Removal of Colloidal Pollutants by Microflotation

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The removal of various colloids (humic acid, silica, polystyrene latex, and bacteria) by microflotation in the presence of aluminum salts has been studied as a function of *p*H. The conditions for efficient separation have been correlated to the stability of these colloids, and it was shown that in all cases rapid flotation occurred when the aluminum salt concentration and the *p*H adjustment rendered the sols unstable. Particularly high removals were observed over the *p*H range of aluminum hydroxide floc formation. Microflotation could be utilized as a nonspecific method for simultaneous removal of mixtures of colloidal pollutants.

Colloids which are found in natural and waste waters ordinarily consist of a heterogeneous variety of particulate matter and can create numerous and rather diverse pollution problems. The purpose of this work is to show that microflotation can be used for efficient separation of a variety of suspended colloidal particles and to relate the colloid stability to floatability.

Flotation has been widely used as a separation process in mineral beneficiation. The major advantage of the process is in its selectivity to various particulate components in a mixture. The purification of natural and waste waters often requires simultaneous removal of many colloidal pollutants, regardless of type. Consequently, mineral flotation technology has found only limited application in water and waste treatment. In those cases in which flotation is employed, it is not common to utilize collectors and/or frothers. A recent study (*1*) describes the state of the art of flotation as applied to municipal waste water treatment. Van Vuuren et al. (*2*) have applied flotation, on a pilot scale, to tertiary waste water treatment.

Few studies have been reported on flotation of colloids. These have been reviewed recently by DeVivo and Karger (*3*). Among these studies, Grieves and co-workers have specifically employed foam separation in the removal of colloidal particulates from natural waters (*4*, *5*). In most of these studies negatively charged colloids, cationic surface-active agents (collectors), and large bubbles were used. It was found that the separation was specific and more efficient with finely dispersed rather than coagulated sols. Also, the presence of electrolytes, and particularly of hydrolyzable polyvalent cationics, adversely affected the floatability of the colloids (*3*).

Several studies have shown that various species of bacteria (*6* to *8*), colloidal silica (*9*), and humic acid (*10*) can be successfully removed from aqueous dispersions by microflotation. The following conditions are essential for an efficient separation by this process: (1) the dispersion to be floated must be rendered unstable (coagulated) by additions of small amounts of hydrolyzing electrolytes and by proper *p*H adjustment; (2) a suitable collector-frother solution must be added to induce bubble attachment, to control the bubble size, and to produce a foam of desirable characteristics; and (3) the bubbles must be small (40 to 60 μ in diameter).

In this paper the use of microflotation to remove a number of colloidally dispersed particles from aqueous suspensions will be demonstrated. Also, the stability domains of the colloidal sols will be given as a function of *p*H and of the aluminum salt concentrations and the regions of these domains defining the conditions for the most efficient separations will be delineated.

The advantages of the microflotation process for colloid separation will be enumerated in the discussion.

EXPERIMENT

Materials

The humic acid used in this work was obtained from Professor Heinrich Thiele, who extracted it from peat according to a method described earlier (*11*). Stock solutions containing 2,000 mg./liter of humic acid were prepared by adding 0.500 g. of dry humic acid to 225 ml. of 0.01 *N* NaOH. This mixture was stirred for two days and then diluted to 250 ml. with distilled water and stored at 4°C. All microflotation and stability experiments were conducted at a humic acid concentration of 50 mg./liter which was obtained by further dilution of the stock solution with distilled water. Humic acid concentrations were determined spectrophotometrically at 550 mμ at which wavelength Beer's law is obeyed for concentrations < 100 mg./liter if the *p*H was maintained at 11.5.

The colloidal silica, Ludox AM (technical grade), obtained from E. I. du Pont de Nemours and Company, was composed of particles averaging 15 mμ in diameter with a density of 2.2 g./cu. cm. A detailed description of this silica is given elsewhere (*12*). The original suspensions were diluted with distilled water to give an intermediate stock solution containing 8.0 g. silica/100 ml. This was further diluted to 0.2 g./100 ml., at which concentration all stability and microflotation experiments were conducted. The concentrations of silica were measured by the colorimetric molybdosilicate method (*13*) modified to eliminate an interference due to the presence of aluminum ions (*9*).

The polystyrene latex (PSL) containing spheres with diameter of 1.09 ± 0.006 μ was obtained from the Dow Chemical Company. The suspension as received from the manufacturer was analyzed for solids content, and a stock solution containing 0.76% solids by weight was prepared by dilution with distilled water and stored at 4°C. This was further diluted to 0.00196% solids, at which concentration all microflotation and coagulation

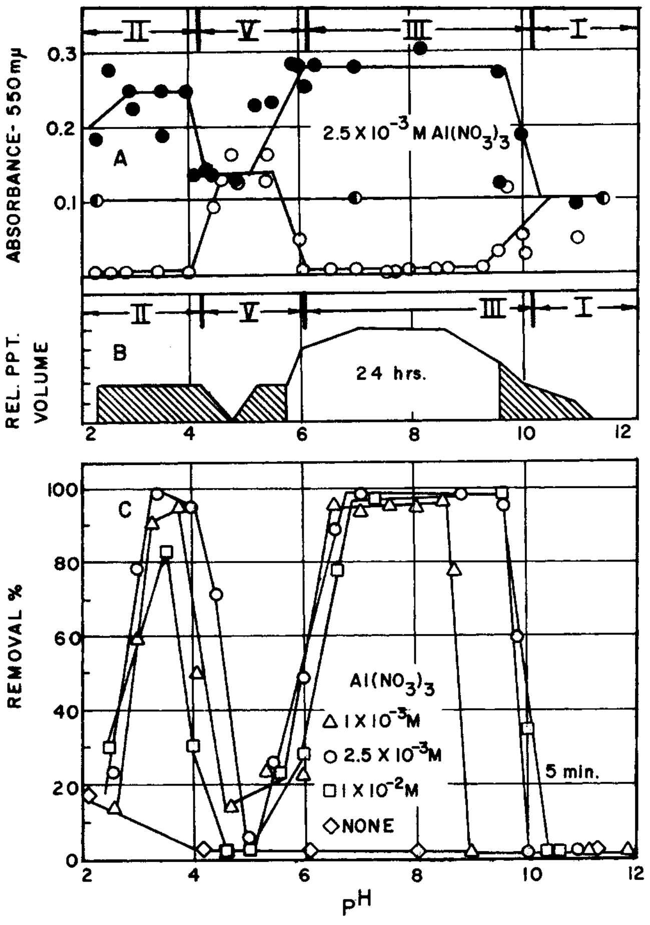

Fig. 1. *A*: Stability of a humic acid sol in the presence of aluminum nitrate as a function of *p*H. Humic acid sol 50 mg./liter, Al(NO$_3$)$_3$ $2.5 \times 10^{-3}M$. Solid and open circles represent the absorbances of the stirred and undisturbed systems, respectively, 24 hr. after mixing the reacting components. Half-filled circles are for the humic acid sol in the absence of Al(NO$_3$)$_3$. This sol did not contain the collector/frother solution.

B: Relative volumes of the precipitate accumulated after 24 hr. of settling for the same run as in part *A*. Hatching denotes compact dark brown and open areas voluminous light brown precipitates.

C: Percent removal of humic acid after 5 min. by microflotation as a function of *p*H at three different Al(NO$_3$)$_3$ concentrations: $1.0 \times 10^{-3}M$ (△), $2.5 \times 10^{-3}M$ (○), $1.0 \times 10^{-2}M$ (□), Humic acid 50 mg./liter, lauric acid $1.25 \times 10^{-4}M$, ethyl alcohol 2.5 ml./liter. Diamonds give the results in the absence of Al(NO$_3$)$_3$.

experiments were conducted. A linear relationship existed between the turbidities measured by the Hach 1830 turbidimeter and the percentage solids by weight at concentrations as high as 0.0030% solids. All turbidimetric measurements of PSL were made on samples whose *p*H was adjusted to ~ 12.

The mixed bacterial culture used in this work was grown in a continuous culturing vessel of the type described elsewhere (*14*). The inoculum was obtained from raw domestic sewage, and the growth medium consisted of a solution of 0.14% dry skim milk solids fed at a rate to maintain a 10-hr. retention period in the culture vessel. The culture was kept in an aerobic state at all times at 20°C. Bacterial densities (numbers per milliliter) were determined by the direct microscopic counting technique in which methylene blue was used as a dye (*15*). Direct microscopic counts were correlated to percentage transmittance (at 400 mμ) so that estimates of bacterial numbers during the experiments could be made spectrophotometrically.

Other chemicals used were of the highest purity grade commercially available. Aluminum salts were Baker analyzed reagents, and the concentrations of their stock solutions were determined by suitable gravimetric procedures. The aluminum concentration during microflotation experiments was determined by means of chrome azurol S (*16*).

Methods

Microflotation. All microflotation experiments were conducted in a laboratory system described in detail elsewhere (*6*, *7*). The flotation cell, designed for batch experiments, was a 600-ml. glass Büchner funnel (100 mm. diam. and 88 mm. deep) having a fine sintered glass frit through which the nitrogen gas was introduced. The dispersion to be floated (humic acid, colloidal silica, PSL, or mixed bacteria) was placed in the flotation cell and a high rate of gas flow was started to provide mixing. The reagents were then added in the following order: aluminum nitrate or aluminum sulfate, and base (NaOH) or acid (HNO$_3$ or HClO$_4$) as required for *p*H adjustment. The total final volume was always 400 ml. After 10 min. of mixing the gas flow rate was set at 30 cu.cm./min. and the collector solution added. The latter consisted of lauric acid dissolved in the frother (ethanol). In the flotation cell the concentration of the collector was 25 mg./liter and of the frother 2.5 ml./liter. The moment at which the collector solution was added was designated as time zero. Samples were withdrawn from the liquid portion of the cell contents immediately before time zero and at preset time intervals afterward. These samples were analyzed for the concentration of the dispersed material in accordance with techniques described above. All measurements of *p*H were made using carefully standardized glass electrodes.

Stability Domains. The stability domain for humic acid was established by observing the physical and optical characteristics of a series of humic acid dispersions as a function of *p*H and Al(NO$_3$)$_3$ concentration. This domain (Figure 2, to be described later) defines the initial electrolyte concentration and the equilibrium *p*H necessary to produce coagulated sols, stable sols, and sols restabilized due to charge reversal. A desired amount of aluminum nitrate was added to 200 ml. of the aqueous humic acid sample, the *p*H adjusted, and the resulting solution shaken for 10 min. Two 50-ml. portions were removed, placed in 80-ml. test tubes, and allowed to settle for 24 hr. The systems were observed visually and information was recorded concerning the relative volume and color of the floc and the resulting sludge. The absorbance of the supernatant solution of one settled sample was determined. The second sample was shaken immediately prior to measuring absorbance. An example of a run is shown in Figure 1, *A* and *B*, discussed in detail in the next section.

The stability domain for the colloidal silica was established in a similar manner as that used for the humic acid. A detailed description of this method is given elsewhere (*17*).

RESULTS

Humic Acid

Figure 1*A* gives an example of the absorbance of a system containing 50 mg./liter humic acid as a function of *p*H in the presence of $2.5 \times 10^{-3}M$ Al(NO$_3$)$_3$. Several *p*H regions, marked by Roman numerals, indicate sols of various degrees of stability. Half-solid circles designate the humic acid dispersions in the absence of aluminum nitrate. The absorbances of the settled and stirred systems are given by the open and solid circles, respectively. Figure 1*B* shows the relative volumes of precipitates which accumulated on the bottom of the test tube after 24 hr. of settling. Hatching denotes compact dark-brown solids, whereas a light-brown precipitate is produced over the open area. Higher absorbances in the stirred samples than in samples containing only humic acid indicate aggregated sols. In region I no aggregation takes place. Systems in regions II and III are unstable and settle and the flocs formed in region V remain suspended.

In region II soluble aluminum species coagulate the humic acid, which upon settling gives compact dark-brown sediment. In region III aluminum hydroxide particles interact with humic acid to produce relatively large volumes of light-brown precipitate. Previous work (*18*) suggests that the stability of humic acid in region V is likely due to charge reversal caused by highly positively charged hydrolyzed aluminum species.

Experiments similar to those shown in Figures 1*A* and 1*B* were systematically carried out in the presence of various concentrations of aluminum nitrate. This enabled the establishment of a complete stability domain as given in Figure 2 for systems containing 50 mg./liter humic acid, 24 hr. after the reacting components were mixed. The solid lines delineate various stability regions which are described below. The dotted lines are the precipitation boundaries of aluminum hydroxide in the absence of humic acid. The dotted line at low *p*H was determined experimentally (*19*), whereas the dotted line at high *p*H was calculated from the complex constant for aluminate ions (*20*).

Within region I the humic acid sol remained stable. At lower *p*H values in this region, the concentration of cationic aluminum species is too small to cause coagulation, whereas at high *p*H values aluminate ions are formed which cannot coagulate the negatively charged humic acid. The boundary between regions I and II has not been precisely determined, but is located at $Al(NO_3)_3$ concentration $\sim 1 \times 10^{-4}M$. In regions II, III, and IV the humic acid sols are unstable. As mentioned above, the instability in region II is due to coagulation by soluble aluminum species; in regions III and IV it is caused by precipitation of aluminum hydroxide which in turn interacts with humic acid. The only observable difference between the last two regions is in the type of settling: in IV discrete particles settle and in III zone settling is observed. Finally region V designates sols of reversed charge.

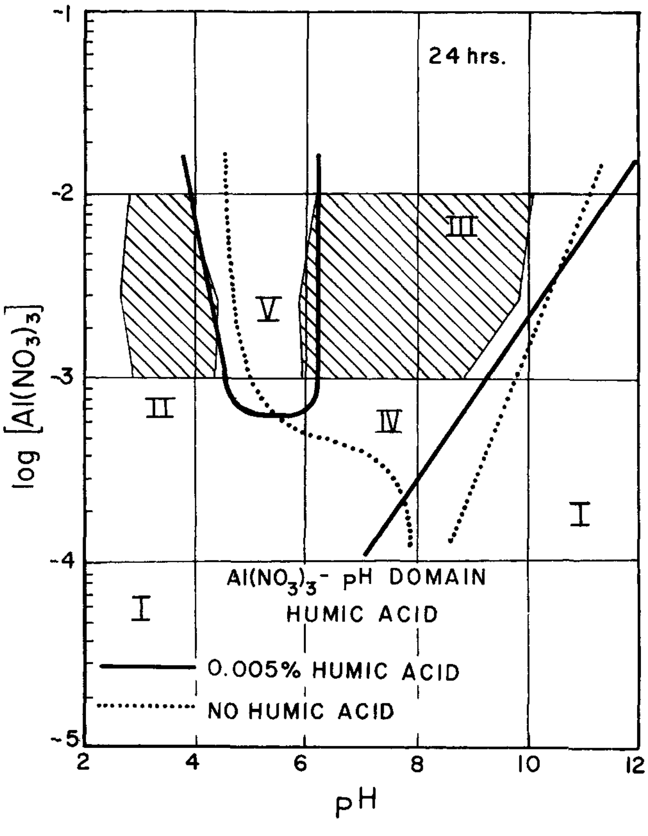

Fig. 2. Aluminum nitrate-pH stability domain for the humic acid sol (50 mg./liter) 24 hr. after mixing the reacting components. Regions: I, stable sol; II, sol coagulated by soluble aluminum species; III and IV, sol coprecipitated with aluminum hydroxide with different settling characteristics; V, sol restabilized due to charge reversal. Dotted lines show the region where the precipitation of aluminum hydroxide occurs in the absence of humic acid. Hatched area represents 50% or greater removal of humic acid after 5 min. of microflotation.

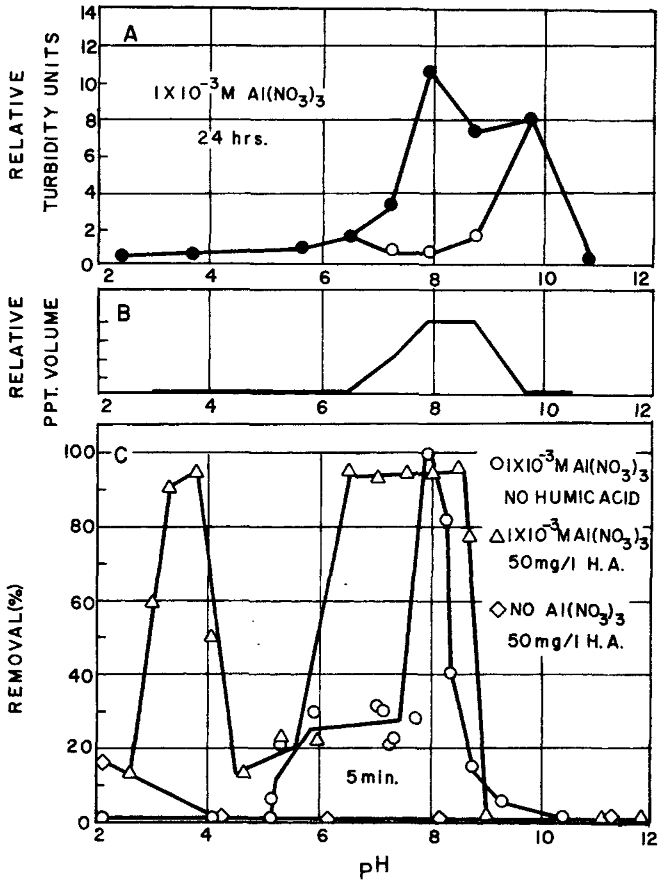

Fig. 3. *A*: Precipitation of aluminum hydroxide. Turbidities of $1.0 \times 10^{-3}M$ solutions of $Al(NO_3)_3$ as a function of pH, 24 hr. after mixing the reacting components. Solid and open circles are for stirred and undisturbed systems, respectively.

B: Relative precipitate volume of the systems described in part *A*.

C: Percent removal aluminum in the absence of humic acid (○), and of humic acid in the presence of $1 \times 10^{-3}M$ $Al(NO_3)_3$ (△) and in the absence of aluminum nitrate (◇) after 5 min. of microflotation. Humic acid 50 mg./liter, lauric acid $1.25 \times 10^{-4}M$, ethyl alcohol 2.5 ml./liter.

Figure 1*C* shows the percentage removal of humic acid by microflotation as a function of *p*H at three different concentrations of aluminum nitrate using the same collector/frother solution in all experiments. Circles designate flotation experiments using systems of identical composition as in Figure 1*A* and 1*B*. Separation of humic acid occurs only when the sol becomes destabilized. This is indicated by the hatched area in Figure 2, defining the conditions under which it is possible to remove at least 50% of the humic acid within 5 min. of microflotation. No systematic experiments were conducted at $Al(NO_3)_3$ concentrations $< 10^{-3}M$, but several runs carried out at $10^{-4}M$ $Al(NO_3)_3$ showed no separation.

Additional flotation experiments were performed with systems containing aluminum nitrate and the same collector/frother solution at various *p*H values but with no humic acid present. Figure 3*A* gives the turbidities when *p*H is varied in $1 \times 10^{-3}M$ $Al(NO_3)_3$ solutions. High turbidities of stirred systems (solid circles) indicate aluminum hydroxide precipitation. The *p*H range over which this precipitation occurs is in good agreement with the dotted boundaries in Figure 2. The open circles in Figure 3A show the turbidities after 24 hr., during which time the systems remained undisturbed. Between *p*H 7 and 9 the precipitate settles out, whereas over the *p*H ranges 5 to 7 and 9 to 9.8 a stable sol is formed. Figure 3*B* gives the corresponding precipitate volumes.

Figure 3*C* shows that efficient removal by microflotation of aluminum hydroxide in the absence of other colloidal systems occurs between *p*H 7.2 and 8.7, the *p*H region of unstable aluminum hydroxide. No aluminum removal is observed below *p*H 5 and above *p*H 9.8. Only low removal efficiencies are found in the *p*H ranges which produce stable aluminum hydroxide sols.

At the same aluminum nitrate concentrations ($1 \times 10^{-3}M$) humic acid is separated over a broader *p*H range (*p*H 6 to 9) than aluminum hydroxide alone (triangles in Figure 3*C*). Aluminum hydroxide particles have been shown to be positively charged at *p*H values between 6.0 and 7.5 (*17, 21, 22*). Apparently the interaction of these positively charged alumina flocs with the negatively charged humic acid results in the formation of an unstable sol which can be floated. The second flotation region of humic acid (*p*H 3 to 4) corresponds to unstable sols coagulated by highly charged soluble aluminum species.

Figure 4 shows the behavior of two systems containing $5.0 \times 10^{-4}M$ $Al_2(SO_4)_3$, one in the absence and the other in the presence of 50 mg./liter humic acid. The microflotation curves of aluminum hydroxide and of the humic acid are nearly identical (Figure 4*A*). The turbidity data for aluminum sulfate solution as a function of *p*H in the absence of humic acid are shown in Figure 4*B*. The solid and open circles are the 24-hr. turbidities of stirred and undisturbed samples, respectively. Aluminum hydroxide is formed over the *p*H range 4 to 9.3, which is in good agreement with results reported elsewhere (*23*). Figure 4*C* shows relatively high precipitate volumes over the *p*H range of high turbidity.

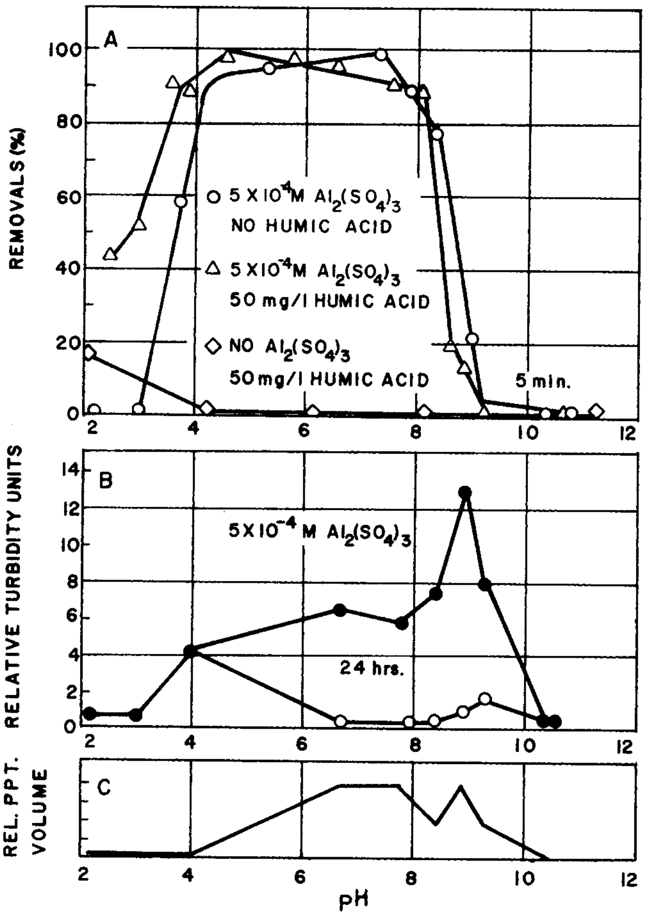

Fig. 4. Plots as in Figure 3 using $5.0 \times 10^{-4}M$ $Al_2(SO_4)_3$ instead of $1.0 \times 10^{-3}M$ $Al(NO_3)_3$. Note that the order of plots is reversed.

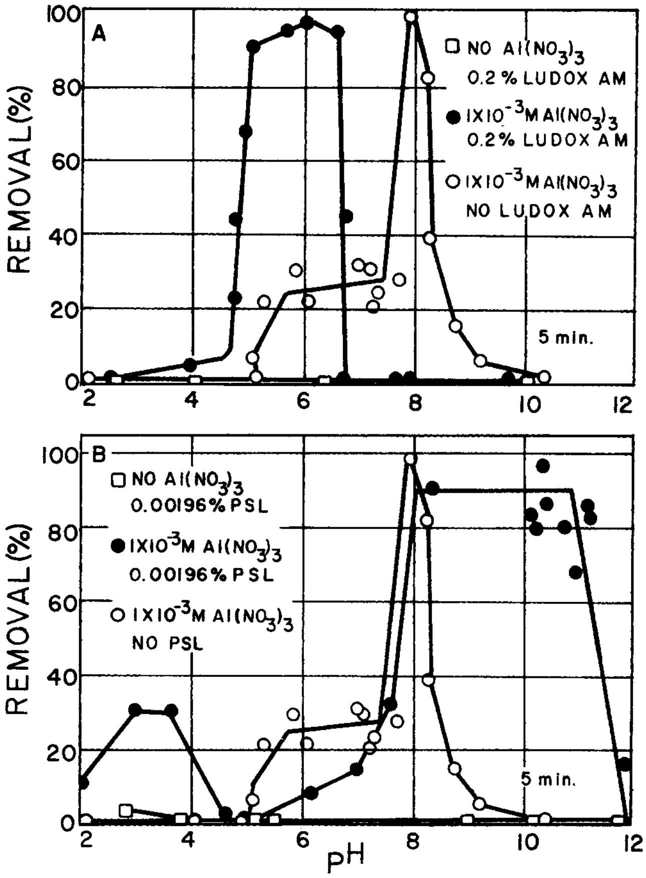

Fig. 5. *A*: Percent removal of aluminum from a $1.0 \times 10^{-3}M$ $Al(NO_3)_3$ solution in the absence of silica (○) and of silica (0.2% Ludox AM) in the presence of $1.0 \times 10^{-3}M$ $Al(NO_3)_3$ (●) and in the absence of aluminum nitrate (□) after 5 min. of microflotation. *B*: The same plot as in *A* with polystyrene latex instead of silica sols.

It is interesting to note that region V in Figure 2 is no longer present when aluminum sulfate is used instead of aluminum nitrate. This is obviously due to the presence of sulfate ions which form complexes with aluminum species in solutions (*24, 25*). These complexes apparently cannot restabilize humic acid by charge reversal. Thus aluminum sulfate promotes floatability of humic acid over a much broader *p*H range than does aluminum nitrate.

Ludox AM

Figure 5*A* is an example of separation of colloidal silica by microflotation as a function of *p*H in the presence of $1 \times 10^{-3}M$ $Al(NO_3)_3$. Superimposed is the removal curve of aluminum hydroxide formed in the absence of silica in a solution containing $1 \times 10^{-3}M$ $Al(NO_3)_3$. The separation of silica and of aluminum hydroxide does not occur over the same *p*H range.

It was possible to relate again efficient flotation of silica to specific regions of the stability domain for Ludox AM in the presence of aluminum nitrate at various *p*H values. This domain is shown in Figure 6. The dotted lines, representing precipitation boundaries of aluminum hydroxide in the absence of Ludox AM, are identical to the boundaries shown in Figure 2. The solid lines delineating various stability regions carry the same designation in Roman numerals as used in Figure 2 and have been discussed in detail earlier (*17*).

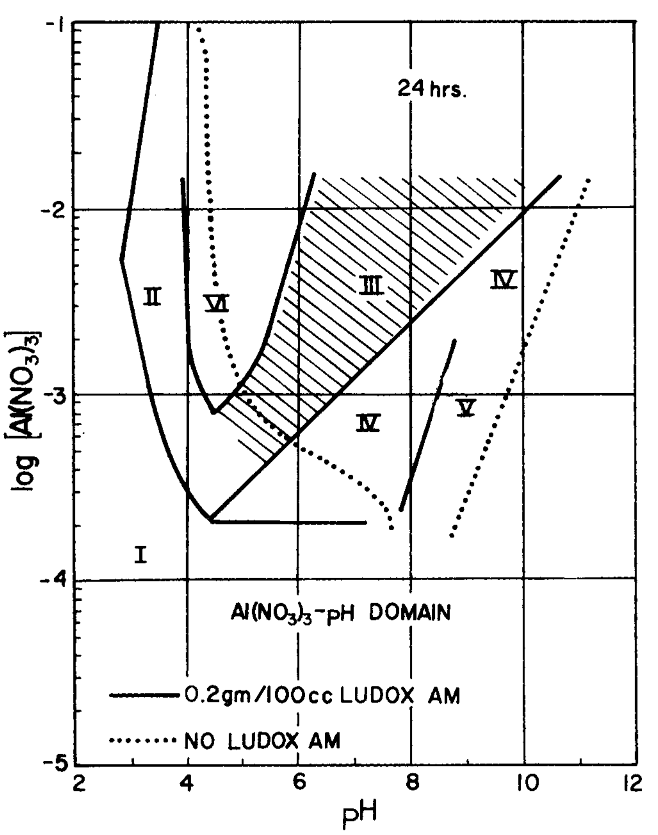

Fig. 6. Aluminum nitrate-pH domain for the Ludox AM sol. The solid lines designate regions of various degrees of sol stability 24 hr. after mixing of the reacting components: I, stable sols; II, sols coagulated by soluble aluminum species; III, coprecipitated silica and aluminum hydroxide; IV and V, silica-aluminum hydroxide precipitates of high negative charge; VI, stable sols of reversed charge. (For details see reference *17*.) Dotted lines show the region where the precipitation of aluminum hydroxide occurs in the absence of silica. Hatched area represents 50% or greater removal of silica after 5 min. of microflotation.

In region I the silica sol remains stable and the particles are negatively charged. The sol is coagulated by soluble aluminum species in region II. In region III rather large floc particles are formed which settle rapidly; the silica sols are partially coagulated in regions IV and V but the flocs are strongly negatively charged and exhibit relatively high stability. The silica sol is stable but positively charged in region VI. This recharging seems to be due to the adsorption of positively charged colloidal aluminum hydroxide particles on silica (*17*). The shaded area in Figure 6 delineates the conditions under which at least 50% of Ludox AM is removed within 5 min. by microflotation. This is almost entirely located within region III where the precipitated aluminum hydroxide interacts with the silica particles to produce an unstable system.

Polystyrene Latex (PSL)

Figure 5*B* is a plot of percent removal of PSL by microflotation as a function of *p*H in the presence of $1 \times 10^{-3}M$ $Al(NO_3)_3$. Removals as high as 90% are accomplished at *p*H values between 8 and 11. Over the same *p*H range the PSL sols are destabilized by the addition of aluminum nitrate. Some removal also takes place over the *p*H ranges 2.5 to 4 and 5 to 8. No stability domain such as shown for the humic acid and silica sols is available at this time. Thus it is not possible at this time to correlate the floatability to the stability characteristics of the PSL system.

Mixed Bacterial Cultures

Figure 7 is a plot of the efficiency of removal by microflotation of bacteria from a mixed culture of microorganisms as a function of *p*H for aluminum sulfate dosages of 0, $2.5 \times 10^{-5}M$, and $5 \times 10^{-4}M$. The mixed culture was a relatively stable dispersion. In the absence of aluminum sulfate, good to intermediate removals of bacteria by microflotation are obtained at *p*H values less than 3 and greater than 8. Similar observations on various pure bacterial cultures have been reported earlier (*6* to *8*, *26*). The addition of at least $2.5 \times 10^{-4}M$ $Al_2(SO_4)_3$ was required at *p*H values between 4.5 and 7.5 before a significant increase in the efficiency of microflotation was observed. In the presence of $5 \times 10^{-4}M$ $Al_2(SO_4)_3$ efficient removals of bacteria were accomplished over the entire *p*H range of 7.5 to 11.5. These results show that the bacteria can be removed nonspecifically. In the absence of aluminum salt the removal of bacteria by microflotation is highly specific (*8*, *26*). Direct microscopic counts indicate that under the same experimental conditions in excess of 95% of the filamentous organisms and about 85% of the small dispersed organisms were separated by microflotation. The more efficient removals of the filamentous species is likely due to the shape rather than the surface characteristics of these organisms.

DISCUSSION

This work deals with the separation of four quite different colloids from aqueous dispersions by microflotation.

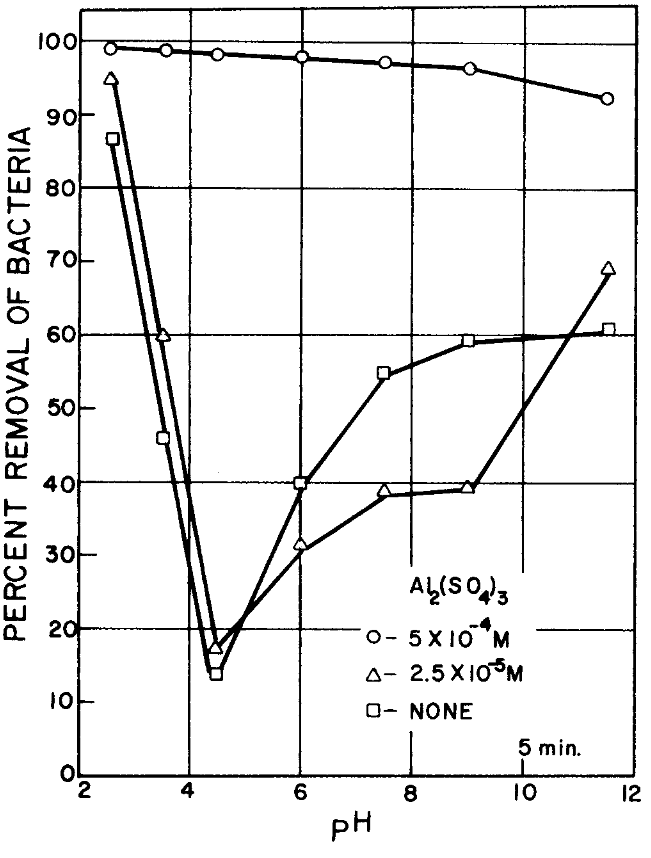

Fig. 7. Percent removal of bacteria from a mixed culture as a function of *p*H after 5 min. of microflotation in the presence of $5.0 \times 10^{-4}M$ $Al_2(SO_4)_3$ (○), $2.5 \times 10^{-5}M$ $Al_2(SO_4)_3$ (△), and and in the absence of aluminum sulfate (□).

The humic acid and colloidal silica systems could be classified as lyophilic sols, whereas the latex particles are lyophobic. Bacterial surfaces differ widely (27) and consequently no proper classification of a mixed culture may be made.

With the exception of the bacterial culture none of the dispersions studied could be separated by microflotation without the addition of aluminum salts. The removal of bacteria without the salt was observed only at low *p*H values. Such results were reported with pure cultures of *B. cereus* (7) and *A. aerogenes* (8). Pure cultures of *E. coli* could not be floated in the absence of aluminum salts regardless of *p*H (6).

Upon addition of $Al(NO_3)_3$ or $Al_2(SO_4)_3$, it was possible to separate by microflotation all the colloids studied in this work. In each case rapid and efficient flotation occurred when the *p*H was adjusted to render the sol unstable. Conversely, it was impossible to float any sol which remained stable upon addition of aluminum salts. More specifically, conditions which were conducive to separation by microflotation could be well correlated to the stability domains of the colloids in question. Figures 2 and 6 show efficient removals only in region III, in which aluminum hydroxide is precipitated.

Figure 3*C* shows that the *p*H range over which humic acid is floated in the presence of $1 \times 10^{-3}M$ $Al(NO_3)_3$ does not entirely correspond to the range over which pure aluminum hydroxide is floated at the same $Al(NO_3)_3$ concentration. Ludox AM exhibits a similar pattern (see Figure 5A). Over the *p*H range 5 to 7 aluminum hydroxide is precipitated as a stable sol of positive charge (17) and is not efficiently separated. However, in the presence of negative sols (humic acid, Ludox AM, etc.), mutual coagulation occurs, producing an unstable system which can be floated.

Between *p*H ~3 to 4 all the sols studied were destabilized by aluminum ions or by their highly positively charged hydrolysis products. However, Ludox AM could not be floated over this *p*H range despite the fact that the sol coagulated. PSL was partially floated, whereas the mixed culture and humic acid dispersion were efficiently separated. The reasons for this are not clear.

The presented results show that aluminum hydrolysis products play an important role in microflotation. The similarity of the behavior of various colloids in this process would indicate that the adsorbed soluble aluminum species and the precipitated aluminum hydroxide are essential in determining the surface properties of the sols, which lead to successful microflotation. Aluminum hydroxide precipitates and the sols mutually coagulate under certain conditions. The collector, a fatty acid, apparently interacts with the hydroxylated aluminum species at the silica surface, forming a cation-hydroxy-soap complex which causes the bubble attachment. The ionization state of the collector seems to play a negligible role. Over the *p*H range of efficient flotation in the presence of aluminum salt, the degree of ionization changes quite drastically. Also, our unpublished work shows that aluminum can be replaced by other metal ions, but the flotation is observed only when heterocoagulation with the metal hydroxide takes place. For example, with lanthanum salts this occurs at considerably higher *p*H (~ 8) in the presence of the same collector/frother concentration. Under these conditions lauric acid is fully ionized. In contrast, at *p*H ~ 5, at which substantial flotation first begins in the presence of aluminum salts, the lauric acid is only weakly ionized.

The small bubbles can attach in large number to aggregates and this provides the necessary buoyancy. The effect of the bubble size upon the efficiency of microflotation will be the subject of another report (28).

The *p*H range of successful flotation can be shifted by using different electrolytes. This will depend on the solubility product and the surface characteristics of the metal hydroxide formed.

This work in conjunction with previous studies demonstrates that a wide variety of different colloids can be effectively separated from water by microflotation under similar conditions of *p*H and aluminum salt concentrations. Thus it appears that microflotation has sufficient versatility to accomplish simultaneously the removal of mixtures of colloidal pollutants commonly found in natural and waste waters at a fast rate.

In addition to this nonspecificity, the microflotation process offers some other advantages when compared to the conventional flotation of colloids. It requires less surfactant materials. This is particularly important as the vast majority of the naturally occurring colloids are negatively charged. Microflotation makes use of anionic surfactants which are considerably less expensive than the cationic surfactants needed in conventional flotation. Because of the small bubbles and low flow rates, the consumption of gas is much smaller. Finally, and quite importantly, the salts, and particularly the hydrolyzable cations, which may be detrimental to conventional flotation, are beneficial to microflotation. This is important as many systems to which microflotation might be applied contain such electrolytes.

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Diffusion of Inert and Hydrogen-Bonding Solutes in Aliphatic Alcohols

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The diffusion of various inert and of hydrogen-bonding solutes into aliphatic alcohols was considered. The diffusivities of benzene, *p*-dichlorobenzene, biphenyl, and triphenyl methane in methanol, ethanol, *n*-propanol, *n*-butanol, *n*-pentanol, and *n*-heptanol were measured at 25°C. for low solute concentrations. An equation was developed for the limiting values of the binary mutual diffusion coefficient in complex-forming mixtures. This equation, used in conjunction with the Wilke-Chang correlation, gave a considerable improvement over existing predictive methods for the diffusivity of inert solutes, mono- and polyhydroxy alcohols, and water in aliphatic alcohols.

This work is concerned with diffusion of inert solutes (that is, solutes incapable of forming hydrogen bonds, such as carbon tetrachloride) and hydrogen-bonding solutes into aliphatic monohydroxy alcohol solvents. It is part of a wider study of diffusion in dilute complex-forming binary liquid mixtures. The study was undertaken because solute-solvent complexes are formed by hydrogen bonding in many organic solutions, and complex formation often leads to large errors in the diffusivity predicted by the literature correlations (*1* to *8*). Alcohol solvents are of special interest, because they have a high hydrogen-bonding capacity.

Consider, for example, Figure 1, where we have compared experimentally observed diffusivities in methanol and ethanol with values predicted by the Wilke-Chang equation (*1*) for inert solutes, for mono- and polyhydroxy alcohols, and for water. The experimental data were taken from Tables 1, 2, and 3. The association parameters for methanol and ethanol were taken as 1.9 and 1.5, respectively (*1*). From Figure 1 it can be seen that the predicted diffusivities for inert solutes are consistently low, often by more than 20%. On the other hand, the predicted diffusivities for mono- and polyhydroxy alcohols and water are always higher than the observed values. This is so because hydrogen bonding between solute and solvent hydroxyl groups tends to retard the diffusional motion of these latter types of solutes—a factor which is not taken into account in the correlation.

Thus the Wilke-Chang equation, which was developed using data for all types of solutes (*1*), performs best for mixtures where moderate solute-solvent interactions are present. However, where interactions are either fairly weak or very strong, this equation can give large errors in the

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