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Simple Relationships among Zeta Potential, Particle Size Distribution, and Cake Specific Resistance for Colloid Suspensions Coagulated with Ferric Chloride

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ABSTRACT

Kaolinite and latex colloidal suspensions were coagulated with various doses of ferric chloride before being filtered on microfiltration membranes. Subsequent improvements of the filtration rate (7 to 25 times) were observed for small coagulant doses (10 to 20 mg Fe^{3+}/g). The variations of three parameters, the cake specific resistance, the particle interaction energy calculated from zeta potential measurements, and the fraction of colloidal particles remaining in suspension, all showed a minimum at virtually the same concentration of ferric chloride. The fixation of iron ions, which brings positive charges onto the originally negative surfaces, resulted in charge destabilization and aggregation of fines. For the latex, however, overdosing caused the breakup of aggregates and an accordingly lower filtrability. The cake structure was found to be more open at optimum ferric chloride dosage as shown by electron microscopy.

INTRODUCTION

Particle characterization is a leitmotiv for better understanding and controlling processes where colloidal suspensions are involved. This is particularly the case in the water treatment industry where coagulation-flocculation represents the most commonly used solid–liquid separation technique (1). Coagulation-flocculation is also the first step of the treatment process which controls the performance of downstream operations. Coagulation

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is brought about by the neutralization of the electrical charge on particles in suspension, which results in small aggregates being formed. The aggregates are further joined together following the addition of a polymeric substance (flocculant) until their size is sufficient for gravity settling to occur. Sedimentation, however, is not a very intensive process. Since downward motion of flocs is slow, the residence time is of the order of hours. Hence, large settling tanks, which take up valuable land in urbanized areas, are required.

In membrane techniques, such as microfiltration and ultrafiltration, the separation principle is based on sieving by size. The selection of an appropriate membrane depends on the size of the species to be separated. Membranes are thus rated in terms of pore size or molecular cutoff. In microfiltration as in other filtration processes, fine particles are responsible for the clogging of filtration media, resulting in low filtration flux (2). This is particularly the case where the particles are small and a highly resistant cake composed of them builds up on the filtration media. Particles smaller than the pore size are very likely to enter the membrane porous network and cause internal fouling (3). A major advantage of crossflow operation is that the solids build-up is less, due to the shearing action of the flowing stream. However, in many systems the permeability decreases even with shearing action. It has been shown that the proportion of small particles tends to be higher with filtration time as measured from deposits collected on the membrane surface (4). Fouling and flux decline can also happen when particles and macromolecules adsorb on the surface. The degree of adsorption depends upon the actual membrane material and the physicochemical conditions by way of their effects on the colloidal forces. This can lead to irreversible deposition which is responsible for significant flux losses (5, 6).

Recent publications (7–9) report that flocculation is an effective pretreatment procedure to improve microfiltration processes. Increasing the size of the solids by flocculation and substituting microfiltration for sedimentation provides advantages which outweigh those of employing these techniques singularly: The separation rate is higher by large and the risks of membrane fouling are reduced. Wiesner et al. (7) studied the membrane filtration of what they called coagulated suspensions. These are really flocculated suspensions because of the polymeric nature of the added polyaluminum chloride. The flux performances which they obtained were least where the zeta potential of the particles was close to the isoelectric point, which is also where the average particle diameter (d_p) was a maximum. At the low solids concentration used in the experiments, penetration of solid matter into the pores was observed from electron microscopic studies. In another paper (9) it was found that at higher solids concentration, but still with the zeta potential close to zero, a filtration cake builds up. At other zeta potential values the floc size was decreased and a standard blocking filtration law behavior was reported.

Mietton Peuchot and Ben Aim (8) were able to triple the filtration rate by carefully adjusting the dose of flocculant and the stirring speed in the filtration cell. As for the other works already mentioned, the increase in filtration flux was concurrent with the increase in average diameter of flocs.

This paper looks at some fundamental aspects of the coagulation of colloidal suspensions with ferric chloride. Measurements are made of the cake specific resistance, the fraction of colloidal particles remaining in suspension, and the interaction energy between particles as a function of the coagulant dose. The comparative trends of these parameters are investigated. The structure of the filtration cake subject to electron microscopic methods is investigated.

THEORETICAL BACKGROUND

Interaction Energy between Colloidal Particles

The DLVO theory provides a general understanding of interfacial phenomena in colloidal systems in terms of the electrostatic interaction and van der Waals interaction (10, 11). The interaction energy (V_t) is the sum of the electrical interaction (V_e) and the van der Waals interaction (V_a). For two identical particles of zeta potential ζ, V_t is given by (12)

$$V_t = V_e + V_a = 16d\pi\epsilon\left(\frac{kT}{z_i e}\right)^2 \tanh^2\left(\frac{z_i e\zeta}{4kT}\right)\exp(-\kappa x) - (Ad/24x) \tag{1}$$

V_t is a characteristic of the repulsion/attraction between particles. The interaction is attractive when the van der Waals component is larger than the electrical component. In practical situations, V_t becomes negative when the zeta potential is close to zero.

Adsorption and desorption of particles on the surface of a collector have been modeled as first-order reactions (13, 14) where the kinetic constants are a function of the interaction energy. This approach translates to coagulation processes where qualitatively the concentration of colloidal particles remaining in suspension is a function of the repulsion/attraction between particles.

Cake Filtration and Permeability

Cake filtration at constant pressure is described by Ruth's law:

$$\frac{t}{V} = \frac{\alpha C \mu}{2S^2 \Delta P} V + \frac{R\mu}{S \Delta P} \tag{2}$$

α is obtained from the slope of the plotting of t/V as a function of V.

The specific resistance of a cake composed of particles of diameter d can theoretically be estimated from the Carman–Kozeny equation:

$$\alpha = \frac{6h_k(1 - \epsilon_p)^2}{d^2 \epsilon_p^3 \rho} \tag{3}$$

The resistance is dominated by the particle size where, for example, a tenfold decrease in diameter equates to a hundredfold increase in the resistance. Recently MacDonald et al. (15) extended the theory to the homogeneous packing of spheres of different sizes. Their expression of the hydraulic resistance takes into account the first and the second moment of the distribution (i.e., the average diameter and the variance). However, when the size distribution is very broad or particles are not spherical, which is typical of wastewaters (1), the theory is unlikely to be valid. The filtration of suspensions with a broad range of particle sizes is somewhat comparable to precoat filtration or dynamic membrane filtration where small particles are filtered through a thin layer composed of much larger particles. The hydraulic resistance is then governed by the fine particles progressively filling the big channels (16).

Analysis of Particle Size Distribution Measurements

Particle size measurements were performed by means of a laser light-scattering apparatus which displays the mass distribution of suspension as a function of 16 size classes. Particles from the colloidal range up to 120 μm can be measured with the apparatus. Caution must be employed in processing the data of the distribution. In fact, a significant error may be generated in calculating the average diameter for various reasons, the more obvious of them being the limited number of channels which lumps particles of various sizes under the same class (17). This is particularly evident for the largest sizes because of the geometric progression of the class width. For these reasons the mass fraction of the first class (0–1.2 μm), which corresponds to the colloidal range, was reported rather than the average diameter.

EXPERIMENTAL

Materials

Two types of colloidal particles were used in this study. The first one was a concentrated suspension of polystyrene latex (40% solid) used in the manufacture of paints (Estapor, Rhône-Poulenc). According to the manufacturer, the suspension is made of a mixture of four single populations whose mean diameters have been measured by electron microscopy. The first population (mean diameter 1.3 μm) represents 18% in weight, the second (1 μm) 23%, the third (0.55 μm) 57%, and the last (0.25 μm) 2%. The second suspension was a purified kaolinite powder (Lab. Ponts et Chaussées, Paris) with a wide size distribution (size from 0.2 μm up to 20 μm) but with a high fraction of colloidal particles (40% in mass of particles < 1.2 μm). The measured specific surface area was reported as 25 m^2/g (BET method using CO_2). The specific mass was 2650 kg/m^3 as measured by helium pycnometry.

The suspensions were prepared with ultrapure water (MilliQ, resistivity 18 megohm cm) adjusted to a ionic strength of 10^{-3} M NaCl. The kaolinite powder was dispersed by magnetic stirring for 2 hours at concentrations of 200 to 1000 mg/L. The as-supplied latexes were diluted with 10^{-3} M NaCl to the desired concentration (17 to 200 mg/L). Small volumes of freshly prepared ferric chloride solutions (1 and 5 mM of $FeCl_3$, $6H_2O$) were added to 200 mL of the suspensions. The pH of the suspensions was not controlled and varied between 4 and 6 due to residual amounts of sulfuric acid present in the ferric chloride.

Experiments

Dead-end microfiltration at constant pressure was performed in order to determine the cake specific resistance. The membrane used was Millipore GVWP 0.2 μm. The pressure was set by connecting the filtration cell to a nitrogen gas cylinder at between 0.6 to 3 bars. The filtration cell (Sartorius) had a 15 cm^2 membrane area, 250 mL capacity, and was not stirred. The mass of filtrate was recorded on a balance as a function of the filtration time. The specific resistance of the filtration cake (α) was determined according to Eq. (2).

The particle size distribution of suspensions was measured by means of a laser light-scattering apparatus (Malvern 2200). For kaolinite suspensions it was possible to carry out the measurements at concentrations up to 200 mg/L. Dilute latex concentration had to be used (17 mg/L) because of the high refractive index of the latex material.

The determination of the zeta potential was carried out by means of an automatic laser light-scattering apparatus (Malvern Zetasizer IIC). Because of the shorter optic path in the Zetasizer IIC, concentrations of latex up to 100 mg/L could be analyzed.

The adsorption of iron was also investigated. Aliquots of suspensions were centrifuged and the iron remaining in the supernatant was measured by atomic absorption (Varian A-20, wavelength 248.3 nm).

The structures of filtration cakes and individual aggregates were studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Samples underwent a gold-palladium coating prior to SEM observation. For TEM, cakes samples were imbeded in a resin and cross-sectioned according to the technique described by Villemin and Toutain (18).

RESULTS AND DISCUSSION

The variations of particle size distribution following the addition of ferric chloride are illustrated in Fig. 1 for the latex. All particles of the original suspension are in the first class (0–1.2 μm). Following the addition of 20 mg Fe^{3+}/g, the distribution broadened to include the 8–10.5 μm class. Only 38% of particles remain in the colloidal range (0–1.2 μm).

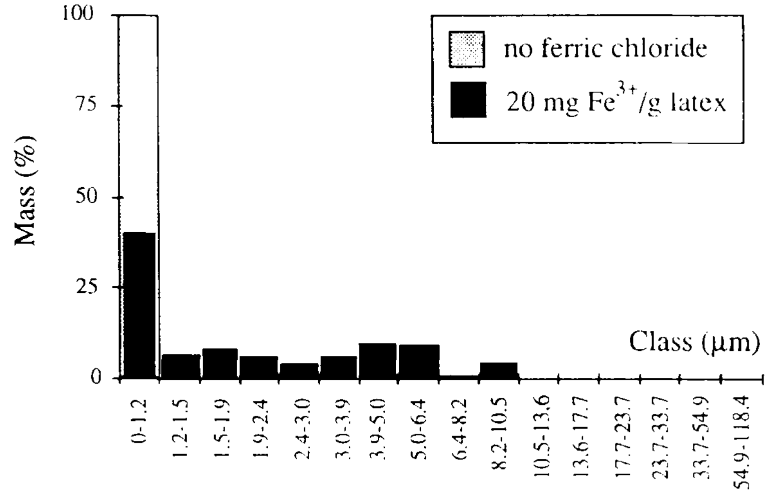

FIG. 1 Particle size distribution of latex as measured by Malvern 2200 (concentration of latex: 17 mg/L).

Meanwhile, the zeta potential shows important variations (Fig. 2). Initially latex and kaolinite particles are negative charged. As $FeCl_3$ was added to the suspensions, the zeta potential increased, passing through the isoelectric point and then becoming positive before nearly plateauing. A characteristic feature is that the fraction of colloidal particles (0–1.2 μm) was high when the zeta potential exhibits a high negative or a high positive value. On the contrary, the fraction of colloidal particles was at a minimum when the zeta potential is close to zero (0 to −5 mV).

The cake specific resistance also undergoes important changes. The results are presented together with those of the interaction energy and the fraction of colloidal particles (0–1.2 μm) to allow for comparison (Figs. 3 and 4). The interaction energy was derived from Eq. (1), taking into account the zeta potential measurements and assuming an Hamaker constant of 5×10^{20} J for the van der Waals interaction. Clearly, the curves bear a certain similarity.

For the kaolinite suspension, the cake specific resistance initially decreased as ferric chloride was added: without ferric chloride the resistance α is 1.7×10^{13} m/kg. A 7-fold drop was observed for an addition of 8.4 mg Fe^{3+}/g, which corresponds to a minimum of the specific resistance. For higher concentrations of ferric chloride, α re-increases but only slightly (4.2×10^{12} m/kg for 24 mg Fe^{3+}/g). The fraction of colloidal particles and the interaction energy show a minimum around the same concentration of ferric chloride as for the specific resistance. However, their relative increase past the minimum was much more marked than for α.

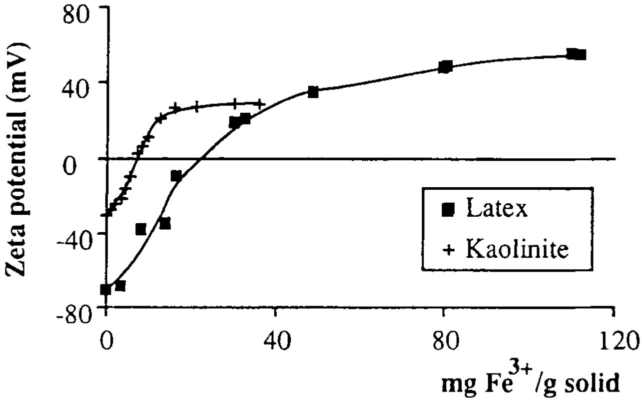

FIG. 2 Variations of the zeta potential of kaolinite (200 mg/L) and latex (100 mg/L) as a function of the concentration of added ferric chloride.

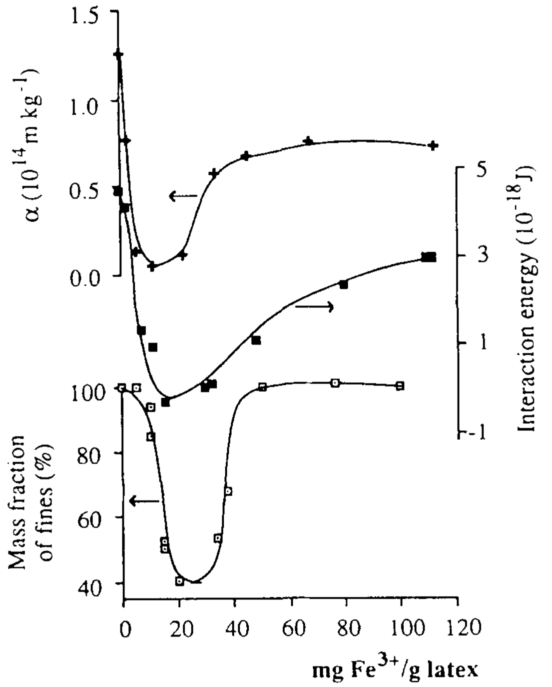

FIG. 3 Variations of latex suspension properties as a function of the concentration of added ferric chloride: (+) specific resistance of the filtration cake (C = 100 mg/L, ΔP = 80 kPa), (■) interaction energy between particles (C = 100 mg/L, x = 10 nm), (□) mass fraction of the 0–1.2 μm class (C = 17 mg/L).

The specific resistance of the latex cake has a sharp initial decrease, then passes through a minimum around 10 mg Fe^{3+}/g which corresponds to a 25-fold reduction. For further additions of ferric chloride, the specific resistance re-increased to reach a plateau of about half the initial value. The behavior of the interaction energy was similar although the increase was more gradual. For the fraction of colloidal particles, the plateau value after the minimum is the same as the initial value, i.e., 100% of particles in the first size class. The possibility that this could be due to the different latex concentration used in particle size measurements cannot be dismissed.

pH variation was shown to have no effect on the zeta potential of latex and kaolinite particles; in the absence of ferric chloride, the value was constant between pH 3 and 7. The variations can then be attributed to

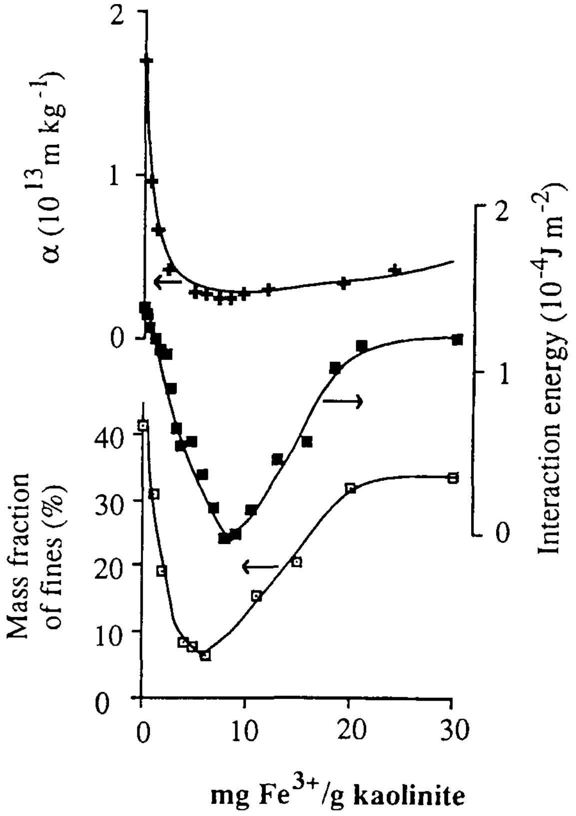

FIG. 4 Variations of kaolinite suspension properties as a function of the concentration of added ferric chloride: (+) specific resistance of the filtration cake (C = 200 mg/L, ΔP = 60 kPa), (■) interaction energy between particles (C = 200 mg/L, x = 10 nm), (□) mass fraction of 0–1.2 μm class (C = 200 mg/L).

the uptake of Fe^{3+} ions (and other cationic iron species) which bring positive charges to the surface of the particles. The uptake of iron was confirmed by chemical analysis. Bringing the zeta potential close to zero reduces the electrical repulsion between colloidal particles, thus exacerbating the effect of attractive van der Waals forces. This causes increased coagulation and a related lower filtration resistance. Overdosing of ferric chloride, however, produces a reverse effect. It brings an excess of positive charges to the surface and results in lessened coagulation and accordingly higher filtration resistance. Iron is assumed to be present mainly in an ionic form as reported in other works (19, 20). Very few granules of iron oxide precipitates (10 to 50 nm) were observed.

Observations under the electron microscope show that coagulated latex forms two types of associations: 1) small latex beads aggregate around a bigger latex bead, 2) latex beads of nearly the same size form small chains of a few beads, typically less than 10. Without the addition of coagulant, the surface of the cake has an ordered, well-packed structure (Fig. 5a). By contrast, with 10 mg Fe^{3+}/g the surface is uneven (Fig. 5b); particle aggregates as well as large openings are visible.

Cross sections indicate that kaolinite cakes without ferric chloride have a dense packing. Platelet particles are oriented in various directions (Fig. 6a). As ferric chloride is added, particles seem to preferably associate in stacks, leaving large gaps in between (Fig. 6b). Over 20 mg Fe^{3+}/g this feature was quite unexpected as the particle size distribution is very close to that of the original suspension.

A possible explanation for the different packing modes lays in the change of the electrical charge distribution. Due to isomorphic substitutions of aluminum atoms by silicium atoms in the crystal lattice, the faces of the kaolinite platelets have a net negative charge. On the contrary, the edges have a positive charge at neutral or acidic pH, which disappears at alkaline pH (21). The heterogeneity of the electrical charge induces edge-to-face interactions or face-to-face interactions depending on the pH and has been shown to have implications for the rheological behavior of clay suspensions (22). It can be speculated that ferric chloride has the same effect as a high pH. In the original suspension, edge-to-face interactions prevail, leading to disordered structures making a maze of small channels in which the pressure drop is high. When kaolinite particles are covered with ferric chloride, the surface charge distribution becomes less asymmetric. Face-to-face interactions allow for the stacking of particles on top of each other. This implies more structure compactness, which corresponds to larger channels.

This fundamental study shows the positive aspects of coagulation and provides hints toward the possibility of using coagulation as a pretreatment for crossflow microfiltration. However, applicability to real processes needs to be assessed by carrying out crossflow microfiltration runs. This aspect is under investigation in our laboratory.

A few implications for filtration processes can be pointed out.

- An important reduction of the cake specific resistance was obtained: 7-fold and 25-fold for kaolinite and latex, respectively. The doses of coagulant necessary for optimum performance are several times less than in flocculation and are of the same order as doses of polyaluminum chloride used by other authors (7, 8).

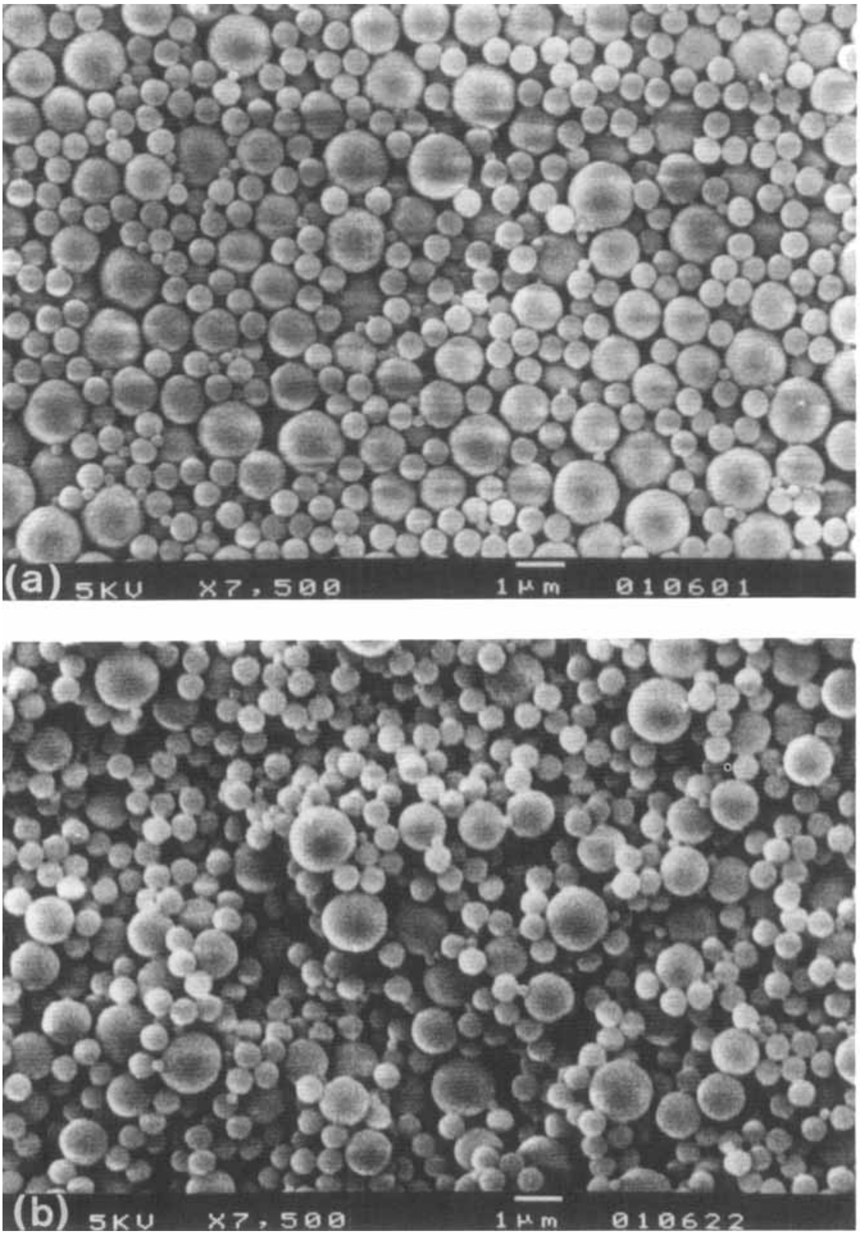

FIG. 5 SEM of the top of a latex filtration cake: (a) without ferric chloride, (b) with 20 mg Fe^{3+}/g.

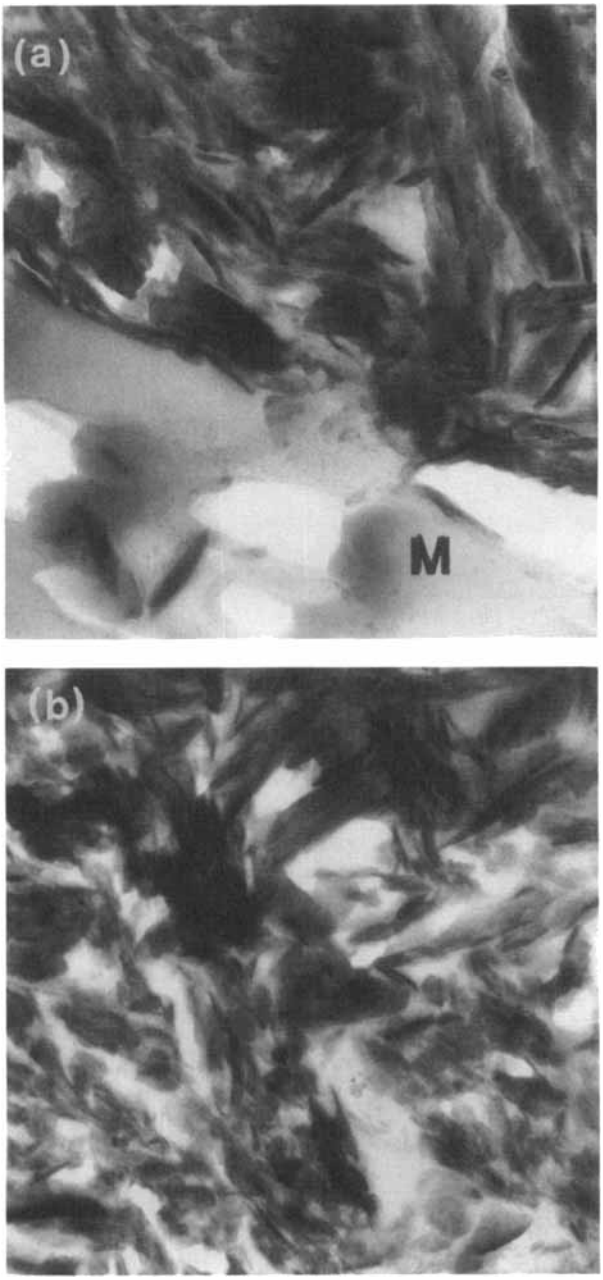

FIG. 6 Detail of cross-sections of the structure of kaolinite cake under TEM: a) without ferric chloride, "M" indicates the membrane; b) with 24 mg Fe^{3+}/g ferric chloride. Scale for a) and b): 15 mm represent 0.4 μm.

- The particle size increases to only a few microns, which is sufficient for obtaining significant filtration improvement. The small size aggregates (5 to 10 μm) render them less sensitive to break-up by shear (23). Suspensions that were vigorously stirred before filtration did not show any reduction of filtration rate.
- The coagulant acts as a binder between the particles and does not form the gelatinous network which is responsible for the formation of compressible cakes. Sludge production is then kept low because the coagulant dosing is small.
- Should ferric chloride deposit inside the pores, it should be easily dissolved by an acid wash.

Coagulation as a pretreatment for microfiltration may not be applicable where the cake resistance curve presents a sharp minimum, as for latex. Overdosing causes the aggregates to break down and the cake resistance to increase (Figs. 3 and 4).

CONCLUSION

Coagulation pretreatment resulted in significant improvement in the filetrability of suspensions. The main impact was the reduction of the colloidal fraction which represents the major component of the resistance to permeation. The change in particle electrical charge was responsible for the coagulation of the suspensions as the minimum for the cake specific resistance and that for the fraction of colloidal and that for the minimum of interaction energy are obtained for a similar dose of ferric chloride. The use of a coagulant is advantageous compared to the use of a flocculant as the small aggregates (a few microns) formed during the coagulation process are less sensitive to shear. In addition, they do not form gelatinous sludges which are subsequently difficult to dewater. Observations under the electron microscope show different modes of packing for the uncoagulated and coagulated suspensions. The technique may not be applicable to all suspensions as possible overdosing might induce aggregate breakage.

SYMBOLS

C	mass concentration of particles ($\mathrm{kg \cdot m^{-3}}$)
d	particle diameter (m)
e	charge of electron (1.610^{-19} C)
h_K	Carman–Kozeny constant (—)
k	Boltzmann constant (1.3810^{-23} $\mathrm{J \cdot K^{-1}}$)
R	membrane resistance ($\mathrm{m^{-1}}$)
S	membrane area ($\mathrm{m^2}$)

t	time (s)
T	temperature (K)
V	volume of filtrate (m^3)
x	distance between surfaces (m)
z_i	valence of ion (—)
α	cake specific resistance ($m \cdot kg^{-1}$)
ΔP	transmembrane pressure (Pa)
ϵ	medium permittivity ($F \cdot m^{-1}$)
ϵ_p	cake porosity (—)
κ	Debÿe–Hückel parameter (m^{-1})
μ	viscosity of suspension ($Pa \cdot s$)
ρ	specific mass of solid ($kg \cdot m^{-3}$)
ζ	zeta potential (V)

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