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T. A. Pinfold[a][b]; B. L. Karger[a]
[a] DEPARTMENT OF CHEMISTRY, NORTHEASTERN UNIVERSITY, BOSTON, MASSACHUSETTS [b] Department of Chemistry, University of Witwatersrand, Johannesburg, South Africa

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The Coagulation of Finely-Divided Ion Exchange Resins and the Use of the Coagulated Material for Rapid Ion Removal

T. A. PINFOLD* and B. L. KARGER
DEPARTMENT OF CHEMISTRY
NORTHEASTERN UNIVERSITY
BOSTON, MASSACHUSETTS 02115

Summary

Finely-ground ion exchange resin particles remove ions from solution much more rapidly than the conventional-size beads. Such finely-divided solids form suspensions when added to aqueous solutions. A method was required for rapidly removing such suspensions once ion adsorption had occurred, and to this end it is shown that the particles (−400 mesh) can be completely coagulated within a few minutes by the addition of suspensions of oppositely-charged solids. Thus anion exchange resins are coagulated by cation exchange resins (200 to 400), montmorillonite (200), kaolin (30), charcoal (10), silica (10), and glass (5), the figures representing arbitrarily defined relative coagulating abilities. Coagulating power is shown to increase markedly with decreasing particle size. Most suitable for ion removal is a mixed finely-divided resin formed by coagulation of anionic and cationic resins from pure water. The mixed resin, when added to 1 liter of $3 \times 10^{-4}\,M$ sodium phosphate solution removes all the phosphorus within 2 min, and when added to 1 liter of $2.5 \times 10^{-4}\,M$ calcium chloride, removes over 90% of the calcium within 3 min.

INTRODUCTION

Ions may be removed from large volumes of dilute aqueous solutions by adsorption on ion exchange resins. The solutions are passed through columns packed with resin beads of about 0.5 mm diameter, and exchange of the counter-ions of the resin occurs with ions of the same

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* Present address: Department of Chemistry, University of Witwatersrand, Johannesburg, South Africa.

sign from the solution. The rate of this exchange is inversely proportional to the square of the radius of the resin particles (*1*), and hence the finer the state of subdivision of the beads, the more rapid the ion removal. There is a practical limit, however, to continued subdivision in that as the particle sizes approach the colloidal range, suspensions are formed. Such particles can no longer be used in columns because the fines are washed out while the larger particles, which are still relatively small, settle and then necessitate the use of high pressures to force the liquid past them. Such suspensions, however, are admirably suited for the rapid removal of ions from large volumes because besides being able to adsorb ions rapidly, they can be dispersed throughout the bulk in a short time with efficient stirring. The advantage in time, however, is dissipated unless a comparably rapid method can be found for subsequently removing the suspension. As filtration of large volumes is too slow, another means was sought for removing the dispersed resins.

Hydrophobic colloids are stabilized by the charges that exist on the surfaces of their particles. It is well known that one hydrophobic colloid can be coagulated by the addition of another of opposite charge since the repulsions between particles of one species are reduced by intervention of oppositely-charged particles of the other. As the resin particles used were not greatly in excess of colloidal dimensions, it was decided to attempt the coagulation of an anion exchange resin (positively-charged) with solids that were negatively-charged. It was found that glass, silica, carbon, and kaolin were suitable. Of markedly greater efficiency were montmorillonite or a cation exchange resin, and the addition of an optimum amount of these led to rapid and complete removal of the suspended particles. The purpose of the present investigation, then, is to examine the above phenomena more closely, both from the standpoint of mutual coagulation of suspensions as well as the rapid removal of ions from aqueous systems.

EXPERIMENTAL

Materials

The anion exchange resins used were Amberlite IRA 400, IRA 401 (both Mallinckrodt Chemical Company) and IRA 904 (Rohm and Haas), all of the $RN(CH_3)_3^+Cl^-$ form. They differ in nominal divinylbenzene (DVB) content being 8, 4, and 16%, respectively. Amberlite IRA 400 and IRA 401 are gelular-type resins whereas Amberlite IRA

904 is a macroreticular resin. The gelular-type loses its pore structure on dehydration while the latter does not. It is relevant to the present discussion that macroreticular resins reduce to samples of uniform particle distribution on grinding because their beads are made up of a number of much smaller beads of uniform size and the grinding process merely breaks down the larger particles into their smaller constituents (*2*).

The cation exchange resins used were Amberlite IR 120 (Mallinckrodt Chemical Company), Dowex-50W-X8 (Dow Chemical Company) and AG50W-X16 (BioRad Laboratories) all of the $RSO_3^-H^+$ type and nominally of 8, 8, and 16% DVB content, respectively. An aqueous suspension of Amberlite XE 254 ultrafine resin (Rohm and Haas) of the $RSO_3^-Na^+$ form was also used; the amount of solid material in the suspension was 23% w/w and the average particle size, as declared by the manufacturers, was 1 μ.

The solid resins, as well as soda glass, silica, charcoal, montmorillonite, and kaolin, were ground and separated into fractions using U.S. Standard sieves of 60, 200, and 400 mesh. Examination of the —400 mesh fraction under a microscope showed the resin samples to be made up of an appreciable range of particle sizes (except IRA 904, which has been discussed), while the other solids were relatively uniform. The montmorillonite, kaolin, and silica were finely divided in relation to the resins, while the charcoal and glass particles were, relatively, of medium and large sizes, respectively. The montmorillonite (coaguloid) was supplied by the Baroid Division, National Lead Company, Texas; the soda glass was obtained by crushing clean watch glasses; and the silica, charcoal, and kaolin were from reliable laboratory stocks.

Procedure

The experimental procedure for the study of the coagulation of suspensions involved the dispersion of a weighed amount of resin in a 1-liter measuring cylinder containing 1 liter of water, using a magnetic stirrer. A known mass of coagulant was wetted with a small amount of water, introduced into the cylinder, and stirred for 5 min; thereafter 5 ml samples were withdrawn at known time intervals from approximately 5 cm below the surface of the solution. The extent of coagulation was estimated in terms of the turbidity of these samples. As a measure of turbidity, the optical densities of the samples were determined in 1 cm cells in a Beckman DU 2 spectrophotometer at an arbitrary wavelength of 500 nm.

Analysis

The phosphorus contents of the solutions were determined colorimetrically using ammonium molybdate (*3*). To 5.00 ml of sample were added 2 ml of 2.5 *M* sulfuric acid, 2 ml of 2.5% ammonium molybdate, and 1 ml of reducing solution (made by dissolving 0.5 g of 1-amino-2-naphthol-4-sulfonic acid in 185 ml of 15% sodium bisulfite and 5% sodium sulfite). The solution was then made up to 25.00 ml with water, allowed to stand for 10 min, and examined spectrophotometrically in 1 cm cells at a wavelength of 660 nm.

The calcium contents of the solutions were determined (*4*) colorimetrically using ammonium purpurate (murexide). A solution of this dye was made by dissolving 40 mg of ammonium purpurate in 75 ml of water and making up to 250 ml. A volume of 10.00 ml of unknown solution was diluted to 80 ml, the pH adjusted to 11.3 with 0.4% sodium hydroxide solution, 10.00 ml of murexide solution added, and the whole made up to 100 ml in a standard flask. The optical density was then determined without delay in 1 cm cells at 506 nm against a blank sample formed from the same reagents.

The zeta-potentials of the particles in a sample were determined by measuring their electrophoretic mobility using a zeta-meter (Zeta-Meter Inc.).

RESULTS AND DISCUSSION

Coagulation

The manner in which suspended particles of one charge could be coagulated by others of opposite charge was examined first. Figure 1, in which the optical density of the solution is plotted against time, illustrates the mutual coagulation of IRA 401 resin and glass (both —400 mesh). Curve A shows the decrease in turbidity as the resin particles settled out in the absence of glass, a slow process which even after 24 hr could not reduce the optical densities to values below 0.38. The addition of finely-divided glass, as shown by Curves B and C, caused a lowering of the repulsions of the positively-charged resin particles by intervention of the glass particles between them. In this way coagulation was enhanced and the optical densities decreased.

It became clear early in the investigation that the state of sub-

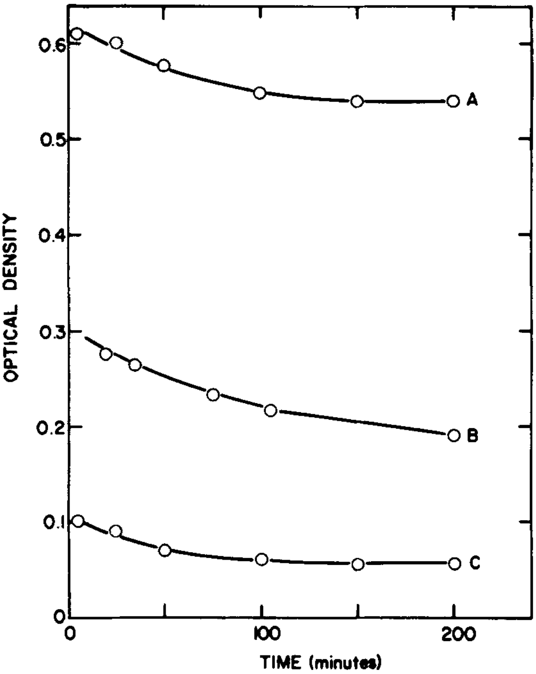

FIG. 1. Coagulation of 0.50 g liter^{-1} of Amberlite IRA 401 resin using glass (both solids —400 mesh): A, nil; B, 3.0 g; C, 6.0 g glass.

division of the coagulant was of importance. In Fig. 2, Curve D shows the rate of settling of 0.50 g of IRA 401 resin (—400 mesh) alone with time, while Curves A, B, and C reflect the coagulating ability of samples of glass of the same mass but of different particle size. The best coagulation was achieved among the measurements made when the particles of glass were smallest, but it is not known how effective glass of a finer state of subdivision would have been because a sieve of smaller mesh was not available.

As explained in the Introduction, it was found that the most efficient coagulations occurred when one suspension of a resin was added to another. The spectacular way in which this happened is shown in Fig. 3. The curve between Points A and B reflects the gradual settling of 0.50 g of IR 120 (—400 mesh). At B, 0.50 g of IRA 401 (—400 mesh) was added and the mixture stirred vigorously for 30 sec. Within a minute, both solids had settled out almost completely.

It was found that when one suspension of resin was added to another of opposite charge there was an optimum ratio of masses of the two

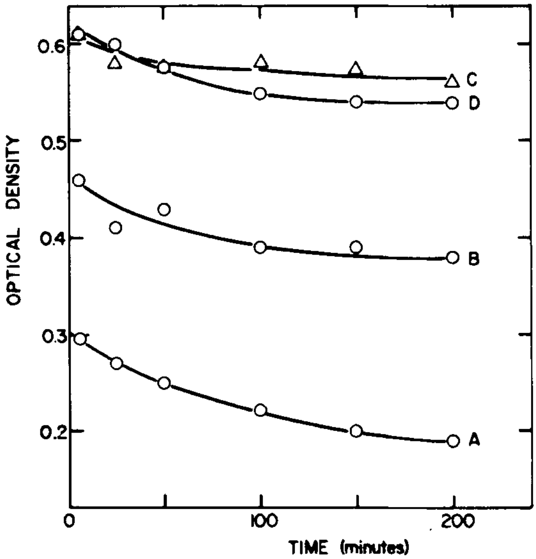

FIG. 2. Coagulation of 0.50 g liter^{-1} Amberlite IRA 401 (—400 mesh) with 3.0 g of glass of various mesh sizes: A, —400; B, —200/400; C, —60/200; D, no glass.

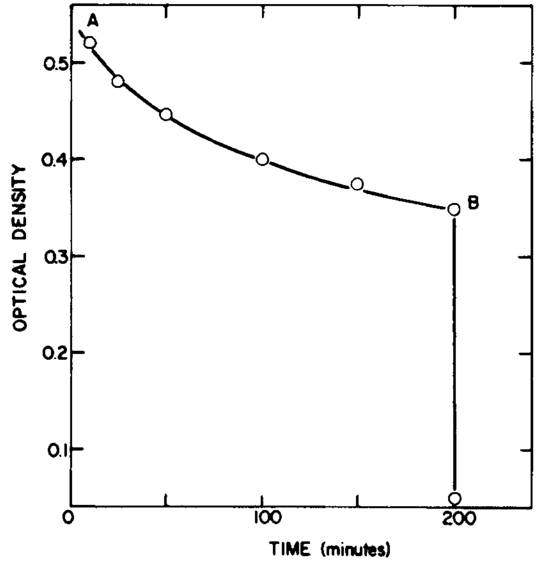

FIG. 3. The effect of mixing resins with opposite charges. A to B: 0.50 g Amberlite IR 120 (—400 mesh) alone. At B, 0.50 g Amberlite IRA 401 (—400 mesh) added.

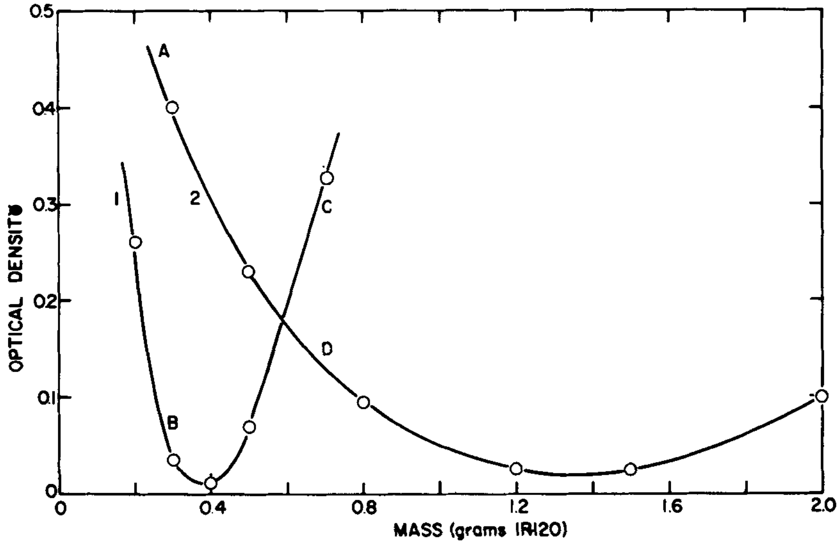

FIG. 4. Coagulation of 0.50 g Amberlite IRA 401 (—400 mesh) with Amberlite IR 120 of two different mesh ranges: Curve 1, —400 mesh; Curve 2, —200/400 mesh.

resins for best coagulation. If too little of the added resin was present, the solution was turbid due to incomplete coagulation. If more of the second resin was added than was required for complete coagulation, the turbidity increased. A minimum in the relationship between turbidity and mass of added resin, as found in Fig. 4, was therefore to be expected. From Curve 1 of this figure, for example, it is clear that the addition of about 0.4 g of IR 120 (—400 mesh) is the most satisfactory for removal of 0.50 g of IRA 401. With less than this amount, coagulation was incomplete, as shown by the positive zeta-potentials of the suspended particles, whereas an excess resulted in turbid suspensions of IR 120, the particles having negative zeta-potentials. In this experiment the oppositely-charged suspensions were mixed by stirring together for 5 min and were allowed to settle for 2 min before the turbidities were recorded. (The coagulated material settled within the 2 min period and a sharp decrease in turbidity was found; it was this value that was recorded, as it reflected the extent of coagulation. Thereafter the usual slow decrease in turbidity occurred, comparable to that shown in Fig. 1, Curve A; no cognizance was taken of this decrease as it was merely a measure of the settling out with time of the uncoagulated resin.)

The importance of particle size of the coagulant is emphasized by Fig. 4, Curve 2, for which the IR 120 resin was in the —200/400 mesh range. Four times as much of this coarser fraction was required for the same extent of coagulation within the 2-min period as for the —400 mesh particles. A more finely-divided sample of IR 120 was not available but a comparison can be made with XE 254 ultrafine resin when used as coagulant. The latter is similar to IR 120 in that both are of the RSO_3^- type although they differ in being of the Na^+ and H^+ forms, respectively. The optimum amount of XE 254 required to coagulate 0.50 g of IRA 401 was 0.20 g as opposed to 0.40 g for IR 120, and the resulting solutions were completely clear. The finer state of subdivision is probably responsible for these results.

The information embodied in Fig. 4 for a resin coagulant can be used to anticipate the probable effect on turbidity of adding greater quantities of glass as coagulant than were used in Figs. 1 and 2. Had the variation of turbidity with time been plotted in Fig. 1 for larger masses of glass, for example, the curves would most likely have been above that for the 6.0 g because, with all the resin coagulated, the increased turbidity would have arisen from excess glass. Turning to Fig. 2, it is shown that, for a fixed mass of coagulant, a decrease in particle size led to lower turbidities, but a study of Fig. 4 indicates that this will only necessarily be true if the fixed mass of coagulant is less than the optimum amount for maximum coagulation for any of the particle size fractions used. For example, in Fig. 4 the turbidity at A for the coarse fraction is greater than that at B for the fine fraction because the mass of resin used was below the optimum amounts of both fractions needed for maximum coagulation. If, however, the fixed amount of resin used had been between the two optimum values, it is possible that a more turbid solution would have resulted with the fine resin (Point C) than with the coarse one (Point D). As the quantity of glass used for Fig. 2 was 3.0 g, which is below the optimum coagulating mass for each of the three fractions considered, the turbidities necessarily decreased with increasing state of subdivision. Figure 4, however, may be used to anticipate that this need not always be the case when masses of glass other than 3.0 g are added to 0.50 g of Amberlite IRA 401.

The importance of particle size on coagulation was again evident when using IRA 400 resin. Two (—400 mesh) samples which had been differently ground showed markedly different particle sizes and size distributions when examined under a microscope. In consequence the masses of IRA 120 resin (—400 mesh) required to coagulate 0.50 g of each sample were about 0.2 and 0.4 g, respectively. Further, 0.50 g of IRA 904 resin required 1.0 g of IR 120 (both —400 mesh) for complete removal. This appreciably greater quantity of IR 120 was due to the finely-divided nature of the macroreticular resin. It is in keeping with the conclusion, which appears to be true as a first approximation, that in the complete coagulation of two oppositely-charged resins, less is required of the one that is more finely divided.

Finally, it is worth noting two results that are to be expected from the experiments described above. Addition of one resin to a suspension of another of the same charge led to increased turbidity in the solution and no coagulation. Second, the ratio of the masses of oppositely-charged resins required for coagulation remained the same irrespective of which was suspended and which was used as coagulant. Reversal of the roles, therefore, led to no unexpected behavior.

The relative abilities of negatively-charged solids for coagulating 0.50 g of IRA 401 (—400 mesh) are shown in Table 1. The values, based on an arbitrary scale of 400 for the best coagulant, were determined by comparing the mass of each solid required for complete coagulation after stirring together for 5 min and allowing 2 min for settling. Some variation in the relative coagulating power is to be expected, depending on how finely the solids have been ground. Thus, although all were —400 mesh, continued grinding would lead to smaller average particle sizes and enhanced coagulating power, as was shown for IRA 400 resin. How much influence efficiency of grinding will have

TABLE 1

Coagulating Power of Some Negatively-Charged Solids

Coagulant	Relative coagulating power	Exchange capacity (meq./100 g)	Density (g cm^{-3})	Negative zeta-potential (mV)
Amberlite XE 254	400	500	1.4	26.1 ± 3.0
Amberlite IR 120	200	500	1.4	44.2 ± 1.2
Dowex 50W	200	500	1.4	34.1 ± 3.3
AG50W-X16	200	490	1.4	28.8 ± 3.4
Montmorillonite	200	40–45	2.8	30.6 ± 1.5
Kaolin	30	10–12	2.6	28.1 ± 0.5
Charcoal	10	—	1.3	18.8 ± 4.8
Silica	10	—	2.4	21.4 ± 1.6
Glass	5	—	2.5	36.0 ± 2.4

on coagulating power will depend on the hardness of the solid, but it is not anticipated that the relative coagulating power would change by more than a factor of 2. The exchange capacities, densities, and zeta-potentials of the solids have been included for comparison. The same sample of IRA 401 was used for all the coagulants.

It is clear from Table 1 that the wide variation in the efficiencies of the coagulants is not matched by similar changes in zeta-potential, exchange capacity, or density. Coagulant particles must have charged surfaces and appreciable zeta-potentials; however, in Table 1 the best coagulants do not necessarily have the highest potentials. It is clear that, in general, there must be a relationship between zeta-potential and the extent of coagulation, but in the system under investigation other factors must also play important roles. As also seen in Table 1, exchange capacity is not related to coagulation. Exchange capacity, of course, is dependent not only on surface charges, but also on charges existing within a particle. Since it is surface charges which keep particles from coagulating, it is not surprising that exchange capacity bears no relationship to coagulation. Note that of the solids listed in Table 1, exchange occurs entirely on the surface for glass, silica, and kaolin; for charcoal and montmorillonite exchange occurs both on and in the solid; whereas for the resins it occurs overwhelmingly in the pores.

It might have been expected that the densities in Table 1 would be significant in that substances with values close to that of the resin would tend to settle at the same slow rate and thus remain in intimate contact with resin particles more readily. The chances of coagulation would then be greater. The particles, however, are small and the electrical effects of their surface charges are of much greater consequence than those caused by gravity.

A clearly dominant factor in coagulating ability is that of particle size, the one bearing an inverse relationship to the other. This result is not surprising as the greater the number of particles for a given mass of coagulating material, the more efficiently they can be packed around a suspended particle, thus reducing its zeta-potential and rendering it more susceptible to coagulation. This cannot, however, be the only effect, as a great difference exists in the coagulating power of montmorillonite and kaolin, although their particle sizes were approximately the same. Further, the silica sample used was more finely divided than those of the resins, although its coagulating power was insignificant in comparison. Had some solids been less easily wetted than others, agglomeration to larger particles may have occurred before coagulation was possible; the increase in particle size of the coagulant would then ostensibly have led to lower efficiencies. The poor coagulants in Table 1, however, are all easily wetted provided their surfaces have not been contaminated. To examine the possibility of such contamination for the case of glass, the powdered sample which had been used was washed repeatedly with ethanol and then tested once again. No change in its coagulating ability was found.

It is tentatively suggested that coagulating power is related to the ability of the solid particles to swell and hence to have sufficient deformability for efficient packing. Totally rigid particles of glass, silica, charcoal, and kaolin may pack around a particle of opposite charge but will do so in a way not conducive to the addition of further layers of alternately charged particles. Strains will develop in these agglomerates which will prevent their growth, thereby reducing the efficiency of the process. This explanation would account for the marked difference in efficiency between montmorillonite which swells and kaolin which does not. It would also account for the marked efficacy of resins. It is clear that more work will be necessary before a complete understanding of the factors involved in the mutual coagulation of two solids can be attained.

Ion Removal

Because of the rapidity with which finely-divided resins adsorb ions and are coagulated, the overall process of ion removal and subsequent resin coagulation was investigated. First it was shown that 2.5 g of underground —20/50 mesh IRA 401 resin required 50 min to adsorb 96% of the phosphorus from 1 liter of a 3×10^{-4} *M* solution of sodium phosphate. (This was done by stirring the resin for the requisite time, allowing it to settle for 2 min, and then withdrawing a 5-ml sample of liquid in the usual way. It was unnecessary to add oppositely-charged resin in this case since the particles settle rapidly on their own and no coagulation is needed.) It was then required to compare this rate of removal to that achieved by a finely-ground resin. In this context, it was necessary to recognize that the resin dried during grinding because the water adsorbed in the pores was released. An adjustment therefore had to be made for this loss of water so that the total exchange capacities of the two samples would be the same. As the unground resin contained 60% of water, 1.0 g of —400 mesh IRA 401 should have the same exchange capacity as 2.5 g of unground resin.

A mass of 1.0 g of —400 mesh resin was stirred with 1 liter of a 3×10^{-4} *M* solution of sodium phosphate and then coagulated by adding an optimum amount of XE 254 ultrafine resin and stirring for 5 min. By performing this experiment a number of times, and on each occasion decreasing the period for which the resin was stirred with the solution prior to coagulation, it was shown that the finely-ground resin required only 0.5 min for 96% removal of phosphate, a rate which was 100 times faster than when using unground resin. If allowance is made for the 5 min required for coagulation of the fine resin, the overall process is about 10 times faster than when using unground resin.

An even more rapid removal can be achieved by the use of a coagulated cationic-anionic mixed resin. This mixture was prepared by coagulating 1.0 g of IRA 401 (—400 mesh) with 0.40 g XE 254 ultrafine resin in pure water. The resulting resins, although coagulated, retain a fine state of subdivision and the concomitant ability to adsorb ions rapidly. The mixed resin was added to 1 liter of the phosphate solution, stirred for 1.5 min, and a sample taken 0.5 min later. As shown in Fig. 5, Curve A, removal of 96% of the phosphate was achieved; recoveries were not as good if the period of stirring was less than 1.5 min. (The sample taken above was withdrawn before the resin had settled completely, which usually took 2 min. This was done because after 0.5 min a sufficient volume at the top of the solution was completely clear of resin.) The optical densities of such samples and of the final solutions were all zero. Curve C in Fig. 5 is for 2.5 g of unground IRA 401 resin as described previously, while Curve B is for 2.0 g of (—40/60 mesh) IRA 401 resin. This latter fraction is the finest to which the resin can be ground and yet retain the ability to settle out rapidly and completely when stirring is discontinued. The mass of 2.0 g used was once again an attempt to maintain comparable exchange capacities, heed being taken of the moisture content of the samples.

Care should be exercised in the choice of the coagulating resin in that if it is in the hydrogen form, exchange with the Na^+ ions in solution leads to a decrease in pH with subsequent hydrolysis of the PO_4^{-3} ion to uncharged H_3PO_4 molecules which are not adsorbed. When, for example, IR 120 resin in the acid form was used as coagulant, recovery of phosphorous was only 50% and the pH of the final solution was 3.4. Using XE 254 resin, however, which is in the sodium form, resulted in 96% removal and a final pH value of 7.3.

If the same quantity of the finely-divided mixed resin described

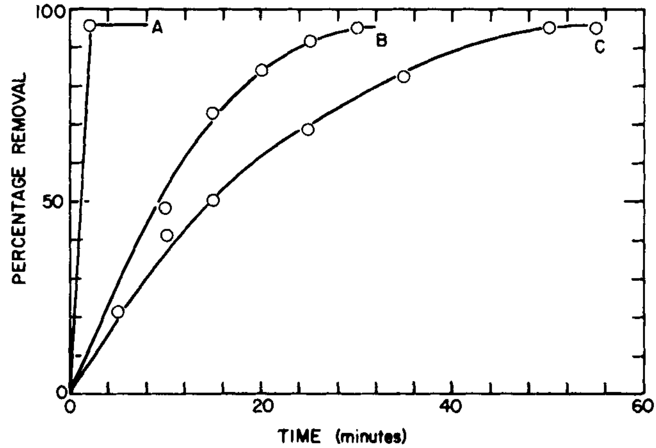

FIG. 5. Removal of HPO_4^{2-} ions by various resins: A, 1.0 g of a coagulated cationic-anionic mixed resin; B, 2.0 g of IRA 401 (—40/60 mesh size); C, 2.5 g of unground IRA 401 (—20/50 mesh size).

above was stirred with 1 liter of a $2.5 \times 10^{-4} M$ calcium chloride solution, over 90% of the calcium present was adsorbed within 3 min.

The rapidity with which ions can be removed by adsorption in finely-divided resins, followed by coagulation of the latter, is so striking that further investigations are to be made. Use of mixed resins in fluidized beds, together with methods for their regeneration, are being considered. With suitable modifications it may be found possible to use mixed, finely-divided resin beds in the processes where coarse resins are currently utilized. Among such processes are the removal of pollutants from municipal and industrial wastes, the concentration of solutions in industrial plants, and the decontamination of waters containing radioactive ions. One aspect in which finely-divided resins may ultimately be superior is the greater use of available exchange capacity. Because of the relative slowness of adsorption of ions by coarse beads, resin beds in current use seldom approach the complete use of their exchange capacity. This potential advantage of fine resins is currently under investigation.

Acknowledgments

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