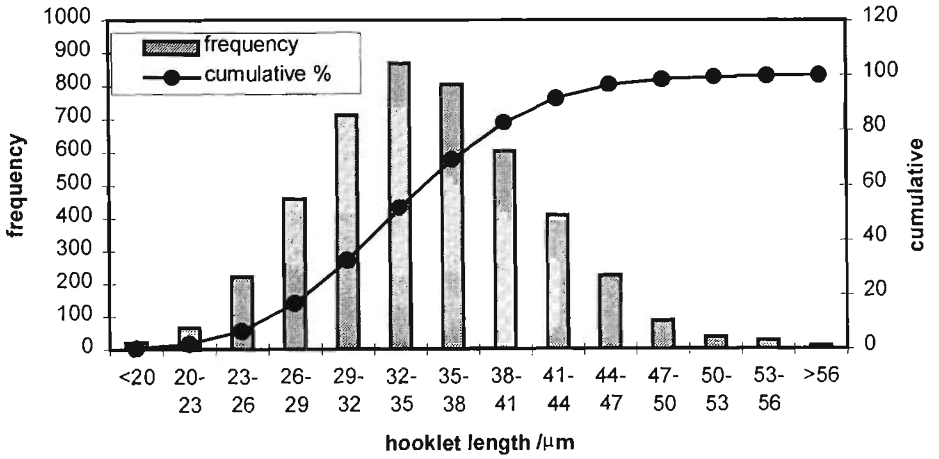


Figure 5.10 : Combined histogram (from tip, middle and base sections) and cumulative curve for 4545 hooklet measurements from an undamaged virgin duck breast feather.

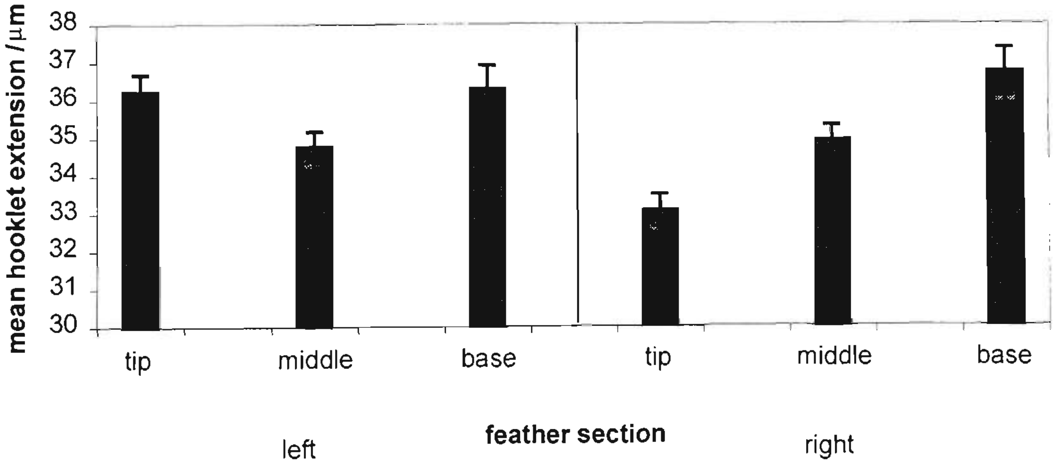


Figure 5.11 : Comparison of trends in mean hooklet extension between two sides of the feather.

5.5 Grid Coherency as a Quantitative Indicator of Feather Damage

Having demonstrated that hooklet extension is not a satisfactory quantitative indicator of feather damage, alternative indicator(s) were considered. It may be reasonably stated that the extent of feather damage may be reflected in the degree of coherency of the feather vane. Therefore, a parameter that is able to quantify the degree of coherency might also provide a quantification of feather damage. To this end, the feather vane may be modelled by a two-dimensional grid, Figure 5.12.

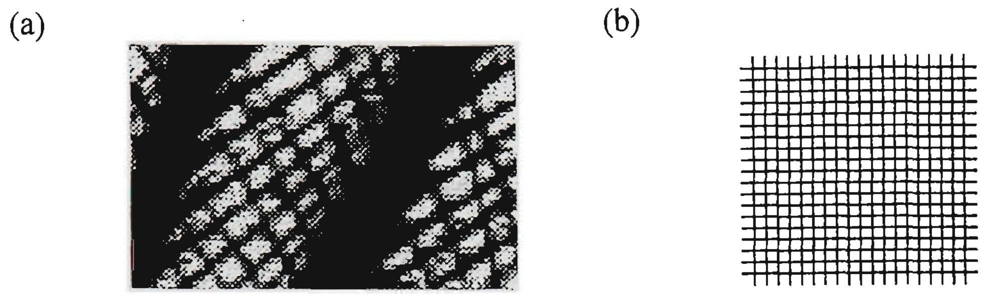


Figure 5.12 : (a) Feather vane (undamaged), and (b) ideal two-dimensional grid.

A perfectly coherent grid has all of the spaces of equal area, Figure 5.12(b). When this is the case, the area distribution is represented by a single vertical line, Figure 5.13(a). Upon disruption (damage), it is postulated that the areas would assume a normal distribution, Figure 5.13(b). It is also postulated that the extent of such disruption is reflected by the width of the distribution.

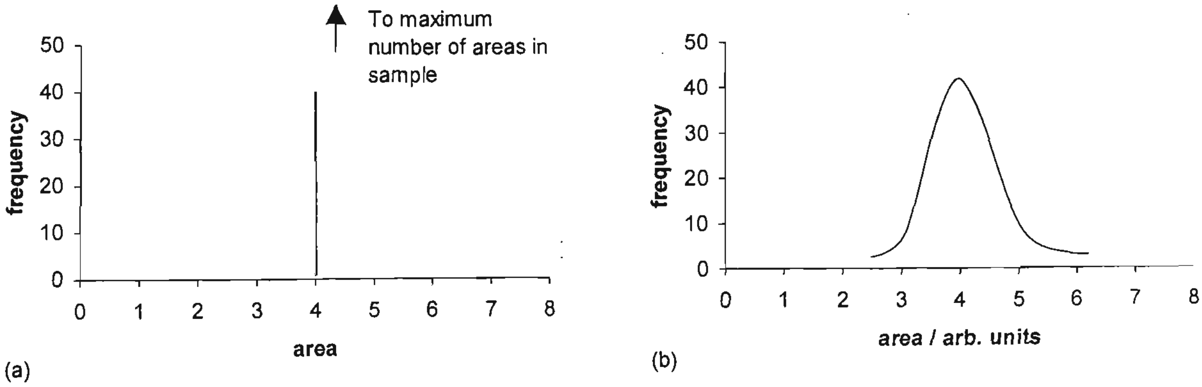


Figure 5.13 : Theoretical area distributions for: (a) a perfectly coherent grid and (b) a disrupted (incoherent) grid.

To explore the above postulates, a mathematical model of this concept was developed. A Monte Carlo computer program was written to calculate the area distribution histogram of the quadrilateral elements in a randomly disrupted two-dimensional grid as a function of the extent of the disruption to the grid. In the program, a square grid of side dimensions, S, containing n × n elements was generated as a series of n + 1 horizontal and vertical intervals drawn between the points P_1 and P_2:

$$\text{horizontal intervals:}\quad P_{H,1}[x_H(i, 1), y_H(i, 1)];\ P_{H,1}[x_H(i, 2\,), y_H(i, 2)] \tag{5.1}$$
$$\text{vertical intervals:}\quad P_{V,1}[x_V(i, 1), y_V(i, 1)];\ P_{V,2}\,[x_V(i, 2), y_V(i, 2)] \tag{5.2}$$

where $0 \le i \le n$, and the subscripts H and V represent respectively horizontal and vertical components.

The allowed deviations of the termini of each interval from its original position on the grid is given by equation (5.3):

$$d = f \times S/2n \tag{5.3}$$

where $0 \le f \le 1$. The constant f is set before the program is run and controls the extent of random disruption to the grid. Horizontal and vertical intervals within the perimeter of square S are randomly disrupted by re-setting the coordinates of their termini to:

$$\text{horizontal intervals:}\quad P_{H,1}[0, i \times S/n + k \times d];\ P_{H,2}[S, i \times S/n + k \times d] \tag{5.4}$$
$$\text{vertical intervals:}\quad P_{V,1}[i \times S/n + k \times d, 0];\ P_{V,2}[i \times S/n + k \times d, S] \tag{5.5}$$

where $0 < i < n$, and the constant k is generated randomly and lies within the limits of $0 \le k \le 1$. The sign of k is also generated randomly and independently.

A matrix of intercepts $\{x(i, j), y(i, j)\}$ is generated for the intersection of each pair of intervals for $\{(i, j)\colon 0 \le (i, j) \le n\}$ using the following system of linear equations:

$$d_1 = x_H(i, 2) - x_H(i, 1) \tag{5.6}$$
$$m_1 = [y_H(i, 2) - y_H(i, 1)]/d_1, \text{ for } d_1 \ne 0 \tag{5.7}$$
$$d_2 = x_V(j, 2) - x_V(j, 1) \tag{5.8}$$
$$m_2 = [y_V(j, 2) - y_V(j, 1)]/d_2, \text{ for } d_2 \ne 0 \tag{5.9}$$
$$d_3 = m_2 - m_1 \tag{5.10}$$
$$x(i, j) = [m_2 x_V(j, 1) - m_1 x_H(i, 1) + y_H(i, 1) - y_V(j, 1)]/d_3, \text{ for } d_3 \ne 0 \tag{5.11}$$
$$y(i, j) = m_1[x(i, j) - x_H(i, 1)] + y_H(i, 1) \tag{5.12}$$

The area of each quadrilateral in the randomly disrupted grid is calculated systematically and stored in the array $A(i \times n + j)$ where $0 \leq (i, j) \leq n$. The area of a quadrilateral $Q(P_1, P_2, P_3, P_4)$ defined by the points $P_1(x_1, y_1)$, $P_2(x_2, y_2)$, $P_3(x_3, y_3)$ and $P_4(x_4, y_4)$ is given by equation (5.13) if where P_1, P_2, P_3 and P_4 lie in sequential order on the perimeter (McLanaghan *et al.*, 1996).

$$A(i \times n + j) = {}^1/_2 \sum_{m=1}^{m=4} (x_m y_{m+1} - x_{m+1} y_m) \text{ ; where } x_5 = x_1 \text{ and } y_5 = y_1$$

$$= {}^1/_2[(x_1y_2 - x_2y_1) + (x_2y_3 - x_3y_2) + (x_3y_4 - x_4y_3) + (x_4y_1 - x_1y_4)] \qquad (5.13)$$

The coordinates of Q are defined for $\{(i, j): 0 \leq (i, j) \leq n\}$ from the matrix of intercepts as given by equations (14) to (17):

$$P_1[x(i, j), y(i, j)] \qquad (5.14)$$

$$P_2[(x(i, j + 1), y(i, j + 1)] \qquad (5.15)$$

$$P_3[(x(i + 1, j + 1), y(i + 1, j + 1)] \qquad (5.16)$$

$$P_4[x(i + 1, j), y(i + 1, j)] \qquad (5.17)$$

Under the conditions allowed in the randomized disruption of the original grid, the maximum area, A_{max}, of any quadrilateral Q, is given by:

$$A_{max} = 4(S/n)^2 \qquad (5.18)$$

A histogram of the distribution of areas $A(i \times n + j)$ can be constructed by dividing A_{max} into z_1 equal divisions, each of width δA where:

$$\delta A = A_{max}/z_1 \qquad (5.19)$$

and incrementing elements of a frequency array $Z(z_1)$ in accordance with equation (5.20):

$$Z(\mathrm{INT}(A(i - 1)/\delta A)) = Z(\mathrm{INT}(A(i - 1)/\delta A)) + 1,\ 1 \leq i \leq n^2 \qquad (5.20)$$

The computer program can be run using a total of T iterations and a cumulative histogram of the area distribution collected.

Figure 5.14 shows three typical grids generated by the program under the condition where there is (a) no disruption, (b) an intermediate extent of disruption and (c) maximum disruption to the grid. Figure 5.15 shows the cumulative area distribution obtained after T = 2000 iterations for a grid where S = 200 and n = 20 under the conditions where: (a) f = 0.2, (b) f = 0.4 and (c) f = 0.8. In these plots z_1 = 200. The plots reveal that the width of the distribution increases and the mode of the distribution decreases with increasing values of the parameter f. The program is listed in Appendix 5.5.

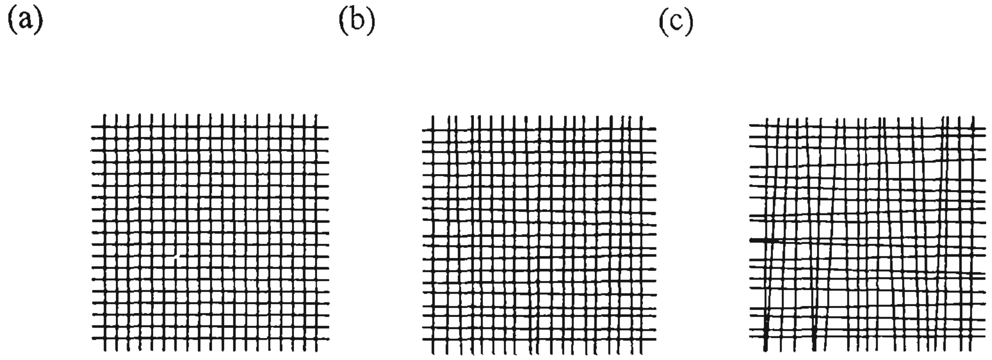


Figure 5.14: Theoretical grids with: (a) no disruption, f = 0, (b) increased disruption, f = 0.5 and (c) maximum disruption, f =1.0.

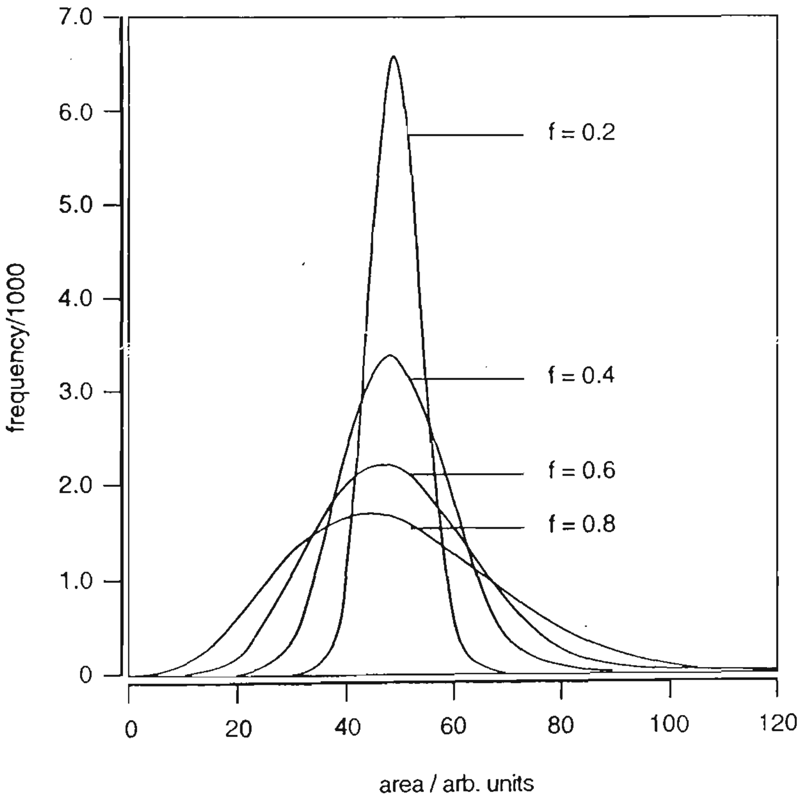


Figure 5.15 : Distribution of areas of theoretical disruption to a grid where the magnitude of f is proportional to the extent of disruption to the grid.

The mathematical model defines an ideal (perfect) grid to have no disruption (f = 0) and to acquire no area distribution, Figure 5.14(a). The model suggests that the degree of disruption may indeed be measured by the width of the distribution. With increasing disruption, the areas become non-equivalent, Figure 5.14(b-c) and the distribution acquires more width and less height, Figure 5.15. In the theoretical analysis we might expect that the distribution will also be right-skewed. This is because, as we vary f, the upper bound (or maximum possible area of a grid segment) may change but the lower bound remains fixed at zero.

The theoretical treatment is suggestive of a high level of sensitivity for the measurement of grid coherency. For example, if the grids for f = 0.5 and f = 0.7 are viewed, Figure 5.16, they can be seen to be essentially visually (quantitatively) indistinguishable with respect to the degree of disruption. However, if one quantifies the relative "squatness" of these distributions by calculating the ratio of the width (at half height) to the height in each case, the values obtained of 0.62 and 1.32 respectively can be seen to be almost 100% different. This notion has been used to develop a damage indicator as follows.

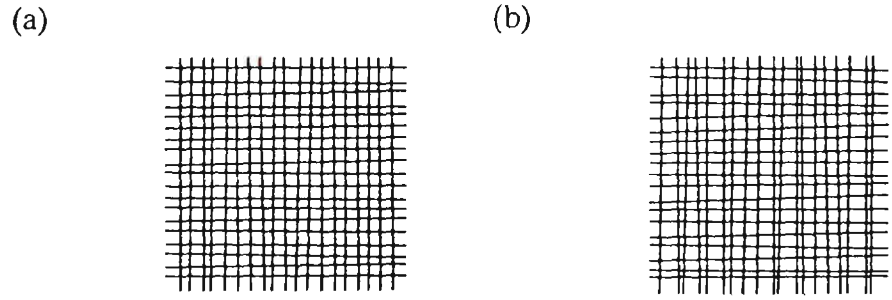


Figure 5.16 : Theoretical grids increasing disruption: (a) f = 0.5 and (b) f = 0.7.

The degree of disruption to the feather vane is reflected in the width at half height of the distribution. In a practical situation, a normalised and more sensitive parameter for describing the relative "squatness" of a distribution is the half-width ($W_{1/2}$) to peak height (H) ratio, Figure 5.17. This ratio (D) may then be used as an indicator for feather damage in practice.

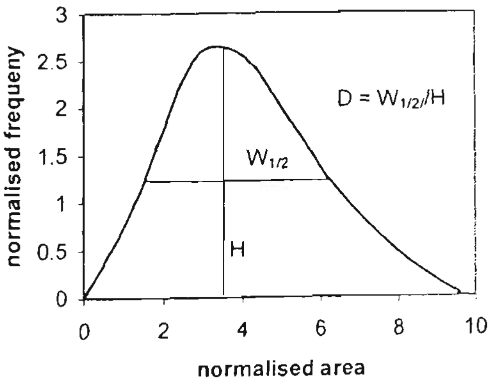


Figure 5.17 : A typical plot of normalised frequency versus normalised area distribution.

5.6 The Development of a Practical "Damage" Parameter for Feathers

An investigation was carried out to obtain experimental data on the distribution of vane areas (primarily triangular and quadrilateral spaces) in duck breast feathers from optical micrographs. Initially studies were carried out on: (i) a virgin undamaged feather, Figure 5.4(a), (ii) a 5%(v/v) detergent-cleansed oiled feather, Figure 5.4(b) and (iii) an oiled feather cleansed with iron powder, Figure 5.4(c). These micrographs were enlarged using a photocopier. Each area was assessed using the "cut and weigh" method. A total of: (i) 321 areas from the undamaged feather, (ii) 293 areas from the detergent-cleansed oiled feather, and (iii) 313 areas from the oiled feather cleansed with iron powder were obtained, Appendices 5.6-5.8.

Each set of data was "normalised" with respect to each axis, since it is the relative shapes of the distributions that are of interest. Along the horizontal axis, areas are expressed as fractions of the total area measured. Along the vertical axis, the *relative* frequency of occurrence of a range of fractional areas is monitored. This normalisation procedure allows different distributions of data to be compared independently of the magnification and total field of view.

The area distributions for undamaged virgin feathers, oiled feathers cleansed with iron powder and 5%(v/v) detergent-cleansed oiled feathers are presented in Figure 5.18 (a-c) respectively. An overlay of these distributions is shown in Figure 5.18(d). It is evident that for the experimental data, the distributions are right-skewed. This originates in a different way to the right-skewing in the theoretical approach. For a feather, this effect is due to the "grid" having various constraints. This will be discussed later.

Figure 5.19 demonstrates that: (i) the treatment with iron powder has had little effect on the coherency of the feather vane, (ii) cleansing with 5%(v/v) detergent leaves the feathers in a disrupted state.

The next step of the investigation was to prepare a series of virgin breast feathers (duck) which had been subjected to treatment with detergent at various concentrations in order to induce controlled amounts of damage. The distribution of areas on the various feather samples was determined using the "cut and weigh" method described previously. A total of: (i) 286 areas from a 3% (v/v) detergent-treated feather, (ii) 267 areas from a 5% (v/v) detergent-treated feather, (iii) 252 areas from a 8% (v/v) detergent-treated feather, and (iv) 251 areas from a 10% (v/v) detergent-treated feather were obtained, Appendices 5.9 to 5.12.

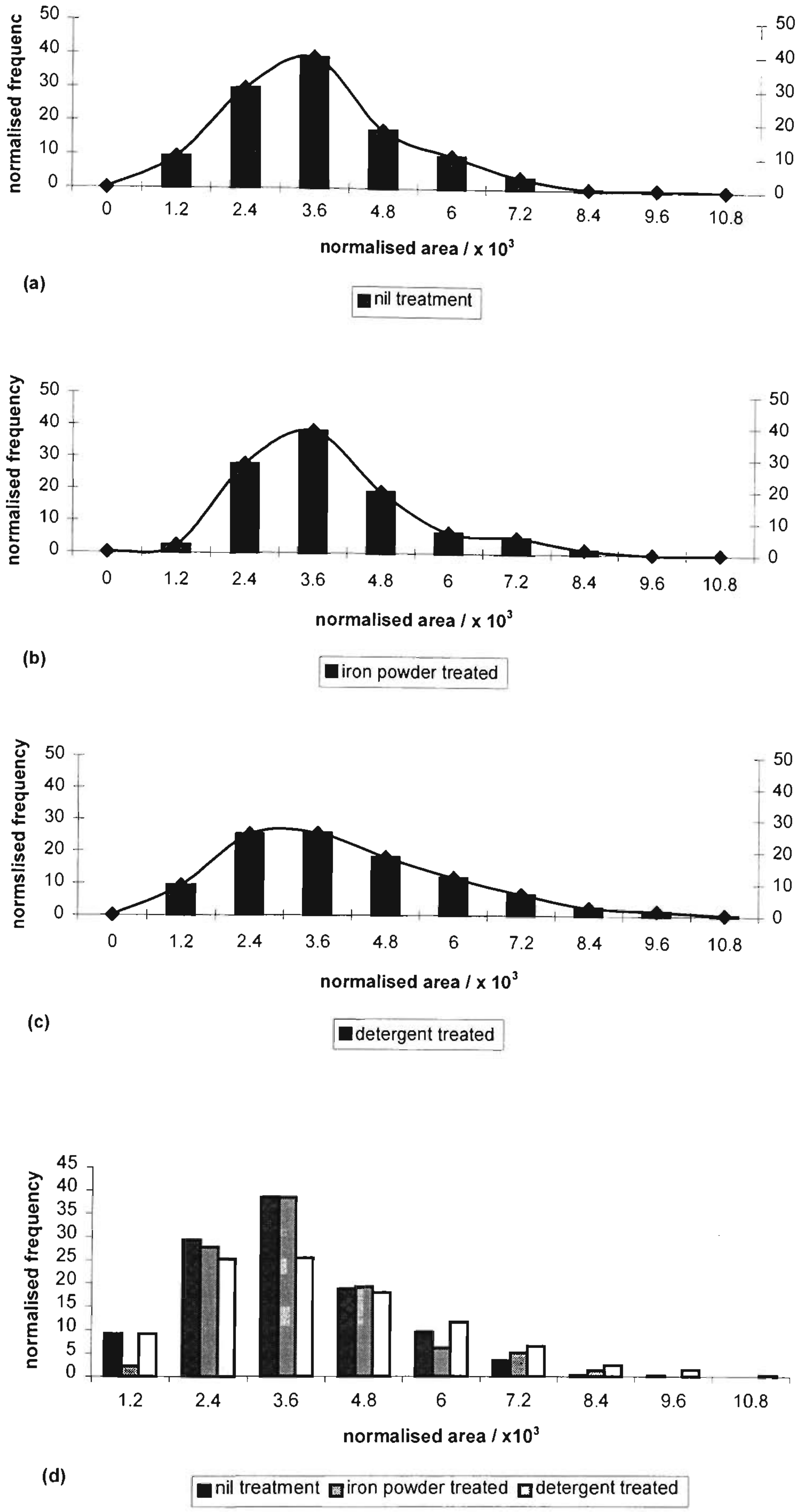


Figure 5.18 : Area distributions between feather barbules in: (a) a virgin feather, (b) an oiled feathers after iron powder treatment, (c) an oiled feather after 5%(v/v) detergent treatment, and (d) the combined of the above three histograms.

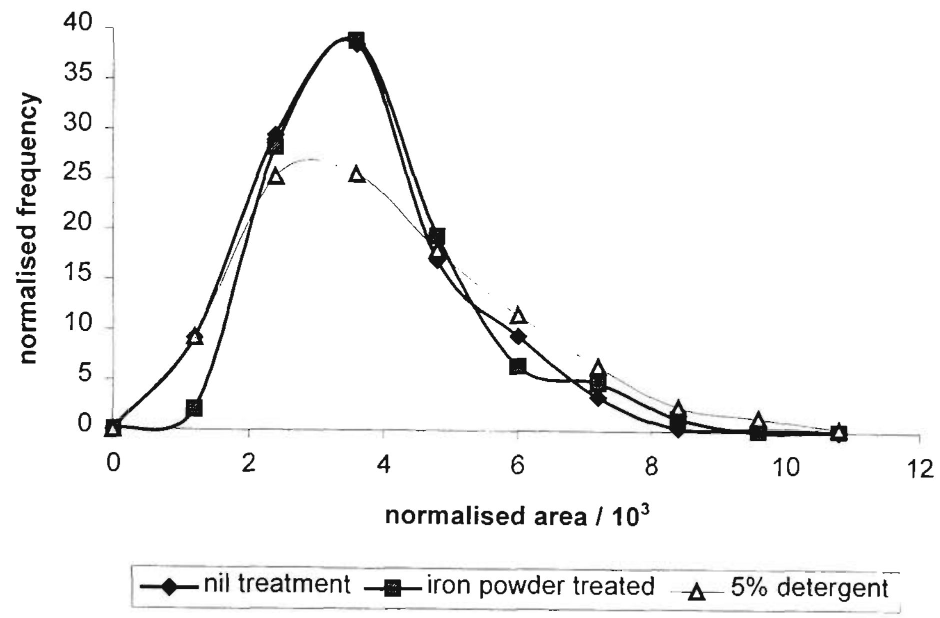
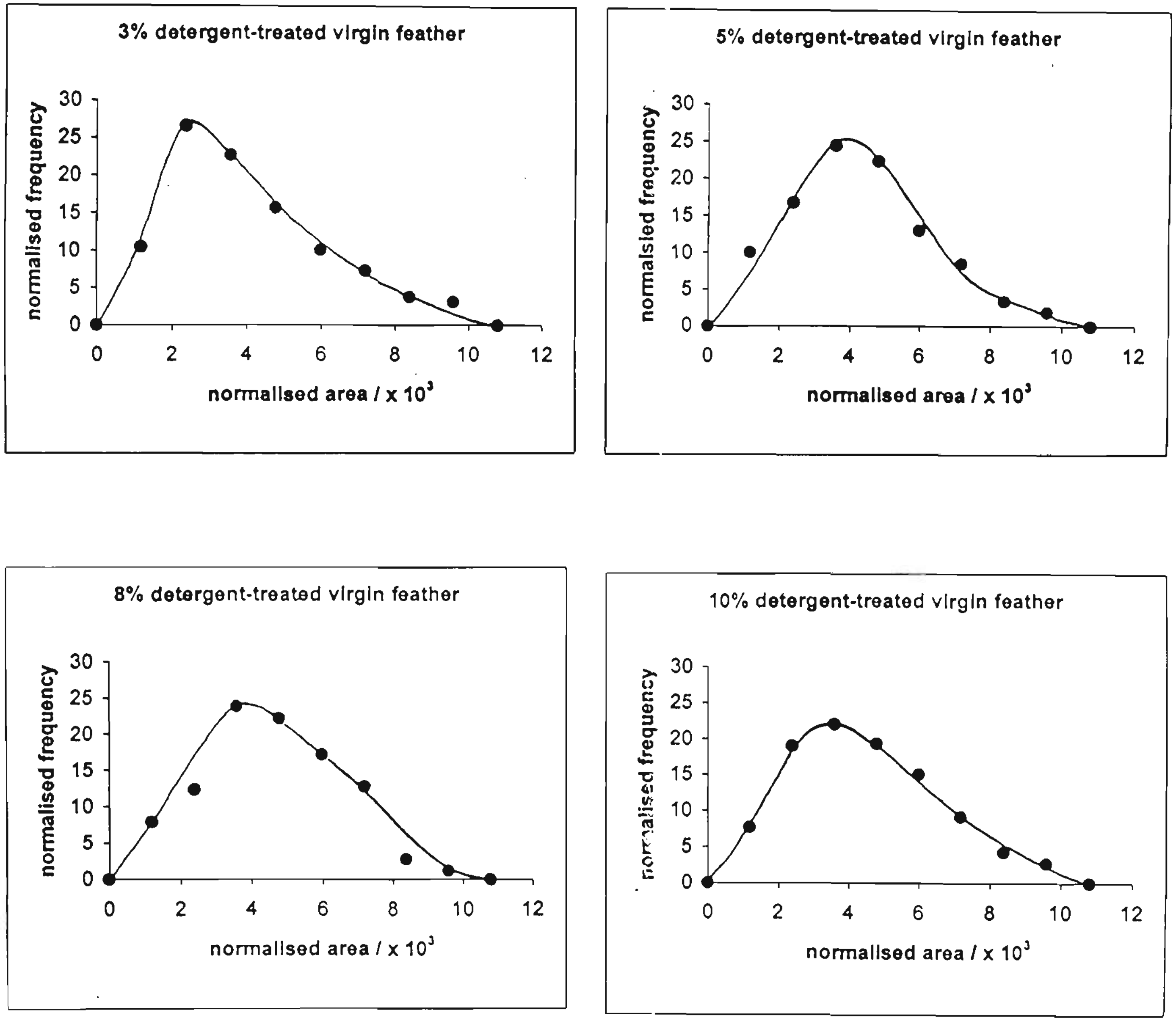


Figure 5.19 : Comparison between the distribution curves of an undamaged feather, an iron powder-treated oiled feather and an oiled feather treated with 5%(v/v) detergent.

From the distribution curves (see Figure 5.20), the D values of various detergent-treated feathers were determined and are presented in Appendix 5.13. When these values are plotted against the detergent concentration, a remarkably linear relationship between D and concentration is observed, Figure 5.21. This suggests that D is a reliable indicator of the damage produced in these feathers by detergent. This confirms the anticipated sensitivity of the method suggested by the mathematical modelling. It should be noted that our results confirm the effectiveness of using iron powder rather than detergent in restoring oiled feathers to their original condition, i.e. D (undamaged) = 0.52; D (5% detergent-treated) = 0.85; D (iron powder-treated) = 0.54, Figure 5.19.

As mentioned earlier the area distributions for the feather are skewed to the right. This observation is not unexpected since the "grid" of a feather is constrained in several ways leading to a higher probability of larger areas remote from the sites of the barb and barbule constraints. Such constraints are shown schematically in Figure 5.22. Two types of constraints are identified and the combined effects of these constraints result in more flexibility of the vane upon moving away from the rachis along the barb. The least constrained areas might be expected to be more easily damaged. Thus the degree of "right-skewedness" would also be expected to increase with increasing damage.

Figure 5.20 : Comparison between the distribution curves of virgin feathers treated with 3%(v/v), 5%(v/v), 8%(v/v), and 10%(v/v) detergents respectively.



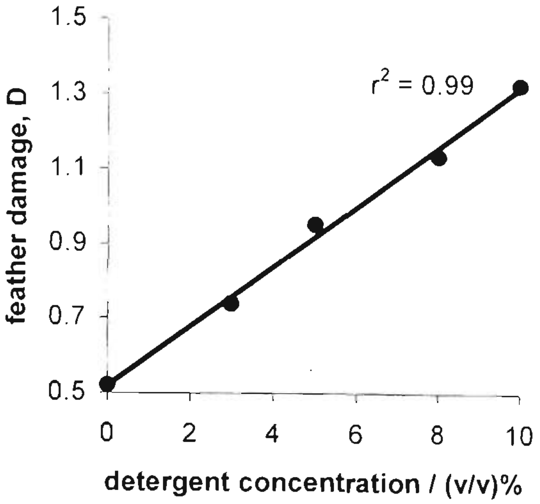
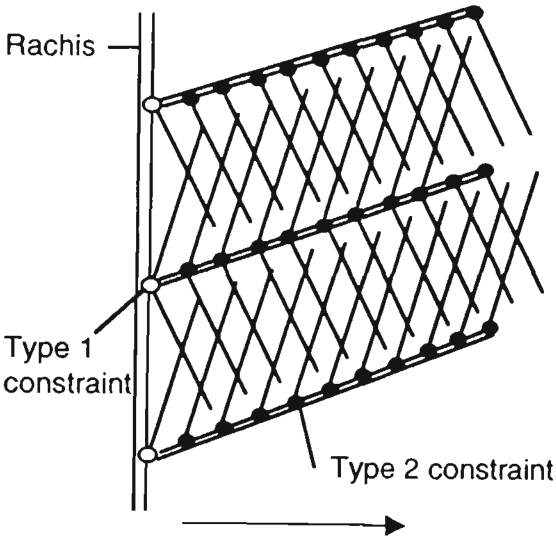


Figure 5.21 : The relationship between feather damage and concentration of detergent.



Increasing probability of larger areas.

Figure 5.22 : Constrained grid.

For these studies, the 'cut and weigh' method was used to determine the area distribution of virgin, detergent-treated and iron powder-treated feathers. A more efficient procedure directed towards the development of an assay would be to exploit digital imaging/pattern recognition technology in order to rapidly scan a given feather and derive its area distribution in an automated manner.

Having demonstrated a 'proof of principle' with respect to the quantification of feather damage, future work is needed to extend these studies to different species and to set bench mark values for what constitutes an undamaged feather in a given species. This would involve considering the age and gender of a given bird (Lucas & Stettenheim, 1972) and the location on the bird from which feathers samples are taken.

5.7 Conclusions

Virgin duck breast feathers, oiled feathers cleansed with detergent, and oiled feathers cleansed with iron powder were qualitatively examined under an optical microscope to assess feather damage. It was found that virgin feathers and oiled feathers cleansed with iron powder show little damage, whereas oiled feathers cleansed with detergent display noticeable disruption. Scanning electron micrograph studies seem to show hooklet elongation for detergent-damaged feathers. However, quantitative studies using digital imaging technology indicate that there is no statistical difference in hooklet extension between virgin and detergent-treated feathers. It was found however, that hooklet extension increases on going from the tip to the base of the feather. It was also found that there is a variation in hooklet extension on either side of the rachis which suggests a role for hooklet extension in feather curvature.

It was postulated that feather damage could be assessed by measuring the degree of coherency of the feather vane. It was suggested that a way of quantifying the degree of coherency was to assess the area distribution of the spaces defined by the barbs of the vane. It was also surmised that the extent of disruption could be measured by the width of the area distribution. A mathematical model was developed to determine the area distribution of a two dimensional grid which models the feather vane. The model shows that the degree of disruption, f, may be measured by the width of the distribution. The model also indicates the high sensitivity of this method and an even more sensitive practical indicator was suggested.

Experiments were designed and conducted to test this indicator on real feathers. Feathers were damaged in a controlled way using different detergent concentrations. The distributions of the areas of the vanes of sample feathers were determined by imaging and the "cut and weigh" method. Analysis of the data enabled an indicator of feather damage, D, to be determined in each case. The D value was found to be directly proportional to detergent concentration over the range of concentrations investigated and appears to be a successful and sensitive indicator of damage, as anticipated from the mathematical model. It was also demonstrated, using this technique, that cleansing oiled feathers with iron powder restored the feathers close to their original condition.

5.7 References

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Chapter 6 Recycling and Reuse of Magnetic Particles

6.1 Preamble

6.2 Oil Removal Using Drained Magnetic Particles

6.3 Methods for Recycling of Magnetic Particles
6.3.1 Solvent Extraction
6.3.2 Supercritical Fluid Extraction

6.4 Oil Removal from Feathers Using Recycled Iron Powder

6.5 Conclusions

6.6 References

6.1 Preamble

Depending upon the specific application, the use of magnetic particle technology for environmental remediation could produce a significant amount of contaminated magnetic particles. These particles can either be recycled, and the contaminant isolated, or be disposed of as waste. For the most economic and versatile application of magnetic particle technology, it is desirable that the particles are recyclable and reusable in an environmentally friendly way, and with a significant retention of function. An initial indication of how recycling and reclamation might be achieved was evident when the oil-laden particles were pooled in a beaker and left to stand, Figure 6.1. It can be seen that after a period of time, for this system, the contaminant drained off the particles and settled at the bottom of the container. This suggests that the contaminant is truly adsorbed and removal is feasible by mechanical means such as centrifugation.

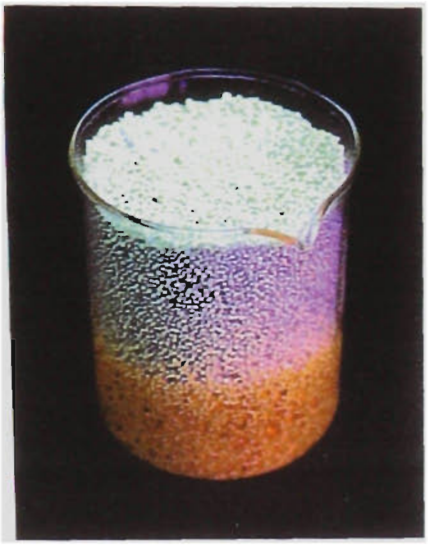

Figure 6.1: Pooled PE-coated particles contaminated with Oil A after standing for approximately one week.

6.2 Oil Removal Using Drained Magnetic Particles

As a preliminary study, "drained" particles of this kind were tested for oil pick-up and their behaviour was compared to the origin particles. Thus the top layer of the particles, Figure 6.1, which were assumed to be the most "drained", was tested for oil affinity using the procedures described previously, Section 2.3. The same testing protocol was applied to the drained PVC-coated particles and iron powder. Oil B was chosen for experimentation with iron powder because it is a moderately heavy crude oil and one of the more challenging oil to remove.

A comparative examination of the percentage pick-up of Oil A for original and drained PE and PVC-coated particles is shown in Figures 6.2 and 6.3 respectively. Figure 6.4 displays the comparative examination of the percentage of Oil B pick-up for original and drained iron powder particles. Various parameters are given in Table 6.1.

The results show that a maximum oil pick-up of approximately 70% and 61% for PE and PVC drained particles respectively. The data also suggest that the removal efficiency of oil by the drained PE and PVC-coated particles is less than that of the original particles, as indicated by their lower E_l and α_0 values, Table 6.1. The decrease in the percentage oil pick-up is approximately 13-14% compared to the pick-up for both original PE and PVC-coated particles. In the case of drained iron powder, an initial pick-up of approximately 32% of Oil B is achieved compared to 46% pick-up of the same oil using the original iron powder particles. A maximum pick-up of approximately 87% of oil using drained iron powder may be achieved for a given R, compared to 99% pick-up of oil using original iron powder, a decrease of approximately 12%.

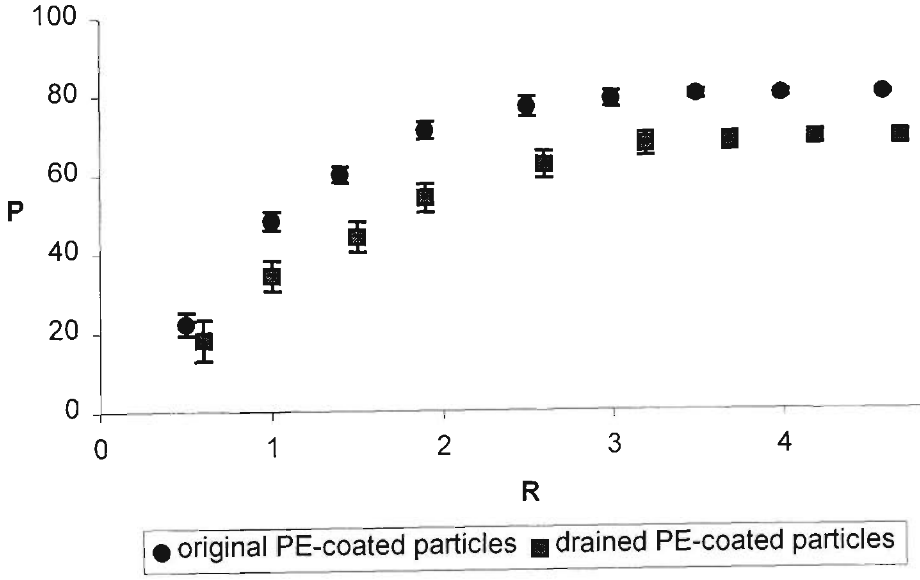

Figure 6.2 : Comparison between the affinity for Oil A of original and drained PE-coated particles. Error bars represent 95% confidence intervals for 5 replicates. The data for the original and drained particles are documented in Appendices 2.5 and 6.1 respectively.

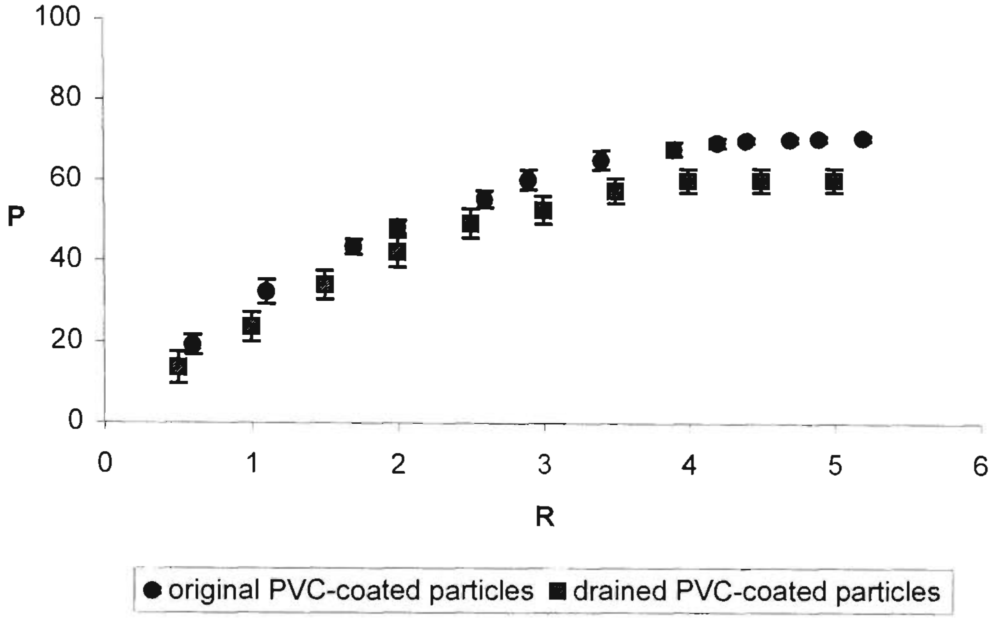

Figure 6.3 : Comparison between the affinity for Oil A of original and drained PVC-coated particles. Error bars represent 95% confidence intervals for 5 replicates. The data for the original and drained particles are documented in Appendices 2.5 and 6.2 respectively.

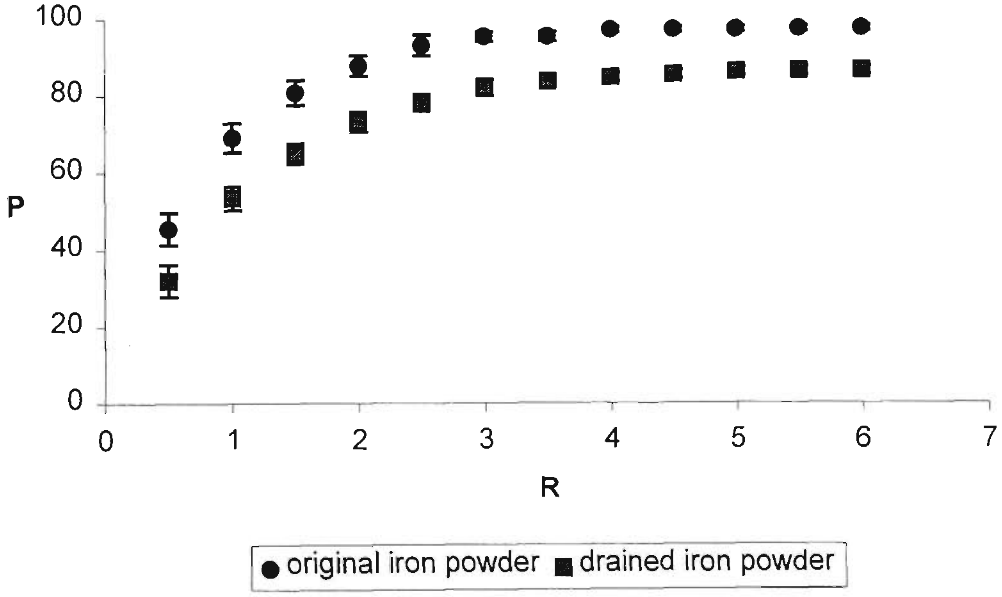

Figure 6.4 : Comparison between the affinity for Oil B of original and drained iron powder particles. Error bars represent 95% confidence intervals for 5 replicates. The data for original iron powder and drained iron powder are documented in Appendices 2.13.2 and 6.3 respectively.

Table 6.1 : Parameters comparing the pick-up of : (i) Oil A between original and drained PE and PVC-coated particles and (ii) Oil B between original and drained iron powder particles.

Particles		**P_c**	**R_c**	**E_l**	α_0
PE	original	80.4	3.5	23.0	3.06
	drained	70.1	3.7	18.9	2.40
PVC	original	70.8	4.4	16.1	2.51
	drained	60.8	4.5	13.5	2.26
Iron powder	original	97.9	4.0	24.5	4.99
	drained	86.0	4.0	21.5	3.54

The results show that simple settling is quite effective in removing the bulk of the oil which is suggestive of an adsorptive mechanism for the pick-up. In order to extend the reprocessing of particles to take into account recycling, two methods were trialled, namely solvent extraction (SE) and supercritical fluid extraction (SFE). The SE method was used because it is a conventional method for extracting organic contaminants (Rulkens, *et al.*, 1998; Nam *et al.*, 2001). The SFE method was selected because it has been used extensively to extract and recover organic contaminants from solid and liquid matrices (Engelhardt & Gross, 1988; Witter, *et al.*, 1998).

6.3 Methods for Recycling of Magnetic Particles

6.3.1 Solvent Extraction

The solvent extraction (SE) method using 20% (v/v) ether/hexane mixture was carried out as follows: the drained PE and PVC-coated particles and iron powder particles used in oil pick-up studies were pooled into three separate filter funnels and allowed to drain further for a week. A sample of 20 g of these drained particles was then washed with 3 × 20 mL of 20% (v/v) ether/hexane to produce recycled particles. The recycled particles were allowed to dry in air for 2 h and were weighed.

6.3.2 Supercritical Fluid Extraction

Approximately 1.0 g of drained PE, PVC and iron powder were contained separately in a filtered paper and inserted into a 7-mL standard stainless steel supercritical fluid extraction

(SFE) cell (Hewlett Packard) respectively. The cell was placed into the SFE module for extraction. The SFE analysis was conducted using the Hewlett Packard 7680A SFE module. A three-step pressure was used for the extraction procedure: step 1, 1117 psia; step 2, 1508 psia; and step 3, 2374 psia. Other parameters used are summarized as follows: chamber temperature, 40 °C; equilibrium time, 2 min; extraction time, 5 min; extraction fluid, CO_2; flow-rate, 1 mL min^{-1}.

The above procedure was repeated until a sufficient quantity of extract of approximately 20g was obtained. The quality of the recycled magnetic particles was assessed in terms of the percentage purity of the recycled particles. The percentage purity is calculated as:

$$\text{Percentage purity} = \text{mass of recycled particles} / \text{mass of original particles} \times 100$$

The percentage purity for (i) PE-coated particles is 98.7%, (ii) PVC-coated particles is 98.5%, and (iii) iron powder is 99.4%.

The recycled PE and PVC-coated particles were then used for Oil A affinity studies using the method previously described in Section 6.1. In the case of recycled iron powder, Oil B was used for the affinity studies. Three replicates were performed for the affinity studies of these particles.

A comparison of the oil pick-up between the original and recycled PE and PVC-coated particles for Oil A is shown in Figures 6.6 and 6.7 respectively. The data in Table 6.2 show that a maximum oil pick-up of 79.0% and 70.0 % is achieved for PE and PVC-coated particles respectively. This is comparable to the original PE and PVC-coated particles which exhibited pick-ups of 80.6% and 70.3 % respectively for a given chemical-to-particle ration, R. However, the overall efficiency has decreased slightly as reflected by their E_l and α_o values, Table 6.2.

The histogram in Figure 6.8 displays the comparative pick-up of Oil B between the original and recycled iron powder. The iron powder subjected SE and SFE shows initial removals of approximately 41% and 40% of Oil B respectively, compared to the initial oil removal of approximately 46% using original iron powder. The data in Table 6.2 suggest that for high values of R the removal of approximately 97% and 96% of oil is achieved using the SE and SFE iron powder respectively, compared to the oil removal of approximately 99% using original iron powder. However, the initial efficiency has decreased slightly as indicated by their lower α_o values, Table 6.2.

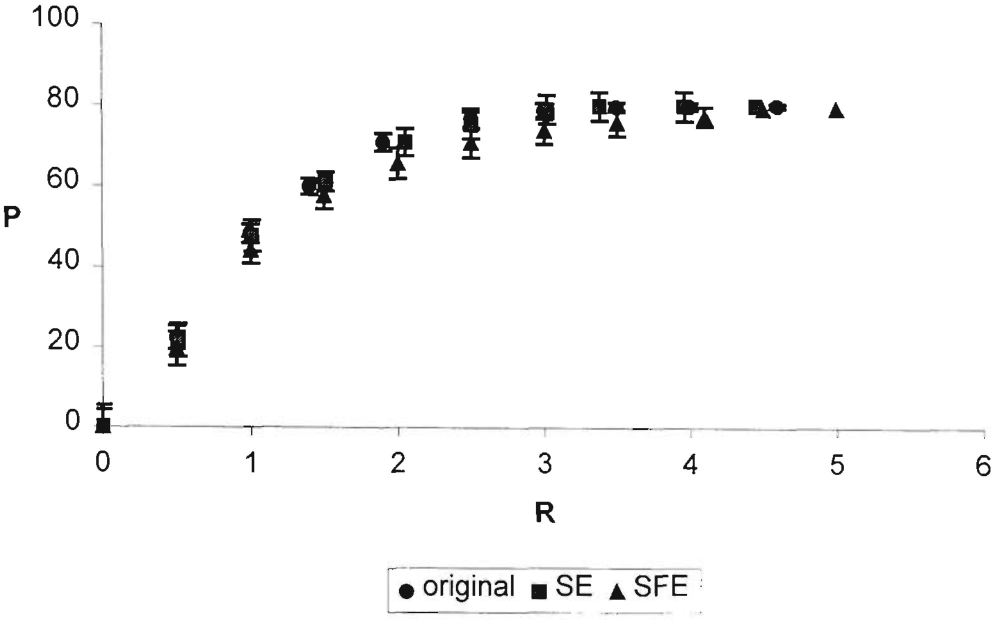

Figure 6.6 : Comparison between the average percentage pick-up of oil A by original and recycled PE-coated particles The data for the recycled PE-coated particles are listed in Appendix 6.4. The error bars for PE-coated particles subjected to SE represent 95% confidence intervals for 5 replicates. The error bars for PE-coated particles subjected to SFE represent 95% confidence intervals for 3 replicates.

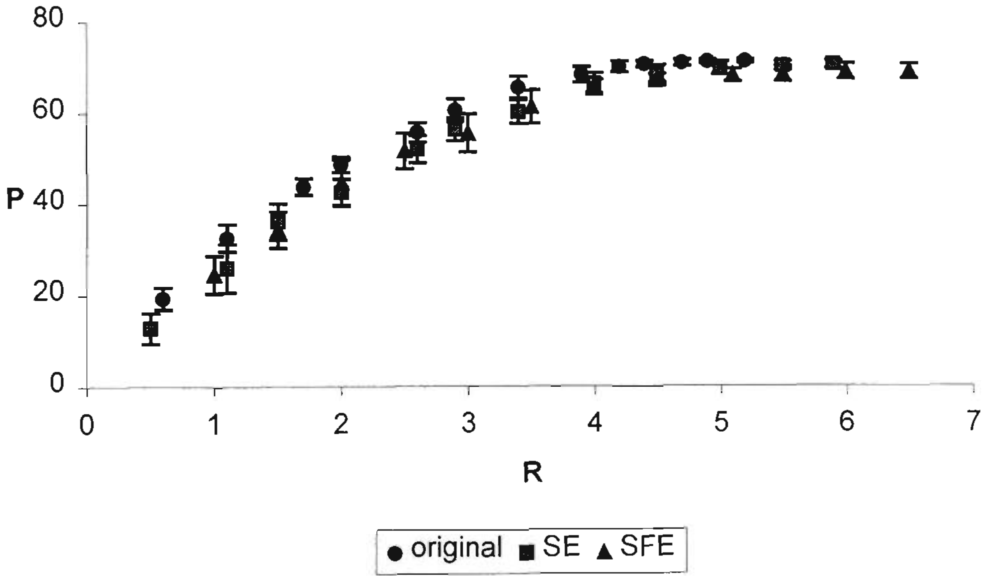

Figure 6.7 : Comparison between the average percentage pick-up of Oil A by original and recycled PVC-coated particles. The error bars for PVC-coated particles subjected to SE represent 95% confidence intervals for 5 replicates. The error bars for PVC-coated particles subjected to SFE represent 95% confidence intervals for 3 replicates. The data for the recycled PVC-coated particles are listed in Appendix 6.5.

Table 6.2 : Parameters comparing the pick-up of Oil A by the recycled PE-coated, PVC-coated and iron powder particles.

Extraction method	**PE-coated particles**				**PVC-coated particles**				**Iron powder**			
	P_c	R_c	E_l	α_o	P_c	R_c	E_l	α_o	P_c	R_c	E_l	α_o
Original (no extraction)	80.4	3.5	23.0	3.06	70.8	4.4	16.1	2.51	97.9	4.0	24.5	4.99
SE	80.5	3.4	23.2	2.72	70.0	4.2	16.7	2.48	96.0	4.2	22.9	3.98
SFE	80.0	4.2	19.0	2.82	69.0	5.3	13.0	2.37	95.6	4.0	23.9	3.66

The profile for: (i) original iron powder is presented in Appendix 2.13, and (ii) iron powder subjected to SE and SFE is listed in Appendix 6.6.

During the course of these studies other potential recycling techniques have been identified. These techniques include microwave-assisted extraction (Pastor *et al.* 1997; Budzinski, *et al.*, 1999) and pressurised liquid extraction (Bjorklund, *et al.*, 1999). These two techniques may also be used to extract and recover organic contaminants from a solid matrix. However, due to time constraints, these alternatives were not pursued as part of the project.

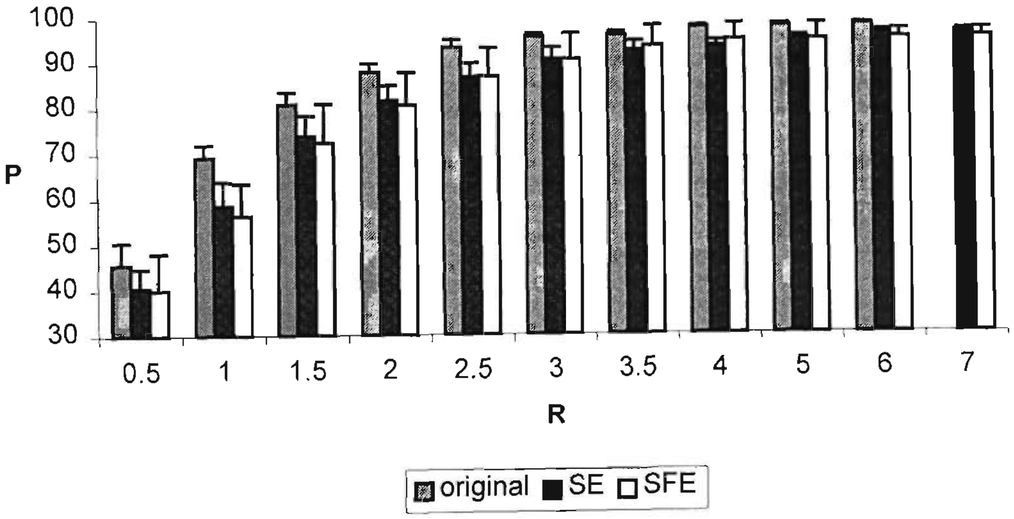

Figure 6.8 : Comparison of the average percentage pick-up of Oil B by original and recycled iron powder. The error bars for: (i) original iron powder and iron powder subjected to SE represent 95% confidence intervals for 5 replicates, and (ii) iron powder subjected to SFE represents 95% confidence intervals for 3 replicates.

6.4 Oil Removal from Feathers Using Recycled Iron Powder

The recycled iron powder particles subjected to SE and SFE were used to remove oil from duck breast feathers. The histograms in Figure 6.9 compare the removal of Oil B from duck breast feathers using original and recycled iron powder. For the first treatment, the SE and SFE methods show a high removal of approximately 68% and 63% of Oil B respectively. These results are slightly lower than the 73% removal obtained using original iron powder. After nine treatments both the SE and SFE methods cleanse the feathers to a maximum value of between 96 and 97%. These results are comparable to the pick-up of 97% for Oil B using original iron powder. The efficiency of the recycled iron powder is only slightly less than that of the original iron powder as indicated by their E_2 and α_o values, Table 6.2.

The profile for the pick-up of Oil B from duck breast feathers using: (i) original iron powder is presented in Appendix 3.6, and (ii) SE and SFE iron powder is presented in Appendix 6.7. The results show that the settling process using PE and PVC-coated particles and iron powder is quite effective in removing the bulk of the oil contaminants. The recycled PE and PVC-coated particles, and recycled iron powder particles are very effective in removing typical oil contaminants.

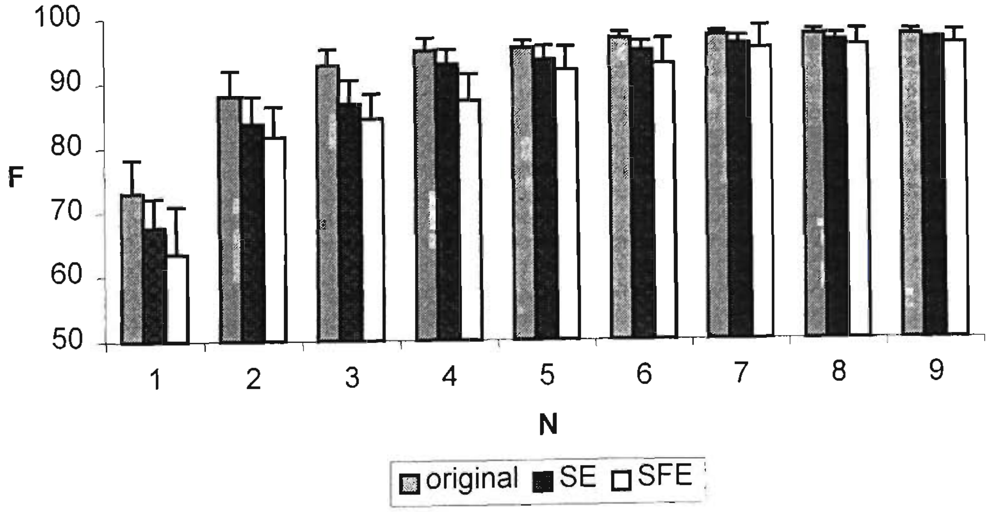

Figure 6.9 : Average percentage by weight of Oil B removed from the breast feathers of the domestic duck (*Anas platyrhnchos*) after successive treatments with recycled iron powder and subsequent magnetic harvesting. The error bars for: (i) original iron powder and iron powder subjected to SE represents 95% confidence intervals for 5 replicates, and (ii) iron powder subjected to SFE represents 95% intervals for 3 replicates.

6.5 Conclusions

As might be expected, the percentage removal of a contaminant (e.g. Oil A) from a glass substrate is lower for recycled (by draining) particles (PE, PVC-coated and iron powder) than for the original particles. However, the removal is still quite high suggesting that a more rigorous recycling could achieve even better outcomes. Therefore two further techniques were trialled, namely solvent extraction and supercritical fluid extraction. Particles recycled by treatment using these techniques showed percentage removals from a glass substrate comparable to the original particles.

The iron powder particles recycled by these two methods was also tested with respect to the removal of oil from duck breast feathers. In this case the removal of the contaminant was found to be comparable to the original particles.

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All oiled birds, mainly penguins are administered a rehydration solution - Vy'trate^{TM}, followed by a Tympanyl^{TM} formulation which emulsifies the ingested oil. When the penguin is not under-weight and appears calm, washing may then commence. DivoPlusV2^{TM} detergent in warm water (35-40 °C) is used. Two persons are required to wash each bird. Normally 20 min is the maximum time permitted to carry out a washing session of the bird. However, if the penguin shows sign of stress, washing is immediately stopped. For "weathered" feathers, multiple washings are required.