

REMOVAL OF PETROCHEMICALS FROM WATER USING MAGNETIC FILTRATION

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ABSTRACT

Magnetic filtration has a long-standing reputation for fast-efficient separations in industrial practice. However, its application to separation of petrochemicals from water requires the development of magnetic extractants that can absorb and “magnetize” the organic compounds. We have investigated several approaches for the preparation of magnetic extractants, including activated carbon/magnetite or nickel ferrite composites and polymer-coated iron and iron oxide powders. Testing with decane/water solutions have demonstrated that these extractants can reduce the concentration of decane rapidly from 104 ppm to low ppb levels. In the case of poly(dimethylsiloxane)-coated hematite, the concentration of decane was reduced below 1 ppb. Magnetic filtration was found to have significant potential for the separation of oil or VOC's from water and for breaking oil in water emulsions.

INTRODUCTION

Magnetic separation has been developed as a recovery and pollution-control process for many environmental and industrial problems including treatment of radioactive water (1) waste water (2) effluents from steel mills (3), desulfurization of coal (4), separation of mining ores and wastes (5), clay processing (6), purification of drinking water (7), and filtration of cooling water in nuclear reactors (8). Magnetic separation has been used since the nineteenth century but the development of high gradient matrix-type separators has greatly extended the range of applications of magnetic separation and magnetic filtration. There are a myriad of designs of magnetic separators that are capable of filtering out even weakly magnetic particles and there are also numerous methods for their application (10).

The application of efficient magnetic filtration to petroleum-related decontamination and waste treatment operations is attractive because it can provide rapid removal of contaminants from aqueous waste streams. This coupled with the ability to switch the filter on and off electronically (avoiding any need for mechanical contact) allows the minimization of exposure of workers to harmful agents. However, since most contaminants of concern to the petroleum industry are not magnetic, magnetic filtering aids must be developed that bind the contaminants and allow their magnetic separation. The magnitude of this challenge is demonstrated by the fact that of 964 papers and patents in the literature concerning magnetic filtration, only 40 address hydrocarbon or oil separations and the majority of these concern separation of metal particles from lubricating oils (see for example ref. 11). This problem has been addressed in coal beneficiation by use of magnetic fluids that are composed of magnetic particles, a suspending agent, and a carrier solvent that selectively wets the contaminant particles (oxide minerals in the case of coal) (12). In the case of oil in water mixtures several approaches have been previously developed. The simplest method was to mix an extremely large excess of magnetite {ratio of 40 Fe_3O_4 :1 oil (fatty acid) by weight} so that the oil absorbed onto the surface of the magnetic powder (13). Subsequent magnetic filtration reduced the oil from 500 ppm to 2 ppm. The success of the absorption method can be attributed to the oil first being emulsified in an ionic form-an approach that is not applicable to normal hydrocarbons. When the same approach is applied to a 3000 ppm B-heavy oil in water emulsion, the final concentration of oil was only reduced to 57 ppm (14). Another method that utilized a magnetic suspension and an acidic coagulant merely achieved a final concentration of 103 ppm (15).

The objective of the research reported herein is the development of single component systems for use as magnetic filtration aids i.e. magnetic materials that can absorb hydrocarbon contaminants and allow their separation from water via magnetic filtration (Figure 1). Our approach is similar to that used for the most common type of magnetic extractants for metal ions in which a magnetic filler is dispersed in a polymeric ion-exchange resin (2). A typical example of this type of material is the MAG*SEP technology developed by Argonne National Laboratory and Selentec, Inc. that uses small magnetite particles coated with an ion exchange resin (16). The MAG*SEP process has been used to remove radioisotopes from milk after the Chernobyl accident and to concentrate radioactive cesium and technetium from dilute aqueous solution (17, 18).

There is a successful application of the magnetic-filler-in-polymer technology that has been used for oil slick removal. In this case the polymer was polystyrene and the filler was iron oxide. The extractant was sprayed onto an oil slick by a water craft travelling through the spill (19). The polymer/oil sludge was then collected on rotating magnetic disks. Using this approach, a 99% recovery of spilt oil was achieved with 20 volumes of oil being collected per unit volume of polymer. In this investigation, several different approaches were used to coat magnetic particles to enhance their absorption of hydrocarbons. The most successful material of this type were polyoctadecylmethacrylate-coated particles and materials with surfaces derivitized with octadecyltrimethoxysilane.

Figure 1. Cartoon of Magnetic Extraction

The binding of organic polymers to a magnetic core is not as common as the magnetic-filler-in-resin technology but such materials have uptake kinetics for metal ions that are five times the speed of the latter extractants (20). A typical magnetic extractant of this type is polyacrylic acid grafted to a magnetite/poly(vinylalcohol) core (21). This material has been successfully used to replace ion exchange columns with magnetic filtration for removal of metal ions from water. The favorable acceleration in kinetics is attributed to much more open access to the active sites of the uncrosslinked shell. The third type of extractant, iron-oxygen polymers, with a magnetic backbone that will be a very minimal fraction of the active extractant, would be expected to display the fastest kinetics since the polymers will be composed primarily of contaminant binding sites rather than magnetic core. In this investigation, polydimethylsiloxane was grafted onto iron and iron oxide particles using a thermally-induced radical process.

Activated carbon has a long-standing history as an absorbent for contaminants, volatile organic compounds, chlorocarbons, etc. Thus, conversion of activated carbon into a magnetically-active material would provide an excellent magnetic filtration aid. Previously, Imshennik *et al.* reported a method for the preparation of porous carbon that was loaded with iron particles (22). These researchers applied this material as magnetic carriers that could be used in conjunction with a magnetic field to deliver medical drugs to target organs or tumors. Based on their results, similar materials for this investigation will be readily prepared but instead of iron, an iron oxide will be deposited in the carbon.

Magnetically-active activated carbon could be dispersed as an extremely reactive fine powder that would absorb petroleum products with enhanced kinetics compared to the granular material used in columns and then the powders could rapidly be separated from the aqueous stream by magnetic filtration.. In this investigation, magnetic activated carbon was prepared by a novel process that yielded magnetite or nickel-ferrite impregnated activated carbons.

Separation of oil/water emulsions might also be feasible using magnetic extraction. The outer shells of the extractants will have a strong affinity for both the oil and the hydrophobic tails of any surfactants that might be present. Therefore, it should be possible to have the surfactant/oil micelles bind strongly to the extractant and be influenced to separate from the water via a magnetic field. This potential alternative to other methods of breaking emulsions such as coalescing filters could provide considerably time and money savings to the petroleum industry.

EXPERIMENTAL

Reagents were ACS grade and were purchased either from the Aldrich Chemical Company or Strem Chemicals. These chemicals were used as received. Water was purified by reverse osmosis and deionization. Toluene and hexane were HPLC grade and were used without further purification. X-ray powder diffraction (XRD) patterns were recorded on a Bruker AXS D-8 Advance X-ray powder diffractometer using copper $K\alpha$ radiation. Gas chromatographic/mass spectroscopic analysis (GC/MS) for decane was performed on a Hewlett Packard G1800A instrument equipped with 30 m x 0.25 mm HP5 column (Crosslinked 5% PhME silicone). The temperature program used was an initial hold of 2 min at 35°C, a ramp of 5°C/min to 170°C, and a final hold of 5 min. The helium flow rate was 1 ml/min and the injection port was set at 250°C. The mass spectrometer was used in the selective ion monitoring mode with the parent ion of decane ($m/e = 142$ a.m.u.). Concentrations of decane were determined by use of a standard solution of decane in hexane and calculation of response factors from peak areas.

Preparation of Polydimethylsiloxane/Iron or Iron Oxide Composites

Composites of polydimethylsiloxane (PDMS) with were prepared by cross-linking a PDMS polymer at moderate temperature with the magnetic substrate. Equal weights of the PDMS (typically 4 g of each) was stirred with either iron metal, hematite, and the resulting mixtures were heated to 280°C for one hour. Afterwards, the material was washed extensively with toluene to remove any unattached PDMS and was then dried in a vacuum oven at room temperature. Two different PDMS oils were used as starting materials: a low viscosity (10 centistokes) material and a moderate viscosity material (1000 centistokes). These yielded strikingly different materials, a homogenous thinly-coated powder in the first case and a rubbery composite in the latter.

Preparation of Poly(octadecylmethacrylate)/Iron Composite

A fine iron powder (10 g) was mixed with 1.0 g of an as-purchased toluene solution of poly(octadecyl methacrylate) (average molecular weight of 170,000) thinned with an additional 3 ml of toluene. The solvent was evaporated under ambient conditions to yield a waxy solid with imbedded iron particles.

Preparation of Octadecylsilsesquioxane-Coated Magnetic Powders

Iron and magnetite powders (30 g) were treated with a solution of octadecyltrimethoxysilane (1.0 g) in toluene (20-25 g). After 12 hours, the derivitized powders were isolated by filtration, washed with toluene, and were dried in vacuo

Preparation of Magnetic Activated Carbons

Paper towels were saturated with an aqueous solution of iron(II) gluconate (10 g in 30 ml) mixture. The towels were hung from a rack to air dry and were then fired to 500°C under a nitrogen atmosphere. After cooling to room temperature, the resulting powders were exposed to air at which point they became quite hot due to rapid oxidation of iron(II) by oxygen. The final result was a magnetite-containing activated carbon. A similar procedure using a nickel gluconate (5g)/ iron gluconate (10 g) mixture in water (45 ml) yielded a nickel-ferrite impregnated activated carbon..

Testing of Magnetic Extractants for Hydrocarbon Removal from Aqueous Solution

A stock solution of approximately 100 ppm decane in water was prepared by stirring the required amount of decane with 250 ml of water. GC/MS analysis was used to determine the actual concentration of decane to be 104 ppm. 20 g of this solution was treated with 0.5 g of extractant and the mixture was stirred for two hours. After filtration, 6 g the aqueous solution was extracted with 1 g hexane and the extracts were analyzed for decane by GC/MS.

Testing of Magnetic Extractants for Breaking of an Emulsion

A stable emulsion was prepared by diluting a 35:20:45 weight percent paraffin oil/triethanolamine/oleic acid mixture to 1000 ppm in water (25). This yielded an indefinitely stable white emulsion. Ten grams of this emulsion was treated with 0.5 g of the nickel ferrite/activated carbon extractant by briefly shaking the two materials together in a glass vial for one minute. The mixture was then passed through a magnetic filter consisting of a glass pipet packed loosely with steel wool and taped to the side of a bar magnet. The solution passed through the filter was much clearer. The extent of emulsion removal was then assessed by measuring the solution's absorption at 500 nm. using a digital Spectronic 20 spectrometer.

RESULTS AND DISCUSSION

Preparation of Magnetic Extractants

A facile method for making magnetically-active activated carbons was developed. These materials were simply prepared by impregnating paper towels with an aqueous solution of iron gluconate mixture and then firing at 500°C under a nitrogen atmosphere. X-ray powder diffraction showed that the resulting material contained nanocrystalline magnetite (Figure 2) while infrared spectroscopy demonstrated the presence of an activated carbon phase. A similar procedure using a nickel gluconate/ iron gluconate mixture yielded a nickel-ferrite impregnated activated carbon. Magnetic testing of the powders with a strong bar magnet indicated that the magnetite and ferrite-containing powders were strongly and completely ferromagnetic. Furthermore, none of the powders demonstrated any remnant magnetization outside of a magnetic field, an important property so that the powder will not stick to non-magnetized steel. Also, in the case of the magnetite, the lack of a remnant magnetization means that we have achieved our goal of creating particles too small to become permanently magnetized. As expected, the nickel ferrite-containing material exhibits the strongest response to a magnetic field.

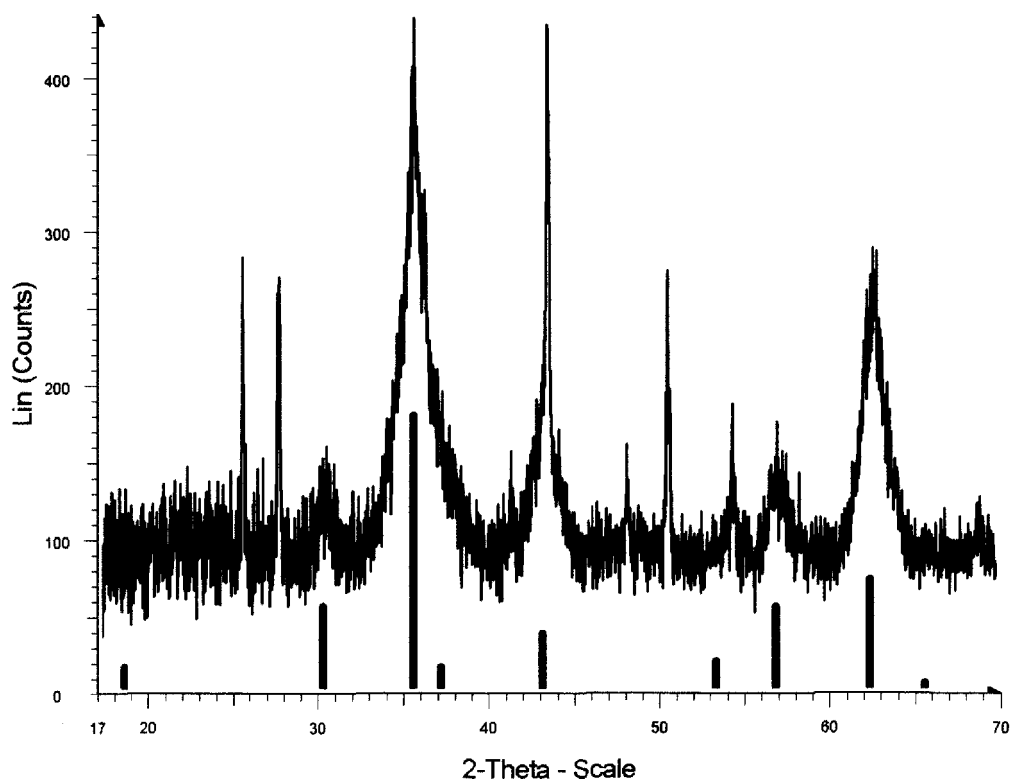


Figure 2. XRD Pattern for Magnetite/Activated Carbon Composite. Solid bars represent the ICDD Pattern for Magnetite

A recent report indicated that polydimethylsiloxane (PDMS) is a good absorbent for phenanthrene prompted us to prepare composites of PDMS with iron metal, hematite, and magnetite (23). These were prepared by cross-linking a PDMS polymer at moderate temperature in a mixture with the magnetic substrate. This is similar to a procedure reported by Soares et al. for coating alumina, calcium carbonate, and hematite with PDMS (24). Two different PDMS oils were used as starting materials: a low viscosity (10 centistokes) material and a moderate viscosity material (1000 centistokes). These yielded powders with substantially different thicknesses of PDMS coatings.

A different polymer-coated powder was prepared by casting poly-octadecyl methacrylate from a toluene solution onto a fine iron powder. The polymer is only physically adsorbed onto the magnetite and can be washed off with organic solvents. However, the coated powders are stable in water and are suitable for use as magnetic extractants. The difficulty with these materials is the problem of removal of extracted organics without displacing the polymer during regeneration.

A second method of incorporating octadecyl residues onto the surface of a magnetic particles was also investigated. In this case the octadecyl groups were covalently anchored to the surface by treating iron and magnetite powders with octadecyltrimethoxysilane. This reagent condenses with surface hydroxyls on the iron or iron oxide surface, leading to a monolayer of pendant octadecyl groups grafted to the metal surface via a cross-linked silica layer. Thus, the particle surface becomes coated with a monolayer of polymerized octadecylsilsequioxane, $(C_{16}H_{37}SiO_{1.5})_x$.

Testing of Magnetic Extractants

The testing of the extractants was performed using aqueous solutions of decane with a concentration of 104 ppm, a point that is below the solubility limit of decane in water. This provides a stringent separation challenge for the magnetic extractants since the decane must be adsorbed from solution and not from a non-aqueous phase that is much easier to separate from water. The ratio of extractant to solution was kept low (2.5%) and the contact time with the aqueous solutions was short, a matter of only a few hours. After filtration, the aqueous solution was extracted with hexane and the extracts were analyzed for decane by GC/MS. The results of these experiments are outlined in Table 1. All of the magnetic extractants removed significant quantities of decane from the aqueous solutions with the best performing materials being the activated carbons and the magnetic materials coated with the thicker poly(dimethylsiloxane) (PDMS-1000). In fact there appears to be a strong correlation between the amount of absorbent present and the performance, thus the 10-centistokes poly(dimethylsiloxane) products (PDMS-10) performed less effectively than the PDMS-1000 series, while the material with only a monolayer of octadecylsilsequioxane performed very poorly by comparison. Nevertheless, the results do show that the magnetic extractants are effective for removing decane, and, by extrapolation, other hydrocarbons from water.

TABLE 1. Results from Treatment of Aqueous Solutions of Decane with Magnetic Extractants

Extractant	Final Concentration	Percent Decane Removal
Magnetite/Activated Carbon	61.2 ppb	99.94%
Nickel Ferrite/Activated Carbon	59.1 ppb	99.94%
Poly(octadecylmethacrylate)/iron	93.9 ppb	99.91%
Octadecylsilsesquioxane/iron	3332 ppb	99.53%
Octadecylsilsesquioxane/magnetite	1037 ppb	99.85%
PDMS-10/Iron	34.6 ppb	99.995%
PDMS-10/Magnetite	187 ppb	97.40%
PDMS-10/Hematite	261 ppb	99.96%
PDMS-1000/Iron	7.8 ppb	99.995%
PDMS-1000/ Hematite	<1 ppb**	100 %
PDMS-1000/ Magnetite	256 ppb	99.96%

* Below detection limit

The nickel ferrite/activated carbon extractant was also tested for its ability to break a very stable emulsion prepared according to the method of Shin and Kim. It was briefly mixed with such an emulsion and then separated by magnetic filtration. The effectiveness of treatment was determined by measuring the transmittance of the solution at 500 nm. Before treatment the absorbance of the emulsion was 1.66 while after it was 0.21. In terms of transmission, an increase from 2 to 62% was observed. Thus, magnetic extractants are capable of breaking emulsions and these initial results suggest that optimization of the magnetic extractant could result in complete breaking of an oil in water emulsion. Notably, the emulsion used in this study was very high in surfactant and extremely stable and it is likely that real world samples may not be as challenging.

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