

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Novel Water Treatment Processes Which Utilize Polymers

B. A. Bolto^a

^a CSIRO Division of Chemical Technology, South Melbourne, Australia

To cite this Article Bolto, B. A.(1980) 'Novel Water Treatment Processes Which Utilize Polymers', Journal of Macromolecular Science, Part A, 14: 1, 107 – 120

To link to this Article: DOI: 10.1080/00222338008063212

URL: <http://dx.doi.org/10.1080/00222338008063212>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Novel Water Treatment Processes Which Utilize Polymers

B. A. BOLTO

CSIRO

Division of Chemical Technology
South Melbourne, Australia

ABSTRACT

The use of insoluble reagents in micro particle form has been extensively investigated in the search for new and simpler processes for purifying water. Very finely divided particles allow rapid rates of reaction to be attained. However, they pose a severe handling problem. To overcome this difficulty, the microparticles may be bound together to form a composite particle of conventional size, held together by a polymeric binder which is permeable to water and the impurities to be removed. Another technique involves incorporating small amounts of a magnetic material such as iron oxide within the micro particles of reagent. When magnetized, the particles flocculate strongly and quickly settle out. Variation of the nature of the reagent allows a wide variety of impurities to be adsorbed. The feasibility of using microparticles suitably modified has been demonstrated for a number of ion-exchange reactions, for a new clarification and decolorization process involving alkali-treated magnetite, and for a selective adsorption process based on a magnetic activated carbon which can adsorb only small molecules.

INTRODUCTION

It is an appropriate time to review the new polymer-associated water treatment processes devised by Weiss and co-workers at the CSIRO Division of Chemical Technology, in research that has spanned more than a decade. Large-scale demonstration plants are planned for three of these processes in 1980. The main aim of the work has been to find new ways of cleaning up waters which are simpler and cheaper to operate than existing procedures.

A central theme has been the use of insoluble purifying agents in microparticle form. Because of their small size, down to 1-5 μm , they react very rapidly. However, they present severe handling problems. When used in packed beds they provide a high resistance to the flow of water, and are difficult to backwash. When used in stirred vessels, they settle out very slowly.

To overcome the difficulty of handling such fine material, two approaches have been developed. In one, the microparticles are bound together to form a larger composite particle, which is held together by a binder which is permeable to water and the impurities in it. This is the method employed for thermally regenerable ion-exchange resins, used for desalting low salinity waters [1].

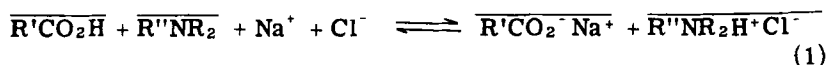
The second technique, which has been used for a variety of adsorption procedures, involves microparticles containing small amounts of a magnetic material, such as iron oxide. When magnetized, the particles flocculate strongly. On agitation, they disperse and react rapidly; when agitation stops they flocculate once more and quickly settle out. The magnetic concept has been applied to a number of processes, including a variety of ion-exchange reactions [2, 3], a new method for clarification and decolorization which is based on alkali-treated magnetite [4], and a selective adsorption process which employs a magnetic activated carbon which can adsorb only small molecules [5]. Magnetic polymers in nonreacting forms have also been developed for use as recyclable filter aids [6], and as absorbents for the recovery of oil spills [7]. All of these processes have been tested on the pilot plant scale.

The two approaches allow the rapid reaction rates of microparticles to be exploited by combining the handling characteristics of large particles with the speedy reaction of finely divided material. A brief review will be made of the way in which this wide range of processes has been developed. It is hoped that this will tie together many of the scattered articles published over the years, as well as give a perspective to a number of the papers presented at this Symposium.

COMPOSITE PARTICLES: THERMALLY REGENERABLE ION EXCHANGE

The Sirotherm desalination process (ICI Limited trademark for thermally regenerable ion-exchange resins and associated plant) has

been extensively discussed in the literature [1], and the complexities of the temperature-sensitive equilibrium between basic and acidic weak electrolyte resins [Eq. (1)]



will not be gone into here. Suffice it to say that, since the formation of the charged sites involves proton transfer from the acidic to the basic resin at near-neutral pH levels where there is a very low proton concentration, the rate of salt adsorption at ambient temperature is slow indeed when resin particles of normal size (300-1200 μm) are employed.

The necessary 100-fold increase in rates can be obtained with particles which contain both the acidic and basic groups within the one particle so as to shorten the path for the proton transfer step. If both types of groups are substituted on the one polymer chain, as in amphoteric resins made from piperidine-4-carboxylic acid and chloromethylated styrene/divinylbenzene (DVB) copolymers, or are present in combinations of a flexible chain and a rigid network, as in the snake-cage resins made by polymerizing acrylic acid within conventional porous amine resins based on styrene/DVB, poor salt uptakes are obtained. This is shown in Table 1 in comparison with mixed resin systems comprised of a crosslinked polyacrylic acid resin, and an amine resin based on styrene/DVB.

Faster rates are certainly obtained with the snake-cage system, but not all the sites are accessible for adsorption of salt, a result which has been ascribed to the sites of opposite character now being in too close proximity so that neutralization occurs with the formation of internal salt structures. Sites so combined are then not available for adsorption of mobile counterions.

Such neutralization is avoided with the mixed micro resins, which have fast rates and adequate thermally regenerable (TR) capacities.

TABLE 1. Comparison of Resin Systems

System	Particle size	Thermally regenerable capacity at 20-80°C (meq/g)	Time to 50% equilibrium (min)
Mixed resins	Normal	1.0	240
Amphoteric resin	Normal	0.05	-
Snake-cage resin	Normal	0.4	1
Mixed resins	Micro	1.0	2

By binding the micro particles together into the so-called "plum pudding" format, using a water- and salt-permeable polymer such as poly(vinyl alcohol) crosslinked with a dialdehyde, it is possible to form composite beads of normal size which can be used in conventional ion-exchange columns [1].

Of course, the capacity of the system is now diminished because of the presence of the inert binder or matrix. This can be alleviated somewhat by the use of base resins derived from triallylamine, which have a 50% higher total capacity than the polystyrene types. In a plum pudding mode with a suitable weakly acidic micro resin, TR capacities of 1.4 meq/g are possible. Nevertheless, further improvement can result if the matrix can be eliminated: a value of 2.1 meq/g is theoretically possible.

Attempts have been made to prepare "no-matrix" resins in which the active materials are bound or grafted together so that they are contained in a three-dimensional mosaic, as shown in Fig. 1.

The major practical problem is to segregate the two types of exchange material and thus avoid interactions which eliminate many sites otherwise suitable for ion exchange. In the idealized version, the preparative route is very simple, involving a one-step preparation from two monomers in homogeneous solution. This is in contrast to the three separate synthetic routes employed in making plum pudding resins. In practice, the need to minimize internal salt formation between the acidic and basic sites adds some complications. If a mixture of acidic and basic monomers such as acrylic or methacrylic acid and an allylamine is polymerized, a resin is obtained which has no TR capacity, because salt formation will have occurred before polymerization, and the product will have the maximum possible interaction between carboxylate and protonated amino groups. If precautions are taken to prevent such interactions, useful resins can be produced [8].

For example, if the same polymerization is carried out in the presence of added anions and cations, particularly multivalent or

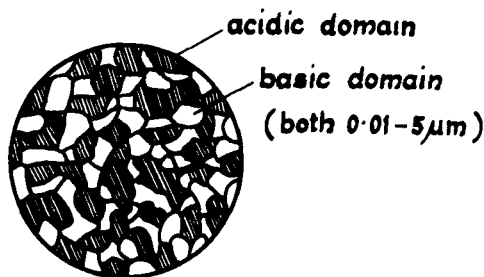


FIG. 1. Diagrammatic representation of a no-matrix resin bead, diameter 300-1200 μ m.

TABLE 2. Comparison of Preparative Routes

System	Preparative route	Thermally regenerable capacity at 20-80°C (meq/g)
No-matrix	Counterion	0.6
No-matrix	Precipitation with solvent	0.6
No-matrix	Neutral precursor	1.2
Plum pudding	Separate polymerizations	1.4

large organic ions, the electrostatic interaction between the monomers can be suppressed in favor of stronger interactions between each type of monomer and a nonpolymerizable counterion. Resins are then produced which, after removal of the counterions, have significant capacities, but only about one-half those of the plum pudding type, showing that a substantial amount of internal salt formation has still occurred.

If the monomers are reacted in the presence of mineral acid so that protons are the only additional cations, the product has no useful capacity, even though under these conditions the acidic monomer is uncharged and should not associate strongly with the protonated amine. When solvents other than water are employed, precipitation of the growing polymer chains occurs, which should encourage block copolymer formation. Appropriate solvents give resins having capacities similar to those of resins made by the counterion method.

Better results are obtained if a noncharged precursor for the acidic groups is employed which is hydrolyzed after polymerization to provide the exchange sites. Resins made from methacrylamide and allylamines have capacities similar to those of plum pudding beads. Electron micrographs clearly show the presence of two separate domains, but neutralization between groups still prevents utilization of one-third of the sites present. It is also evident that one polymer is formed and precipitated as fine particles, around which the other polymer forms so that it operates as an active binder [8]. The capacities obtained are shown in Table 2.

Photografting of triallylamine onto polymethyl acrylate which contains photolabile groups has yielded resins of capacities of 0.7 meq/g [9]. As with the other no-matrix approaches, all of which utilize homogeneous solutions of the reactants, the preparative methods are relatively simple, but for reactions in solution, the chances of interaction between species of opposite character are too high. Inferior capacities are the result.

A more useful route is the two-step approach in which one of the polymeric species is formed as a solid particle and in a separate

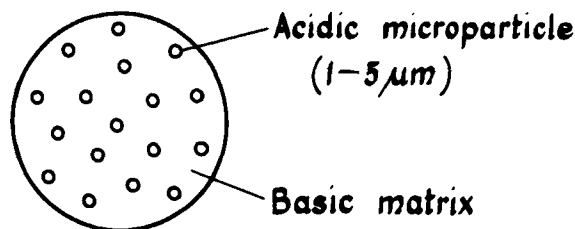


FIG. 2. Representation of an active matrix resin bead, overall particle size 300-1200 μm .

TABLE 3. Comparison of Matrices

Microparticle	Source of matrix	TR capacity at 20-80°C (meq/g) ^a
Polytriallylamine	Ethyl acrylate/DVB	1.2
Crosslinked poly(acrylic acid)	Diallylamine/Hexa	1.2
Crosslinked poly(ethyl acrylate)	Diallylamine/Hexa	2.1

^aAfter hydrolysis, where necessary.

stage the second polymer is intentionally polymerized around it as an active matrix, to give a product as shown in Fig. 2. Heterogeneous two-monomer systems, obtained by using two immiscible liquids or one monomer as a solid, have been studied. However, these are awkward and cumbersome in practice, although a high TR capacity (1.5 meq/g) has been obtained [10].

There are several routes for obtaining the maximum possible TR capacity, based on the encapsulation of microparticles with the precautions against internal neutralization already outlined for no-matrix resins. As examples, data are given for polytriallylamine within an ethyl acrylate/DVB copolymer, and crosslinked polyacrylic acid particles within a diallylamine/bisdiallylaminohexane (Hexa) copolymer. If in the latter case an ester particle is used instead of the acid, the target figure of 2.1 meq/g can be achieved, as indicated in Table 3 [11].

The Sirotherm process is being commercialized by ICI Australia, who have constructed the first large-scale plant treating 600 m³/day of salty surface water. This batch plant has been operated for two years in Adelaide, South Australia. It is now evident that, to better

compete with membrane processes, a continuous mode of operation, which has many advantages [1], will be essential. Several continuous pilot plants have been studied over the years. It is hoped to construct a large-scale continuous demonstration plant in Perth, Western Australia in the near future.

MAGNETIC MICROPARTICLES

Continuous Magnetic Ion Exchange

In addition to the rate and handling properties already alluded to, magnetic resins have a third feature of great practical importance. The magnetized particles, shown in Fig. 3, possess a very high voidage or space within the flocs. As a result, there is a certain amount of give in the structure which allows the materials to be transported in continuous contactors with very little attrition resulting. This has allowed the development of novel procedures for carrying out a variety of ion-exchange reactions in a truly continuous manner, in simple equipment which is well suited to operation on a very large scale.

Magnetic resins have been prepared in a variety of physical forms, and the details are outlined in a recent review [12]. There are three general physical types: "homogeneous" resins comprised either of magnetic material uniformly distributed within the crosslinked ion-exchange resin, or of magnetic material and micro ion exchangers uniformly distributed within an inert crosslinked polymer, and "heterogeneous" resins of the shell or whisker type, consisting of active polymeric chains grafted onto a core of magnetic polymer formed by embedding magnetic particles within an inert crosslinked polymer. The latter structure is depicted in Fig. 4. It can be seen that the core polymer is that utilized as the matrix in Sirotherm resins of the plum pudding type.

Many monomers can be grafted to the magnetic core, with varying degrees of success [13]. A simple redox method is adequate. Acrylic acid and acrylamide give the most successful products, although certain basic monomers, both strong and weak electrolyte types, result in practical grafting levels. The acrylic acid resin can be esterified with isothionic acid in 50% yield to introduce sulfonic acid groups, or reacted with diethylamine and epichlorhydrin to form a weakly basic resin. In both cases the active group is bound to the polymer chain by an ester link, which is too easily hydrolyzed for the products ever to become practical resins. However, a whisker resin can be formed from the polyacrylamide form by reaction with hypochlorite to convert the amide groups to primary amino species [14]. Although devoid of ester groups, it is still unstable in alkali.

The pioneering work on magnetic ion exchange has been performed on the dealcalization reaction in which hard, alkaline bore

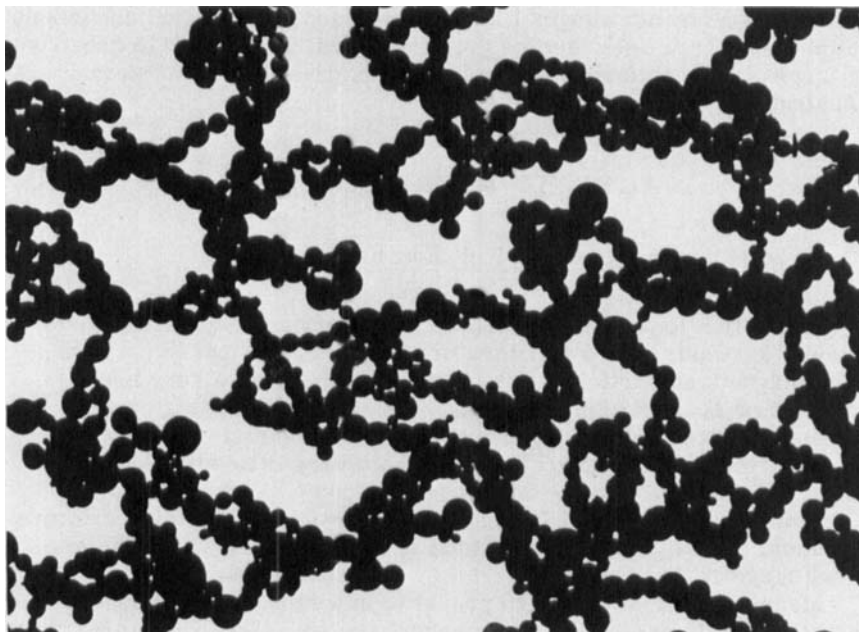
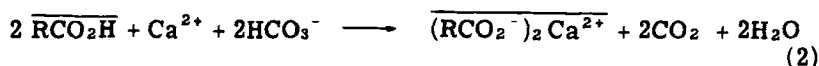


FIG. 3. Magnetic ion-exchange resin beads, about 50 μm in diameter, containing $\gamma\text{-Fe}_2\text{O}_3$. Shown here in magnetized form, the beads are separate, free-flowing spheres when not magnetized.

water is treated with a carboxylic acid resin to remove bicarbonate and an equivalent amount of calcium or other cations.



Regeneration is achieved with mineral acid.

The resin used was the polyacrylic acid whisker resin of the general structure depicted in Fig. 4. The final particle contained 50% by weight of the iron oxide, and was of overall particle size 100-300 μm . In a stirred cell the magnetized resin reacts more than 10 times as fast as normal carboxylic acid resins, which have a particle size of 300-1200 μm . Its settling rate, in the magnetized form, is three times that of conventional resin beads.

With the advent of magnetic resins which can be easily moved about, in contrast to conventional resins, a number of continuous modes of operation become feasible. Pilot plant studies have been made using several types of equipment including fluidized bed, pipeline reactor, and conventional commercial systems which are

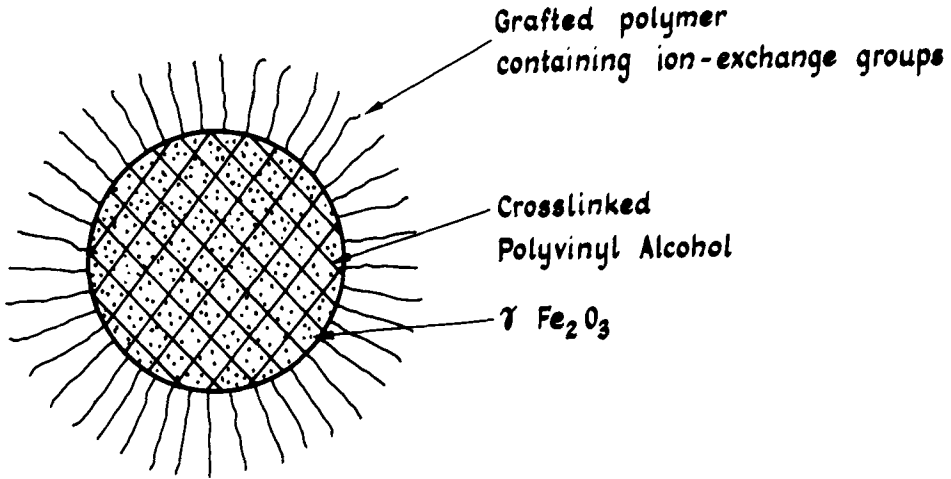


FIG. 4. Depiction of a magnetic shell or whisker resin bead, showing active ion-exchange material grafted onto the magnetic polymeric core.

actually intermittent in their operation and possess many disadvantages. One system advocated [3] involves a simple pipeline for the adsorption reaction, in which the magnetized resin and the raw water are pumped through a pipe at such a flow rate that turbulence results and the flocs are broken apart, so that the reaction is complete when the mixture leaves the pipe. The slurry flows into a settling vessel, whereupon the magnetic flocs reform and rapid sedimentation ensues. The purified water flows over the top of the vessel, and the exhausted resin is pumped from the bottom into the regenerator, where similar contacting procedures may be employed. The resin is always present in its magnetized state. The major advantage of this system is its simplicity, both of construction and operation. Operation is truly continuous, and because rapidly reacting micro particles are employed, the same job can be done using much less resin than is required for batchwise operation.

Unfortunately, the pilot studies over a prolonged period showed that the shell resin is not stable to mildly acidic conditions. This has been identified as arising from cleavage of the grafted chains at the link point to the magnetic core [15]. Resins containing the magnetic material embedded in small weak acid resin beads of conventional chemical structure are now employed. The process is being commercialized by ICI Australia, and it is planned to construct the first demonstration plant in northwestern Australia in the near future. The technique is also being applied to other ion-exchange processes, including Sirotherm.

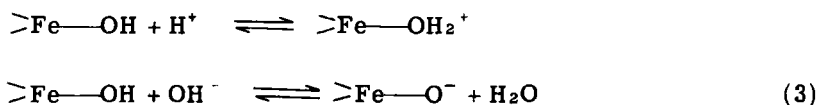
Water Clarification and Decolorization

The standard process for the removal of turbidity and color involves formation of an adsorptive flocculant precipitate of aluminum or ferric hydroxide at a pH where the floc has an opposite charge to that of the colloids to be removed. The colloids thus bind to the floc and are removed through sedimentation. This process, the most widely used of all water treatment processes, has many problems. Perhaps the major disadvantage is that the sludge formed is voluminous and difficult to dewater, since it contains not only the turbidity and color removed from the feed water, but also a much larger amount of the metal hydroxide floc.

As a direct result of the magnetic ion-exchange work, magnetic adsorbents have been prepared which will very effectively remove both turbidity and color in the one step. Good results are obtained with organic polymers of the quaternary ammonium type grafted onto magnetic polymeric cores to give structures as depicted in Fig. 4. A suitable monomer is 2-hydroxy-3-methacryloyloxypropyltrimethylammonium chloride [13]. The positively charged whiskers which are formed are very effective at adsorbing the colloids and color, which are normally negatively charged. Unfortunately, although the resin can be regenerated with brine, the cost of the whisker resin renders the method uneconomic.

Cheaper, inorganic materials have now been prepared from finely divided magnetic particles treated with alkali [4]. This has led to a completely new approach which should overcome many of the disadvantages of the conventional method. Called Sirofloc, it offers promise of a faster and more efficient process with greatly accelerated sedimentation, and a significantly reduced volume of sludge. The particles may be reused repeatedly by regeneration and reactivation with alkali. For the adsorption step, a very small amount of acid is added, which gives the treated unmagnetized magnetite a positively charged surface. The impurities in the water, in general, have a negatively charged surface, and hence adhere to the magnetic material. The mixing may be done in either a pipeline or a series of stirred vessels. When magnetized and transferred to a settling vessel, the solids sediment rapidly, leaving a clear, colorless water to be taken off from the top of the vessel. The slurry at the bottom is treated with dilute alkali at pH 10.5, which reverses the charge on the surface of the treated magnetite, thereby repelling the accumulated impurities. After this regeneration, more alkali at pH 11.5 is necessary to reactivate the magnetite prior to the next adsorption step, before which the particles are demagnetized.

Magnetite particles of size 1-5 μm are employed, after treatment with 0.1 M sodium hydroxide in the cold for 15 min. It is proposed that hydrolysis of the metal oxide occurs to form a highly hydroxylated surface. A charge can then be developed by the addition of acid or alkali [Eqs. (3)].



The positive surface charge results at pH levels less than about 6.5. The lower the pH, the greater the degree of charge formation, and the better the coagulation effect. When the pH is raised in the regeneration step, the net surface charge on the coated magnetite becomes increasingly negative. The adsorbed species also become increasingly negatively charged, so that electrostatic repulsive forces cause their separation from the magnetic particle. Thus on alkali treatment, the surface is regenerated and made ready for reuse.

It has been found that waters of high color and low turbidity can be successfully treated at pH 4 without the addition of other chemicals. With a more turbid water, the surface of the oxide is inadequate to cope with all the impurities, and another coagulant must be added. Alum is effective, but cationic polyelectrolytes are better, in that they avoid the sludge problem.

Polyelectrolytes containing predominantly weakly basic groups are the logical flocculants to employ, in that they possess a positive charge at the pH level used for clarification, which is 5 or above when these materials are present. They assist in bridging the residual turbidity to form flocs, which must still be overall negative in charge, in order to become bound to the positive oxide surface, as shown diagrammatically in Fig. 5a. When the pH level is raised to 10, the weakly basic groups are deprotonated and lose their charge and binding power, so that regeneration occurs as depicted in Fig. 5b, much as already described for the case when the flocculant is absent. The optimum polyelectrolyte structure depends on the nature of the impurities in the water.

A pilot plant has been successfully operated on a highly colored and turbid underground water in Perth during 1978. A large-scale plant is scheduled for operation by the end of 1979. The process has been licensed to Davy Pacific and ICI Australia.

The use of Sirofloc particles for the analogous adsorption of other pollutants such as virus, bacteria, algae, heavy metal ions and organic micropollutants is under active study.

Selective Magnetic Carbons

Some early experiments on the crosslinked poly(vinyl alcohol) used as the matrix in plum pudding resins were conducted to test whether the polymer would be useful as a support in gel-permeation chromatography, as its network density may be readily altered by varying the degree of crosslinking. It was found that beads of poly(vinyl alcohol), reacted with a dialdehyde in an amount equivalent to 20% of the hydroxyl groups in the polymer, would separate inorganic hydrous

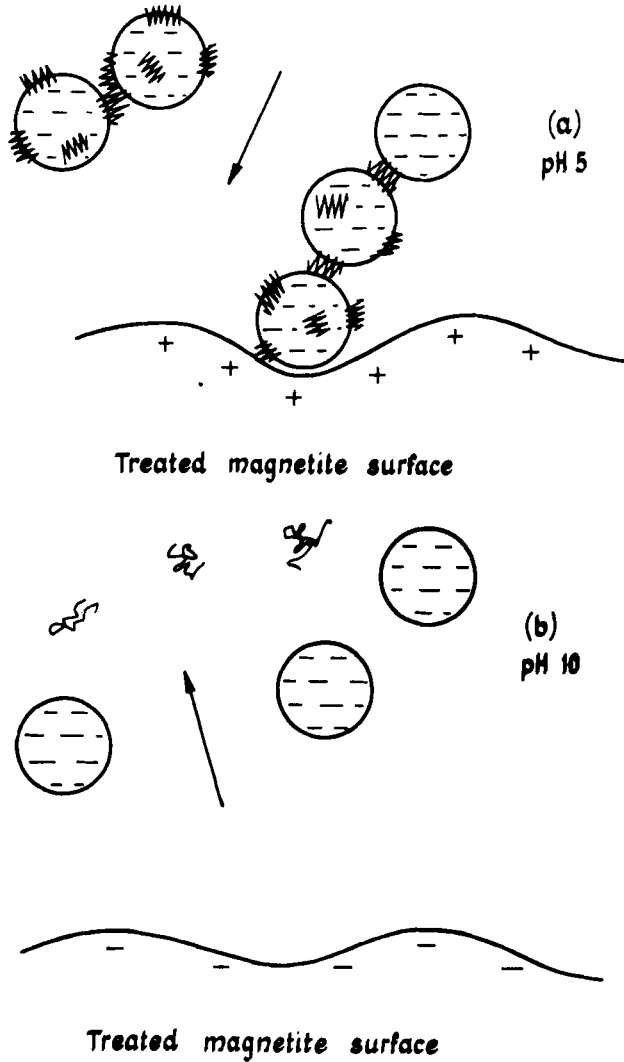


FIG. 5. Schematic representation of (a) bridging of negatively charged clay particles by a cationic polyelectrolyte, which is positively charged at the acidic pH levels used for the clarification step; (b) separation of the clay from the noncharged polyelectrolyte and the negatively charged magnetite under the alkaline regeneration conditions.

oxide polymers from accompanying proteins of MW > 12,000, which were completely excluded from the polymer network.

The phenomenon has been put to good use in an application in the food industry, where it is essential to adsorb small nuisance molecules on activated carbon, but not larger molecules such as vitamins, proteins, and nucleic acids which have a high nutritional value [5]. The finely divided activated carbon, together with magnetic material, is encased in the crosslinked polymer [16]. Only small organic molecules can penetrate the binder, which excludes the valuable macromolecules. The magnetic handling aspects allow the ready separation of the loaded adsorbent from dead cells and other insoluble material. Regeneration is possible with alkali or solvent.

Further Magnetic Particle Systems

The use of hydrophilic yet insoluble polymers containing magnetic material as a recyclable filter aid takes advantage of the high voidage in the magnetized bed (cf. Fig. 3). However, it is essential to use magnetic polymer particles of irregular shape, rather than spheres. The work is adequately described elsewhere [6].

Hydrophobic magnetic polymers likewise make use of the high voidage to absorb oil within the interstitial space. The particles must be vesiculated also, so that the final density is such that they will float on water. A craft has been designed and built to demonstrate their use in the retrieval of oil spills from harbor waters [7].

Other applications such as selective magnetic adsorbents, magnetic enzyme resins and magnetically supported microbes are possible [12].

CONCLUSIONS

The advantages of microparticle reagents are many, if modifications can be made to allow simple contacting techniques to be employed. The major return is in enhanced reaction rates, which means that the same job can be done with less reagent and smaller equipment. Both the composite particle approach and the magnetic concept have resulted in the development of completely new contacting systems which are truly continuous in their operation, and are applicable to a wide range of treatment processes. The most important benefit is that the simple equipment required makes for easy operation on a very large scale. The principle has potential also in nonreacting systems.

REFERENCES

- [1] B. A. Bolto and D. E. Weiss, in Ion Exchange and Solvent Extraction, J. A. Marinsky and Y. Marcus, Eds., Vol. 7, Dekker, New York, 1977, p. 221.

- [2] B. A. Bolto, D. R. Dixon, R. J. Eldridge, L. O. Kolarik, A. J. Priestley, W. G. C. Raper, J. E. Rowney, E. A. Swinton, and D. E. Weiss, The Theory and Practice of Ion Exchange, Society of the Chemical Industry, London, 1976, paper 27.
- [3] B. A. Bolto, D. R. Dixon, A. J. Priestley, and E. A. Swinton, Progr. Water Technol., 9, 833 (1977).
- [4] L. O. Kolarik, A. J. Priestley, and D. E. Weiss, Proc. 7th National Convention, Australian Water and Wastewater Association, 1977, p. 143.
- [5] D. R. Dixon, S. West, and D. E. Weiss, Austral. Pat. Appl. 20,760/76.
- [6] B. A. Bolto, K. W. V. Cross, R. J. Eldridge, E. A. Swinton, and D. E. Weiss, Chem. Eng. Progr., 71, 47 (1975).
- [7] H. A. J. Battaerd, B. A. Bolto, D. R. Dixon, R. J. Eldridge, E. A. Swinton, D. E. Weiss, and P. H. Young, J. Polym. Sci. Polym. Symp. Ed. 49, 211 (1975).
- [8] B. A. Bolto, M. B. Jackson, R. V. Sludak, H. A. J. Battaerd, and P. G. S. Shah, J. Polym. Sci. Polym. Symp. Ed., 55, 87 (1976).
- [9] M. B. Jackson and W. H. F. Saase, J. Macromol. Sci.-Chem., A11, 1137 (1977).
- [10] M. B. Jackson, J. Macromol. Sci.-Chem., A12, 853 (1978).
- [11] M. B. Jackson, ACS Polym. Preprints, 20, No. 1, 624 (1979).
- [12] B. A. Bolto, in Ion Exchange Processes in Pollution Control, Vol. 2, C. Calmon and H. Gold, Eds., CRC Press, Boca Raton, Fla., 1979, p. 213.
- [13] B. A. Bolto, D. R. Dixon, and R. J. Eldridge, J. Appl. Polym. Sci., 22, 1977 (1978).
- [14] R. J. Eldridge, paper presented to Division of Organic Coatings and Plastics Chemistry, Symposium on Modification of Polymers, American Chemical Society Meeting, Hawaii, April 1979.
- [15] J. S. Bates and R. A. Shanks, J. Macromol. Sci.-Chem., A14, 137 (1980).
- [16] D. R. Dixon and J. Lydiate, J. Macromol. Sci.-Chem., A14, 153 (1980).