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## Electroflocculation: the effect of zeta-potential on particle size

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### Abstract

Electroflocculation (EF) of wastewater or water for reuse with colloidal particles, such as kaolin and iron with the right pH, might be optimal for aggregation during water treatment. In this paper, the EF process was compared to chemical flocculation (CF) through  $\zeta$ -potential and particle size parameters. The results demonstrate that the particle became larger, except in the case of pH 4, where, after 50 min of flocculation, there was a jump in the value and the particle attained a diameter of more than 800 nm. Throughout the entire flocculation time, the  $\zeta$ -potential values indicated a stronger negative charge on the particle. Basically, there was a gradual rise in absolute  $\zeta$ -potential with the increase in particle size. The reason for this behavior can be explained by the solubility of kaolin with a decreasing ionic strength, when certain iron ions are released from the electrode and the charge of the particle is altered. The aggregation process, whereby a few small particles with a negatively-charged surface are rendered into a larger-sized particle, results in a larger total negative charge. It has long been recognized that  $\zeta$ -potential is a very good index of the magnitude of the repulsive interaction between colloidal particles. Measurements of  $\zeta$ -potential are commonly used to assess the stability of colloidal and particle size produced by EF. Thus, the coupling of the EF of kaolin and iron with the right pH might be optimal for producing particles.

*Keywords:*  $\zeta$ -potential; Particle size; Wastewater treatment; Chemical treatment; Flocculation; Electroflocculation

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## 1. Introduction

The determination of the rheological characteristics of clay (kaolin)–iron–water suspensions exhibits very significant properties due to aggregation under varying conditions. EF as CF is a coagulation process involving the in situ generation of ions (coagulants) by the electrolytic oxidation of an appropriate anode material or from chemicals [1,2]. This process creates chemical and physical conditions for the separation of the colloids in waste or contaminated water for reuse, where a high negative charge is usual [3].

The availability of reproducible colloid systems and an integrated approach to the study of surface properties have given us more confidence in EF's value as a characterizing parameter [4]. The stability of a colloidal particle is determined by the balance between the repulsive and attractive forces that the particles experience as they approach each other. The  $\zeta$ -potential decreases and a quite sharply defined coagulation concentration can be identified [5,6]. This is the point at which the potential energy barrier opposing coagulation disappears, and it is called the critical coagulation concentration (c.c.c.) [7]. An estimation of the c.c.c. can be obtained by using an approximate expression for the potential energy of attraction and the potential energy of repulsion. An empirical relation between  $\zeta$ -potential and coagulation behavior was first provided by Eilers and Korff [8] using published data on a variety of systems [2,9]. Theoretical justification was provided by Derjaguin [10,11] on the basis of the Debye–Huckel approximation. Assuming that  $\zeta$ -potential measures the potential characterizing the diffuse part of the double layer, it is hardly surprising that it should provide a good description of the coagulation process, since it is the diffuse layer potentials that are involved in double-layer overlap. A much more exacting test of the use of  $\zeta$ -potential to characterize coagulation behavior would require not merely a correlation with the c.c.c., where rapid (i.e., particle diffusion rate) controlled coagulation begins, but rather an understanding

of the region of slow coagulation [12]. The scope of this present study is to examine the effect of flocculation on iron and kaolin solutions while examining the correlation between  $\zeta$ -potential and particle size during EF.

## 2. Materials and methods

A large number of samples of calibrated water, prepared in the laboratory were used in this study. Ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), which served as a chemical coagulant produced by Merck at minimum 99% purity, was used for synthesis with other impurities such as sulfate, Pb and zinc (less than 0.005% each) and nitrogen compositions (less than 0.01%).

In EF,  $\text{Fe}^{3+}$  ions generated by electrolytic oxidation from an SAE1020 steel electrode were used as coagulant and were added to six cups, 800 ml each, of calibrated water (Fig. 1). The calibrated water was tap water that underwent a few stages of purification: 50-micron filtration and reverse osmosis true MWCO (KDa), UF-PA 50 H, hydrophilic membrane from polyaramid (PA) with permeability of 570 (l/h.m.bar) at 20°C. The water was then passed through a polisher made from a mixture of emberlit IR120 and IRA400. In EF, sodium nitrate was used to adjust the suspension conductivity. The samples' initial pH values were varied by adding NaOH or HCl; pH



Fig. 1. Jar-test device used in the experiment.

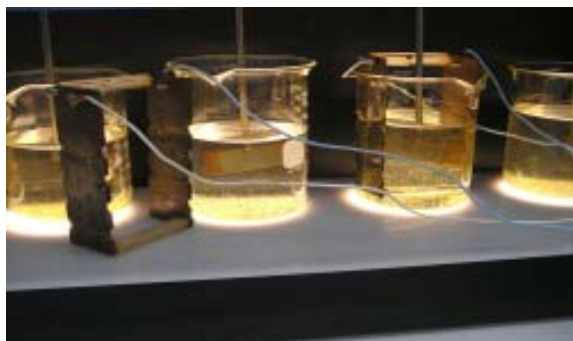


Fig. 2. Jar-test device made suitable for EF.

was adjusted (to 4, 6, 7.5 and 9) and a buffer, sodium carbonate, was added to the solution to stabilize the pH. Twenty  $\text{mg l}^{-1}$  of kaolin were added to the calibrated water used in this study. All the conditions of the experiments were the same in CF and in EF. The jar-test device was fitted to EF by adding two electrodes to each cup (see Fig. 2).

The electrodes were fitted so that the paddle could rotate freely and were connected to a DC power generator that provided current and voltage over the ranges of 0–5 A and 0–30 V. In CF ferric chloride as flocculant was added at the first 3 min only and in EF the current was applied only at the first 3 min.

The calibrated water and additives were mixed in conventional jar-test procedure at 100 rpm for 1 min. The paddle speed was adjusted thereafter to 30 rpm for the next 20 min. Observations of floc formation were carried out. The slow mixing was stopped and the suspension was allowed to settle for 30 min. After settling, samples were drawn from 4 cm below water surface and checked for  $\zeta$ -potential and particle size.

### 2.1. Determination of particle size

Particle size was determined by using ZetaPlus and Particle Sizer (Brookhaven Ins. Corp.), in the range of 10–1000 nm, where a dilute suspension of clay and iron was dispersed in water. Rossi et al. [12] measured the diameter of over 100 different clay particles in the micrographs and found

an average particle aggregate-diameter of 220 nm. These were the values that were obtained in this study.

### 2.2. Electrokinetic measurements

The electrophoresis measurements were carried out after the jar-test procedure by injecting a small amount into the cell of the ZetaPlus instrument at room temperature. Multiple measurements of the electrophoretic mobility of particles were made at different positions across the cell and scans were conducted. After obtaining a series of measurements for each sample, an extended calculation was made, adjusting all the data to a model that would enable the effective  $\zeta$ -potential to be calculated. The bulk  $\zeta$ -potential may be derived from the Schmoluchowski formula [13] for a solid nonconducting particle of arbitrary shape and with a curvature radius greater than the double-layer thickness at any point on the surface.

$$\mu_e = \epsilon_r \epsilon_o \zeta / \eta_l \quad (1)$$

where  $\mu_e$  is the electrophoretic mobility,  $\eta_l$  is the liquid viscosity, and  $\epsilon_r$  and  $\epsilon_o$  are the dielectric constants of the medium and free space, respectively. The resultant effect is a decrease in the electrophoretic mobility and/or  $\zeta$ -potential of the particles. The decrease in  $\zeta$ -potential may be related to a shift in the shear plane, which corresponds to the hydrodynamic thickness of the adsorbed layer. This postulation is valid if it is assumed that the presence of the coagulant does not affect the surface charge density, specific adsorption of ions in the Stern plane, and the charge distribution in the diffuse part of the double layer.

## 3. Results and discussion

The average particle size was found to be 350 nm and  $\zeta$ -potential was found to be negative,  $-35$  mV, as described in Figs. 3 and 4. One might be tempted to conclude that the species involved in coagulation are the insoluble metal hydroxide precipitates. Although precipitation reactions are of

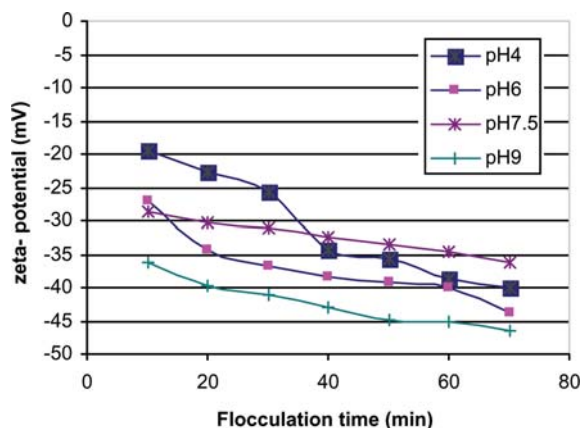


Fig. 3. Effect of EF on  $\zeta$ -potential; comparison of the  $\zeta$ -potential of EF at pH 4, 6, 7.5 and 9.

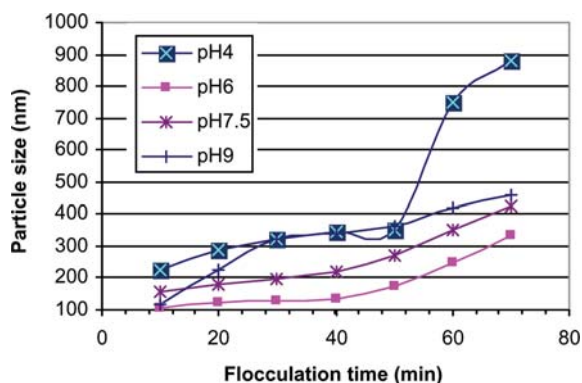


Fig. 4. Effect of the EF process on particle size; comparison of particle size in EF at pH 4, 6, 7.5 and 9.

doubtless importance in certain cases (e.g., iron), destabilization reactions are often other than that of precipitation. The rate of transition from aqua metal ions to metal hydroxide precipitates is dependent on the pH and applied concentration of the solution [6]. For the concentration used in water treatment, true equilibrium may in some cases require time spans longer than those required to attain destabilization. For this reason, the use of stability constants for identifying the species effective during destabilization in water treatment processes may not be valid.

Figs. 3 and 4 illustrate  $\zeta$ -potential and particle size as a function of flocculation time at different pH values. When the results are plotted in this way, it is possible to follow the change in  $\zeta$ -potential as the particles become gradually larger. It can be seen that the particles became larger, except in the case of pH 4, where, after 50 min of flocculation, there was a jump in value. Throughout the entire flocculation time, the  $\zeta$ -potential values indicated a stronger negative charge on the particles. Basically, there is a gradual rise in absolute  $\zeta$ -potential and increase of particle size with the flocculation time. The reason for this behavior is not quite clear. It is possible that the aggregation process could be the result of one of three main mechanisms responsible for the charging of the surface:

1. Ion adsorption, due to an ionic charge taken from the electrolyte solution and applied to the surface;
2. Surface dissociation, i.e., departure of ions from the surface and their transfer to a bulk electrolyte solution;
3. Isomorphic replacement of ions in the solid phase with others having a different charge, accompanied by the sorption of electrons from outside.

The surface hydroxyl group of the adsorbent has the main effect on the adsorption process, so it would be useful to review the surface hydroxyl groups. Fig. 5 demonstrates the relationship between  $\zeta$ -potential and the particle size at a given pH. From these results, it may be observed that the largest particle size, with a diameter of more than 800 nm, is achieved at pH 4. Basically, there is a gradual increase in the absolute  $\zeta$ -potential with a rise in the particle size. The reason for this behavior can be explained by the solubility of the kaolin with a decreasing ionic strength, when certain iron ions are released from the electrode and the charge of the particle is altered. The aggregation process, whereby a few small particles a negatively charged surface are rendered into a

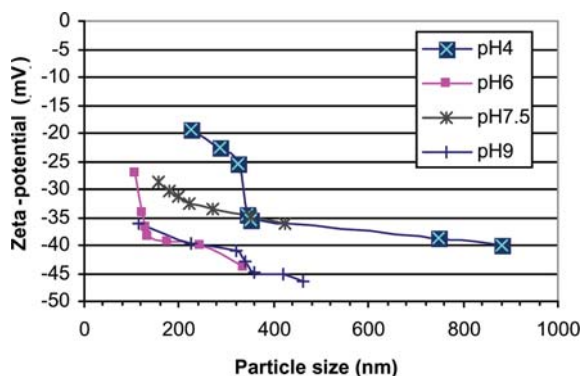


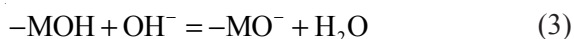
Fig. 5. Effect of  $\zeta$ -potential in EF on particle size; comparison of  $\zeta$ -potential and particle size of EF at pH 4, 6, 7.5 and 9.

larger-sized particle, results in a larger total negative charge.

### 3.1. Effect of solution pH on $\zeta$ -potential

It has been established that the influent pH is an important and clear factor of the  $\zeta$ -potential in EF. For a purely electrostatically stabilized system, it is important to know the exact location of the isoelectric point (iep) i.e., the pH value at which the particle has zero  $\zeta$ -potential. The iep also indicates that at this point (or pH) there is no charge on the surface, i.e., that the total positive charges are equal to the total negative charges. This demonstrates that the kaolin surface maintains its neutral character while most silicate or clay minerals have an iep of pH 2–4 [12].

The electrical charge on the aqueous oxide surface is transferred to the protonation/deprotonation of the hydroxyl surface and can be described as:



and at isoelectric point (iep)



Table 1

Results of  $\zeta$ -potential and particle size of the experiments

Particle size (nm)	$\zeta$ -potential (mV)	pH
226÷882	-19.34÷-40.11	4
106÷335	-27.0÷-43.0	6
155÷425	-28.6÷-36.2	7.5
116÷460	-36.11÷-46.4	9

The fact that there was no iep shows that the reactions responsible for the surface charge of the solid is mainly the reaction in Eq (3).

The electrostatic results (and particle size) of these experiments show that increasing the suspension pH (Table 1) results in an increase of the negative charge of kaolin. This can be ascribed to either the adsorption of  $\text{OH}^-$  ions onto the positive charge centers of kaolin or the deprotonation of surface hydroxyl groups. An addition of  $\text{OH}^-$  with dissolved cations to form metal hydroxides may result in a decrease in the pH. The decrease of the suspension pH results in a decrease of the negative potential owing to the  $\text{H}^+$  adsorption on the negative charge centers. At around pH 7.5, the  $\zeta$ -potential — the curves of all four pH values — changes direction, from an increase to a decrease of  $\zeta$ -potential. These “broken” points will have to be explained in future experiments.

Fig. 6 illustrates the effect of pH on the variation of the  $\zeta$ -potential of kaolin with iron. As shown in this figure, the kaolin with iron samples has no point of zero charge and exhibits negative  $\zeta$ -potential at all pH values. This result corresponds with that obtained in electrokinetic measurements of clay minerals taken in other studies, which have also served as a reference here.

## 4. Conclusion

In the present study, we examined the influence of the addition of iron to calibrated water and kaolin in jar-test device, paying particular atten-

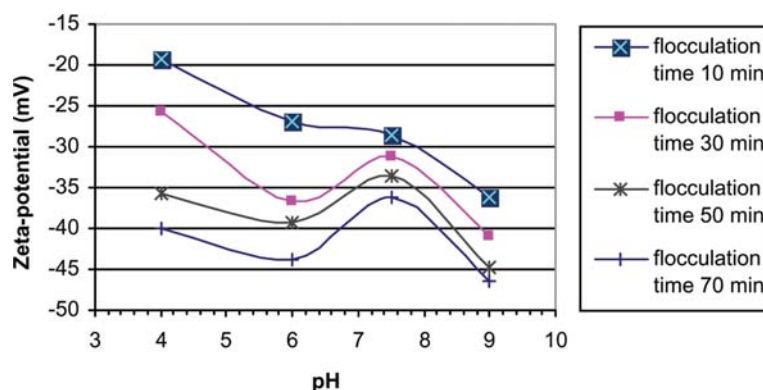


Fig. 6. Effect of  $\zeta$ -potential in EF in the variation of flocculation time at pH 4, 6, 7.5 and 9.

tion to  $\zeta$ -potential and particle size.  $\zeta$ -potential increases in absolute values while the particle size of colloid suspensions increases. This observation provides evidence that iron adsorbed by clay particles tends to cause aggregation resulting from the interaction between the positive iron ion and the negative edges of the clay particle. In addition,  $\zeta$ -potential studies carried out parallel to particle size studies have yielded the same results, i.e., that there is a very clear correlation between both parameters. The correlation between  $\zeta$ -potential and the particle size of iron and kaolin oxide and the hydroxide colloid in EF is not quite clear and requires clarification in future experiments.

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