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Selective Magnetic Adsorbents

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ABSTRACT

There are many practical situations, particularly in the food and pharmaceutical industries, in which it is desirable to adsorb low molecular weight, unwanted, constituents from a turbid process stream without reducing the concentration of larger product molecules. The preparation of magnetic adsorbents, as described in this paper, has provided materials capable of such adsorption.

INTRODUCTION

Materials such as activated carbon, kaolin, silica, and many other mineral oxides are frequently used to remove unwanted impurities from a process stream by adsorption. However, these adsorbents have two major disadvantages: a lack of specificity, resulting in

competition between the desired product molecules and the contaminant for the adsorption sites, and difficulty in removal of the loaded adsorbent from the usually turbid process stream. By encapsulating both the adsorbent and a magnetic material in a polymer matrix of controlled porosity, it is possible to overcome both problems. The size of the molecules which come into contact with the adsorbent can be controlled by the degree of crosslinking of the polymer matrix, while the presence of a magnetic material enables rapid recovery of the loaded adsorbent beads, without accompanying solids from the slurry. For practical purposes, the magnetic adsorbents should be mechanically strong, spherical, of small particle size for rapid kinetics and chemically inert (i. e., should not affect product quality). An idealized version of a magnetic carbon microbead is shown in Fig. 1. The subject of this paper is the manufacture of these materials and the synthetic problems encountered during their preparation.

SYNTHESIS

Experience in the preparation of magnetic ion-exchange resin microbeads indicates that the best preparative method for magnetic adsorbents appears to be a two-phase crosslinking process. The polymer and crosslinker are usually in an aqueous phase. The simplest polymer and to this stage the most useful is poly(vinyl alcohol), nominally 88% hydrolyzed and of low molecular weight. There are many known reagents for crosslinking poly(vinyl alcohol), including aldehydes and dialdehydes; of these, glutaraldehyde proved the most convenient, used as a 25% (w/v) aqueous solution. The rate of crosslinking depends on both pH and temperature.

The organic phase must be immiscible with water. Liquids such

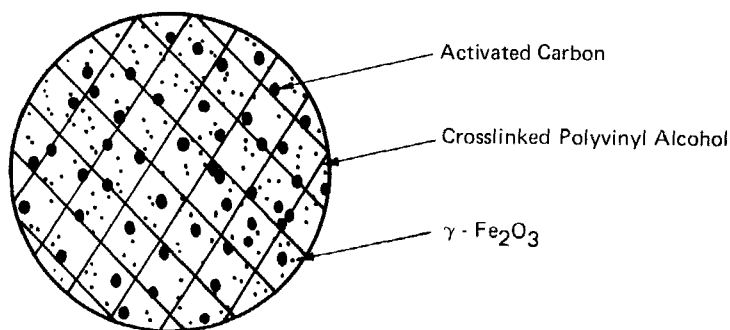


FIG. 1. Idealized version of a magnetic carbon microbead.

as o-dichlorobenzene (o-DcB), m-dichlorobenzene (m-DcB), xylene, or other hydrocarbons can be used, the choice depending on the nature of the product, its density and particle size, and the scale of preparation.

A wide range of adsorbents has been used and doubtless there will be others with specific adsorption properties used in the future for particular applications, but activated carbon remains the most common adsorbent and most attention has been focussed on this material; in particular on the grades commonly used in the food industry.

A variety of magnetic materials could be utilized, but for maximum adsorption per gram of adsorbent, a material of high magnetic remanence is needed. Of the oxides available the most suitable is γ -Fe₂O₃ which is supplied as a brown powder of less than 1 μ m particle size.

For the successful preparation of individual microbeads it is essential that a surfactant be added to both phases to prevent aggregation. The selection of dispersants with suitable properties is discussed in the next section.

In a typical preparation, the aqueous suspension (e. g., 15% PVA solution with equal weight of carbon and γ -Fe₂O₃) adjusted to the desired pH and the organic solvent with dissolved surfactant were prepared separately and then mixed in the reaction vessel. The crosslinking agent was subsequently added, and the reaction proceeded to completion. The mixture was then filtered and washed with acetone and distilled water.

The reaction vessel in our studies was a stainless steel beaker equipped with baffles and agitated by an overhead stirrer. The design of the blades, i. e., the impeller style, was changed frequently until agitation was optimized. Evaluation of the products was based on microscopic examination, attrition tests, adsorption and regeneration capacity measurements, kinetic studies, and finally pilot-plant experiments. Details are reported elsewhere [1].

RESULTS AND DISCUSSION

The products obtained initially were of poor quality, being aggregates of irregular shape and less than adequate mechanical strength. This was found to be due to adsorption by the activated carbon of both the dialdehyde and the acid catalyst, hindering the crosslinking reaction. Thus it was necessary to pretreat the adsorbent particles with a material which adsorbs strongly on the adsorbent but which can be readily removed from the composite material. The nature of the protecting agent depends largely on the particular adsorbent being used, but in general aliphatic acids were found to be particularly useful. Alternative materials such as starches or gelatin were also used successfully, these materials being removed later enzymatically.

TABLE 1. Effect of Pretreatment of Activated Carbon^a

Nature of pretreatment	Temperature (°C)	Nominal degree of crosslinking (%)	Gelation time (hr)	Product
None	45	15	16	Aggregates
None	45	150	16	Aggregates
Saturated with glacial acetic acid	25	30	2.5	Some spherical particles

^aAll other experimental parameters were unchanged throughout the series of experiments.

In a typical preparation, the adsorbent was stirred with the protecting agent, e. g., acetic acid, filtered and washed. Alternatively, spray drying of a mixture of the adsorbent and a starch solution could be used to produce material precoated with starch. The pretreated adsorbent was then added to the aqueous phase and the preparation continued as described above. Finally the adsorbent was reactivated by removal of the protective material (alkali for acetic acid, enzymes for the starch). As a result of this pretreatment step, the amount of crosslinking agent needed to effect gelation was reduced, as were the temperature and time (Table 1). However, the products were still inclined to aggregate, suggesting that even the precoated carbon and to some extent the mineral oxide were hindering the action of the surfactant or dispersant. To prevent aggregation a high ratio of organic phase to aqueous phase and prolonged, rapid stirring were required at a given surfactant concentration as shown in Table 2.

Since these conditions were unacceptable for economic reasons, the solid/liquid ratio of the aqueous dispersion was increased, improving both the yield per unit total volume and the rate of gelation as well as product quality. Furthermore, the type of impeller was varied to increase the amount of shear and turbulence (from S-type impeller to P-type and C-type) with accompanying changes in the nature of the product i. e., shape, particle size, and mechanical strength as shown in Table 3. Thus the conditions determined for successful laboratory preparations were (1) moderately high organic to aqueous phase ratio; (2) as rapid a rate of gelation as possible, i. e., concentrated aqueous dispersion, low pH, highest possible temperature; (3) high shear stirring. However, these reaction conditions are not practicable and in particular are not amenable to large-scale preparations. For larger preparations it is difficult to prevent aggregation of partially gelled products by imposing high shear conditions on the beads, simply

TABLE 2. Conditions Necessary for Preparations with 4% PVA Suspensions^a

Phase ratio o-DcB: H ₂ O	Stirring speed (rpm)	Time (hr)	Organic phase surfactant	Product
6:1	1225	1.5	2% Span 85	Aggregates
12:1	800	16	2% Span 85	Aggregates
12:1	1225	4	2% Span 85	Some spheres
12:1	1225	16	2% Span 85	Mainly spheres 100 μm size

^aAll other experimental parameters were unchanged throughout the series of experiments.

TABLE 3. Conditions Necessary for Preparations with 8% PVA Suspensions^a

Phase ratio 0-DcB: H ₂ O	Impeller design	Product	
		Shape	Size (μm)
12:1	Paddle (straight) blade	Mainly spheres	150
6:1	Paddle (straight) blade	Mainly spheres	250
6:1	S-type impeller	Spheres	200
6:1	P-type impeller	Spheres	170
6:1	C-type impeller	Spheres	140

^aAll other experimental parameters were unchanged throughout the series of experiments.

because of the scale of the preparation. For this reason, attempts were made to optimize the chemical parameters, in particular the type of surfactant, so that aggregation could be prevented.

In all preparations two dispersants were used, one in each phase. Teric PE68 (ICI) was used to prevent clumping of the particles in the

TABLE 4. Effect of Polymeric Surfactants^a

Phase ratio o-DcB:H ₂ O	Organic phase surfactant	Product	
		Type	Size (μ m)
6:1	3% Span 85 in o-DcB	Aggregates	
6:1	6% Span 85 in o-DcB	Aggregates	
6:1	1% EA/HEMA	Spheres	120
6:1	0.1% EA/HEMA	Spheres	200
2:1	2.5% EA/HEMA	Spheres	80
6:1	1% LM/HEMA in xylene	Spheres	150

^aAll other experimental parameters were unchanged throughout the series of experiments.

aqueous phase, and Span 85 (o-DcB) or Tween 81 (hydrocarbons) (both from ICI) was used in the organic phase to prevent aggregation during gelation. Despite a massive increase in the concentrations of surfactants (from 0.5% up to 5.0%) the final products from large-scale preparations (ca. 35 l total volume) were aggregates. Samples taken prior to gelation were found on microscopic investigation to contain spheres, however. It seemed that without the conditions of high shear attainable in small scale preparations, the surfactant was incapable of stabilizing the interface during crosslinking.

At this stage polymeric dispersants were introduced [2, 3]. The particular polymeric dispersant used most commonly was an ethyl acrylate-hydroxy ethyl methacrylate copolymer (EA/HEMA) formed in the ratio of 9:1. The use of this copolymer even at low concentration (0.5%) in the o-DcB phase prevented aggregation as shown in Table 4.

It was also shown that solvents other than o-DcB could be used, provided an appropriate polymeric surfactant was chosen, e. g., toluene with EA/HEMA or xylene with LM (lauryl methacrylate)/HEMA. The mode of stirring was still critical with respect to particle size distribution but the dispersion was now stabilized primarily by the surfactant, a situation which is much more satisfactory for large scale preparations. Furthermore, the phase ratio could be reduced (e. g., 2:1), thereby greatly increasing the product yield from a given reaction volume.

Attention was then given to the preparation of the aqueous slurry with the aim of improving the stability of the dispersion with a polymeric surfactant such as methoxy polyethylene glycol methacrylate-acrylic acid copolymer (10:1 ratio). Subsequent experiments using

this surfactant were successful, even when a low molecular weight surfactant was used in the organic phase.

The adsorption and desorption properties of the products from these preparations were examined using a variety of adsorbates of economic importance, e. g., inosuhumulone, riboflavin, penicillin, and vitamin B₁₂ [1]. In particular, the specificity of adsorption brought about by electrostatic and steric effects was investigated, using solution mixtures, as a function of the size, composition and porosity of the particles. The physical properties, e. g., mechanical strength, attrition rate, have also been examined in both laboratory-scale experiments and in pilot-plant studies [1].

From this work it appears that these magnetic materials do adsorb specifically; can be recovered after uptake of the desired material from the suspension to be treated; can be regenerated with subsequent recovery of the adsorbate and can be readily transferred (pumped) back to the adsorption vessel for reuse. There are many potential applications for these novel adsorbents, some of which are currently being evaluated.

CONCLUSIONS

The preparative conditions required for the production of selective magnetic adsorbents have been determined both on a laboratory scale and on a larger scale, and the effects of many preparative parameters have been examined. The influence of the active carbon on gelation rate etc. has been demonstrated and has necessitated a pretreatment step in which the carbon is protected by acetic acid. The problem of aggregation during gelation has been overcome by high shear stirring in small-scale preparations and by the introduction of polymeric surfactants on a larger scale.

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