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Adsorbing Colloid Flotation of Pb(II). Feasibility of Utilizing Streaming Current Detector

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ABSTRACT

A feasibility study was conducted to assess the application of a streaming current detector (SCD) in the flotation of dissolved heavy metals. The adsorbing colloid flotation of Pb(II) with iron oxide and sodium dodecylsulfate was investigated. Both zeta potential and streaming current (SC) readings of each colloidal system were measured. For colloids of goethite or of amorphous iron oxide, the results show SC changed with pH values and can be well correlated to the zeta potential. The removal of Pb(II) increased with increasing pH. Judging from the experimental results, it is proposed that when pH is at 3.0 or lower, Pb(II) is mainly removed by foam fractionation. When pH values are between 4.0 and 7.0, Pb(II) removal can be attributed to both foam fractionation and adsorbing colloid flotation. When pH values are higher than 7.0, Pb(II) is mainly removed by precipitate flotation in the form of $Pb(OH)_2(s)$ or Pb–Fe coprecipitate. Advantages and limits of utilizing SCD in flotation processes are discussed. Preliminary results show it is feasible for SCD to be utilized in the flotation of Pb(II).

Key Words. Adsorbing colloid flotation; Lead; Streaming current detector; Surfactant; Zeta potential

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INTRODUCTION

In our previous work we explored the feasibility of utilizing the streaming current detector (SCD) in the adsorbing colloid flotation of As(V) (1). It has been demonstrated that an SCD could replace a zeta meter in assessing surface electrical properties of colloidal systems in flotation processes. Since flotation processes have also been extensively examined and used in heavy metal pollution control, the current study was conducted to investigate the applicability of SCD in the flotation of Pb(II) from aqueous solution.

Heavy metals are found in industrial wastewater as well as in natural water bodies. They may be present in various forms, such as hydrated metal ions, complexes, and colloidal species (2). As these different metal forms will generally exhibit different physical and chemical properties, their behaviors in flotation processes are different from anions, such as As(V). Take the lead ion as an example, it undergoes different reactions in aqueous solution. The extensive literature shows that adsorption, precipitation, complexation, and ion exchange could possibly be involved in the fate and transport of Pb(II) in aqueous solution (2). Lead can be removed from water by utilizing various separation processes, such as adsorption (3, 4), neutralization-precipitation (5, 6), and foam fractionation (7–9).

When applied in heavy metal flotation, the foam separation process has proved satisfactorily for the removal of Pb(II) from wastewater. Important parameters, such as pH, activators, surfactant, and gas flow rate, are well known to significantly affect flotation processes (10–16). Among all these variables, the surface charge of a colloidal system plays a key role in determining the optimum condition for separation. The zeta potentials of colloidal systems are commonly measured to study how solution pH, colloid, surfactant, and contaminants in the aqueous phase interact, and consequently determine the removal efficiency. Recent developments in online detection of the surface charge of a colloidal system, such as the streaming current detector (SCD), have facilitated the automatic control of the coagulation reaction (17), sludge conditioning, and dewatering (18–20). Following our previous work on As(V) flotation, the major objective of the current work is to study the feasibility of utilizing SCD in the adsorbing colloid flotation of Pb(II). In addition to zeta potential measurement, streaming current (SC) will be detected and correlated to zeta potential. To remove Pb(II) from an aqueous solution, either α-FeOOH(s) (goethite) or $FeSO_4$(aq) was added to provide colloids, and sodium dodecylsulfate (SDS) was used as the collector. Experimental results will be compared with theoretical prediction. The flotation mechanism will also be discussed.

MATERIALS AND METHODS

Colloid Characterization

The colloid first utilized in the current work was reagent grade iron oxide (Hanawa). X-ray diffraction analysis (Philips MP-710) showed the crystal structure to be α-FeOOH (goethite). The BET specific surface area of iron oxide was determined to be 15 m^2/g by N_2 adsorption (Quantachrom AV-14). Size distribution of α-FeOOH was analyzed (Malvern 2600), and an average diameter of 0.356 μm was obtained. For comparison, $FeSO_4(aq)$ was utilized to form amorphous iron oxide colloid instead of α-FeOOH. Experimental procedures for zeta potential and streaming current measurements were described in our previous work (1).

Adsorbing Colloid Flotation Experiment

The cell utilized in the flotation experiment was based on a developed technique (4). Stock solutions of 2 g/L α-FeOOH, 2 g/L $FeSO_4$ (Nacalai Tesque), 1 g/L SDS (J. T. Baker), 1 g/L TX-100 (Merck), 1 M $NaNO_3$ (Merck), and 1 g/L $Pb(NO_3)_2$ (Nacalai Tesque) were prepared. A 500-mL solution with a different concentration was utilized each time. After the pH value was adjusted with 1 M NaOH and 1 M HNO_3, the solution was poured into the flotation column for the removal of Pb(II). Samples were taken at certain time intervals. They were filtered through a 0.45-μm membrane filter (MFS) before the residual Pb(II) concentration was analyzed by an atomic absorption spectrophotometer (GBC 904AA). To prevent clogging the sintered-glass disk used as the gas disperser (Kimble) was wetted before each experiment and cleaned by ultrasonic vibration for 4 hours after each experiment.

RESULTS AND DISCUSSION

Streaming Current and Zeta Potential Correlation

The zeta potentials of colloidal systems as affected by pH are shown in Figs. 1A and 1B. The iron oxides (α-FeOOH) were positively charged under acidic conditions. The isoelectric point (IEP) at pH 5.7 was found (Fig. 1A). This is consistent with a reported value (21). In the presence of 12 mg/L $Pb(NO_3)_2$, the zeta potential of the colloidal system did not change significantly. Neither was the IEP shifted. However, when 20 mg/

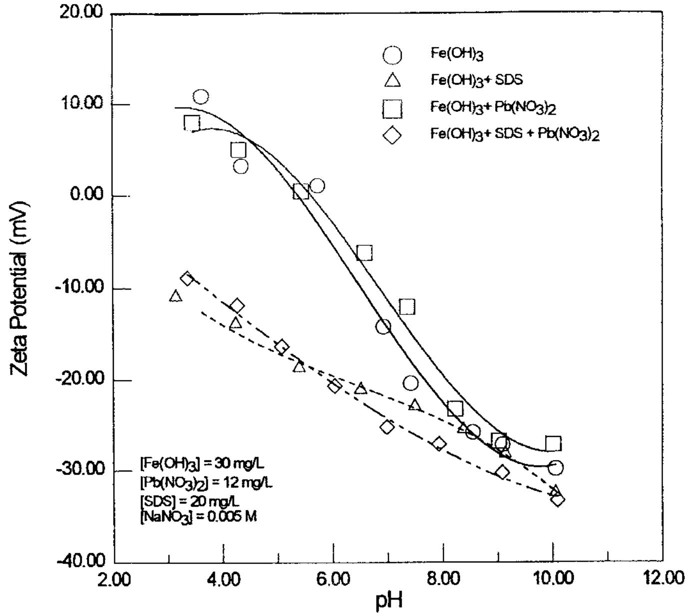

FIG. 1A Zeta potential of systems as functions of pH. Experimental conditions: [$Fe(OH)_3$] = 30 mg/L, [$Pb(NO_3)_2$] = 12 mg/L, [SDS] = 20 mg/L, [$NaNO_3$] = 0.005 M.

L SDS was added to the iron oxides colloidal system, the IEP was shifted to the acidic range as a result of the adsorption of SDS (22). The zeta potential of the iron oxide system in the presence of SDS and $Pb(NO_3)_2$ under all pH conditions was almost identical to the system of iron oxide and SDS. The IEP was less than 3.0. The presence of SDS affected the surface charge of iron oxides more significantly than $Pb(NO_3)_2$. The results when $FeSO_4$ was utilized instead are shown in Fig. 1B. The IEP of amorphous iron oxides is 8.2. Again, this is in conformity with previous findings (21). The value was shifted slightly to 9.5 in the presence of 12 mg/L $Pb(NO_3)_2$, and similarly, the adsorption of SDS could shift the IEP of iron oxides to a more acidic condition, i.e., 6.5. In the presence of both $Pb(NO_3)_2$ and SDS, the IEP of the colloidal suspension system was 8.4.

The SCD reading of various colloidal systems as affected by the pH value are shown in Figs. 2A and 2B. Generally speaking, patterns of SC are similar to those of zeta potential among the four colloidal systems, respectively (Fig. 2A). A very similar pattern was also observed when $FeSO_4$ was utilized (Fig. 2B). However, compared with zeta potential data, either no positive IEPs could be located or IEPs were not the same as

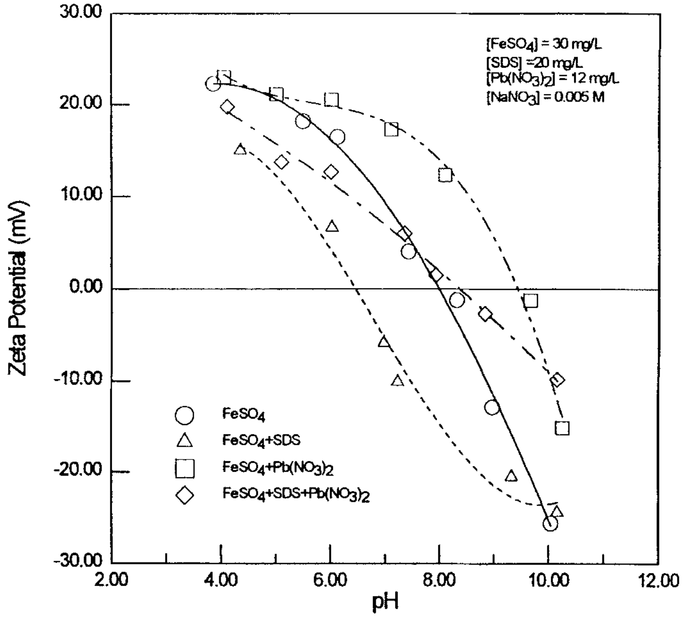

FIG. 1B Zeta potential of systems as functions of pH. Experimental conditions: [$FeSO_4$] = 30 mg/L, [$Pb(NO_3)_2$] = 12 mg/L, [SDS] = 20 mg/L, [$NaNO_3$] = 0.005 M.

previously determined from zeta potential measurements. This has been reported and could be explained in terms of the offset of streaming current measurements (1, 17, 23). For the colloidal system consisting of iron oxide (α-FeOOH), SDS, and $Pb(NO_3)_2$, which was examined in the flotation experiment, SC decreased with increasing pH value throughout a pH range of 3.0 to 10.0. The SC can be linearly correlated to the zeta potential (ZP) (Fig. 3A) and written as

$$[SC] = 0.0527[ZP] - 0.429 \qquad (R^2 = 0.828)$$

or

$$[SC] = 0.000325[ZP]^3 - 0.0208[ZP]^2 - 0.358[ZP] - 2.808$$
$$(R^2 = 0.890)$$

And for the amorphous iron oxide colloidal formed from $FeSO_4$ (Fig. 3B):

$$[SC] = 0.0197[ZP] + 0.316 \qquad (R^2 = 0.938)$$

Colloids formed by $FeSO_4$(aq) show better correlation between the streaming current reading and the zeta potential than that of α-FeOOH.

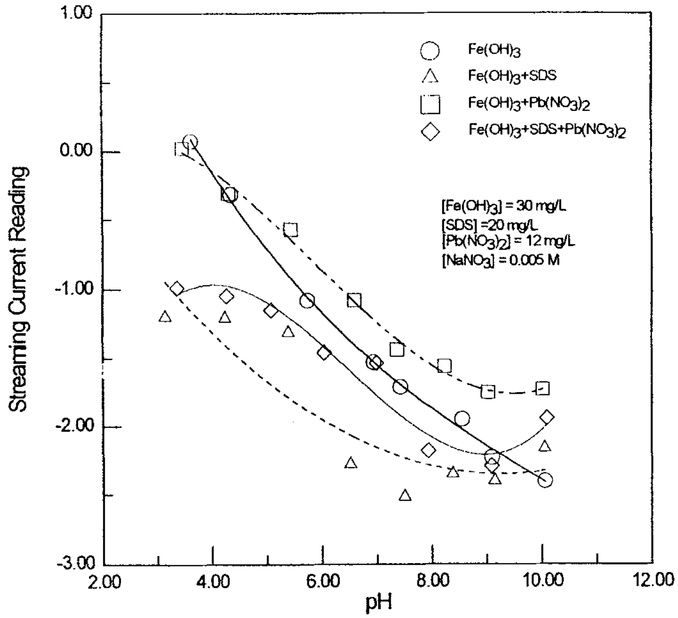

FIG. 2A Streaming current reading of systems as functions of pH. Experimental conditions: $[Fe(OH)_3] = 30$ mg/L, $[SDS] = 20$ mg/L, $[Pb(NO_3)_2] = 12$ mg/L, $[NaNO_3] = 0.005$ M.

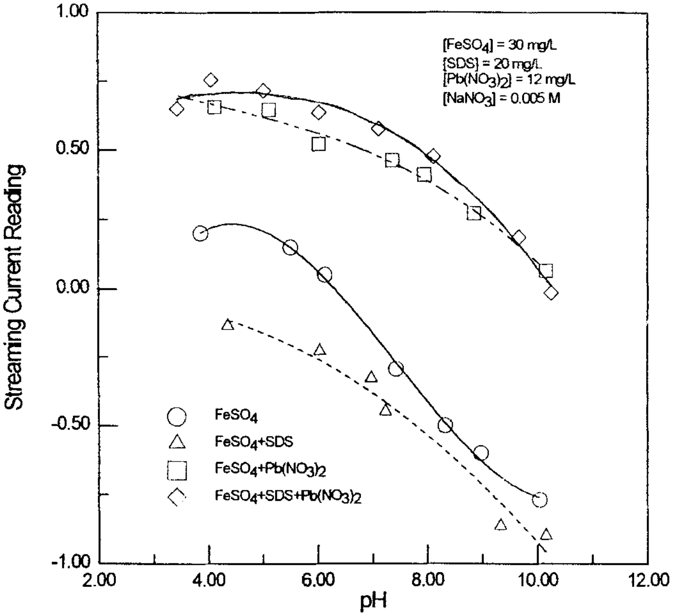

FIG. 2B Streaming current reading of systems as functions of pH. Experimental conditions: $[FeSO_4] = 30$ mg/L, $[SDS] = 20$ mg/L, $[Pb(NO_3)_2] = 12$ mg/L, $[NaNO_3] = 0.005$ M.

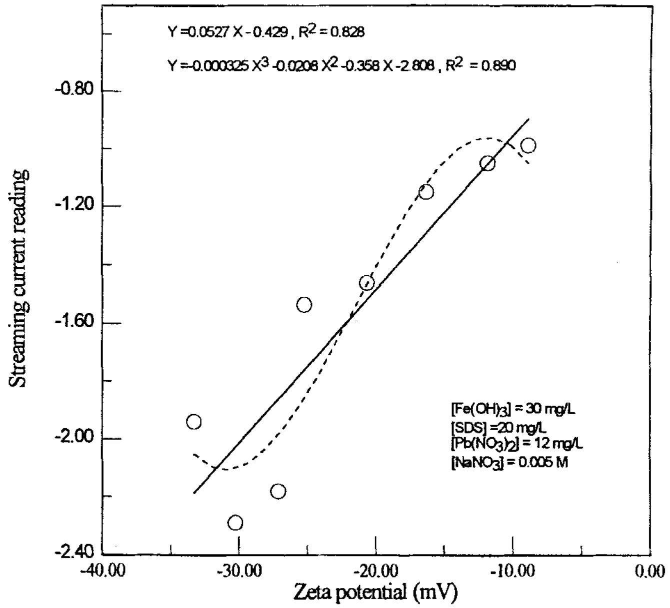

FIG. 3A Correlation between streaming current and zeta potential of colloidal systems. Experimental conditions: [Fe(OH)$_3$] = 30 mg/L, [SDS] = 20 mg/L, [Pb(NO$_3$)$_2$] = 12 mg/L, [NaNO$_3$] = 0.005 M.

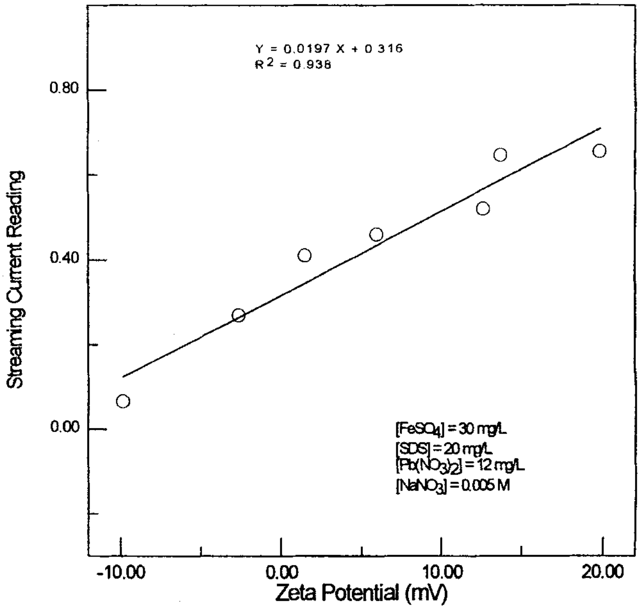

FIG. 3B Correlation between streaming current and zeta potential of colloidal systems. Experimental conditions: [Fe(OH)$_3$] = 30 mg/L, [SDS] = 20 mg/L, [Pb(NO$_3$)$_2$] = 12 mg/L, [NaNO$_3$] = 0.005 M.

The observations in the current work show that SCD could replace zeta meter in assessing adsorbing colloid flotation of Pb(II) and other heavy metals. It is also possible to apply SCD in the automatic control of flotation processes. Dissimilar to our previous work when the removal of As(V) was of interest, it is acknowledged that several pathways exist in the flotation of Pb(II) and other heavy metals. Adsorbing colloid flotation is one of the them (10, 12, 14). Heavy metals may be removed through homogeneous phase foam fractionation from aqueous solution (8, 15). They may also be removed through precipitate flotation (7, 16). SCD could possibly be applied in flotation processes when colloids are involved, such as adsorbing colloid flotation and precipitate flotation. Since complicated colloidal systems are commonly encountered, it is especially helpful in determining the surface charge of colloidal systems in any adsorbing colloid flotation process. Through streaming current monitoring, the optimum conditions for separation can be predicted. Additionally, on-line monitoring of both pH and SC could keep track of colloidal systems during flotation processes. Consequently, better automatic control of flotation processes will become possible. Further research on the flotation process by using an on-line SCD to continuously optimize the chemical dose by feedback control can delineate these proposed advantages.

Adsorbing Colloid Flotation of Pb(II)

The removal of Pb(II) as affected by pH is shown in Fig. 4. At pH 3, the removal efficiency gradually increased to ca. 20% in 20 minutes of reaction time. A more rapid reaction and a higher removal percentage (40%) of Pb(II) was observed at pH 7. However, when the reactions were carried out at pH 8 and pH 10, rapid removal of over 85% Pb(II) was found. In order to elaborate on the mechanism of adsorbing colloid flotation of Pb(II), chemical speciation of Pb(II) was further evaluated by using GEOCHEM software (24). The results are shown in Fig. 5. Soluble lead ion [$Pb^{2+}(aq)$] is the dominant species when the pH is lower than 6.4, while lead exists mainly as hydroxide precipitate [$Pb(OH)_2(s)$] when the pH is higher than 6.4. $PbOH^{+}(aq)$ exists only under neutral conditions. This implies that both flotation and precipitation reactions are possibly involved in the removal of Pb(II) under neutral to alkaline conditions. Furthermore, to examine the flotation mechanism under acidic conditions, the effect of the presence of SDS on Pb(II) removal at pH 3 was studied (Fig. 6A). In the absence of SDS, no Pb(II) was removed, while ca. 20% Pb(II) was removed in the presence of 20 mg/L SDS. However, no significant difference in Pb(II) removal was found at pH 3.0, either in the absence or presence of iron oxide colloid (Fig. 6B). While it is acknowledged that Pb(II) does not adsorb onto iron oxide surfaces under acidic conditions

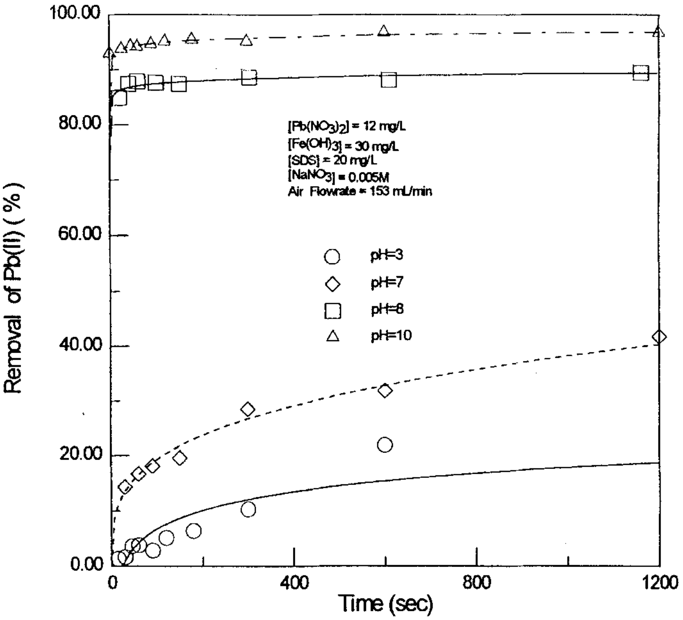

FIG. 4 Removal of Pb(II) as affected by pH. Experimental conditions: $[Pb(NO_3)_2]$ = 12 mg/L, $[Fe(OH)_3]$ = 30 mg/L, [SDS] = 20 mg/L, $[NaNO_3]$ = 0.005 M, air flow rate = 153 mL/min.

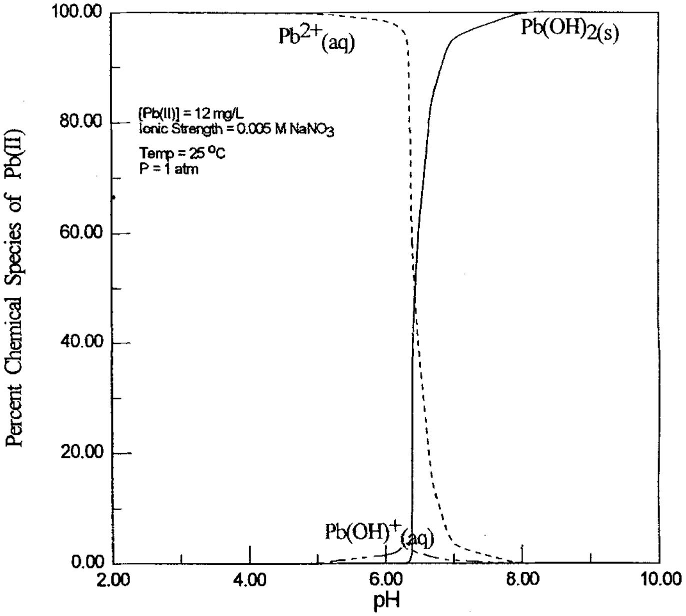

FIG. 5 Chemical speciation of lead predicted by GEOCHEM. [Pb(II)] = 12 mg/L, $[NaNO_3]$ = 0.005 M, 25°C, 1 atm.

(3, 4), it is proposed that at a pH of 3 or lower, Pb(II) is mainly removed from the solution through foam fractionation. This could well explain the results in Figs. 6A and 6B.

To examine the flotation of Pb(II) under neutral pH conditions, Pb(II) removal in the presence of 30 and 60 mg/L of α-FeOOH, respectively, at pH 7 was studied. The results are shown in Fig. 7. It was found that a higher concentration of α-FeOOH could make for better removal efficiency. This indicates that adsorbing colloid flotation is significant at pH 7.0. Next, the effects of SDS and α-FeOOH concentrations on the removal of Pb(II) at pH 8.0 were examined and are shown in Figs. 8A and 8B. In the absence of SDS, the removal of Pb(II) was ca. 72%. When the SDS concentration was increased to 10 and 20 mg/L, respectively, a Pb(II) removal efficiency of over 82% was achieved. Concerning the effect of α-FeOOH concentration on the removal of Pb(II), it was found that there was no significant effect when the α-FeOOH concentration exceeded 5 mg/L (Fig. 8B). It is obvious that Pb(II) was removed from the aqueous phase mostly via $Pb(OH)_2$ precipitation (12, 13, 16). To verify this proposed mechanism, flotation experiments at pH 8.0 and under different

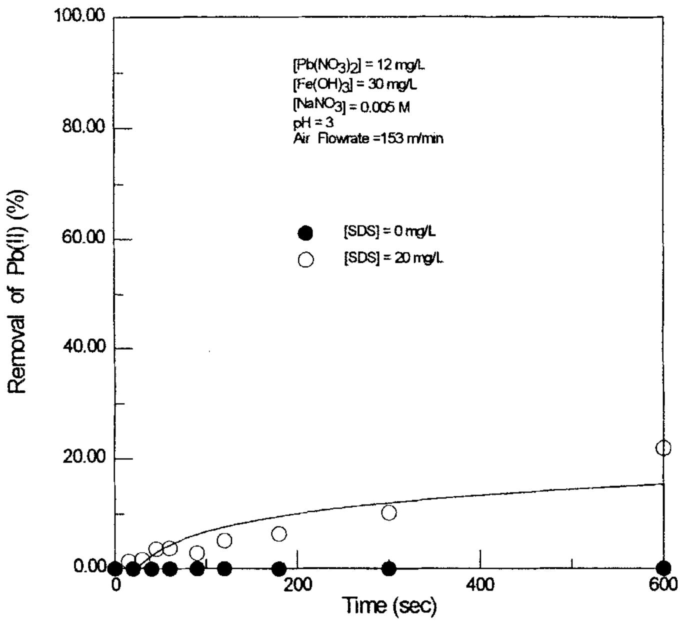

FIG. 6A Removal of Pb(II) as affected by 20 mg/L of SDS. Experimental conditions: $[Pb(NO_3)_2]$ = 12 mg/L, $[Fe(OH)_3]$ = 30 mg/L, $[NaNO_3]$ = 0.005 M, pH = 3, air flow rate = 153 mL/min.

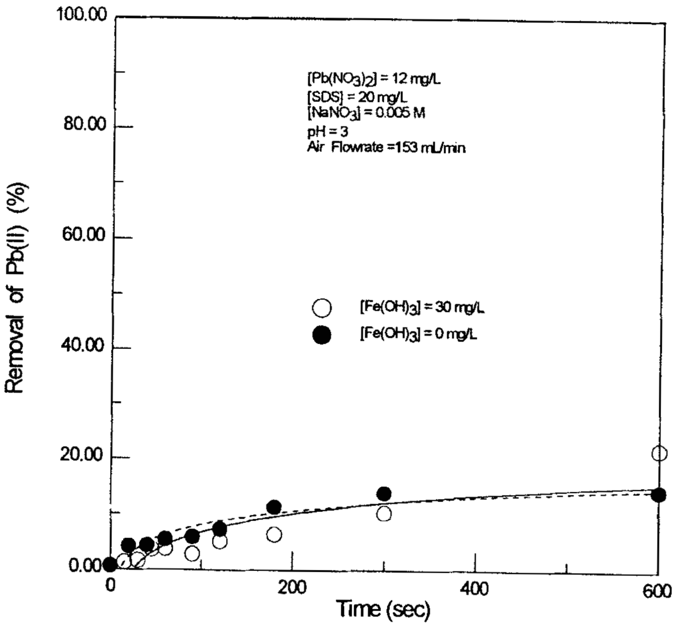

FIG. 6B Removal of Pb(II) as affected by 30 mg/L of [Fe(OH)$_3$]. Experimental conditions: [Pb(NO$_3$)$_2$] = 12 mg/L, SDS = 20 mg/L, [NaNO$_3$] = 0.005 M, pH 3, air flow rate = 153 mL/min.

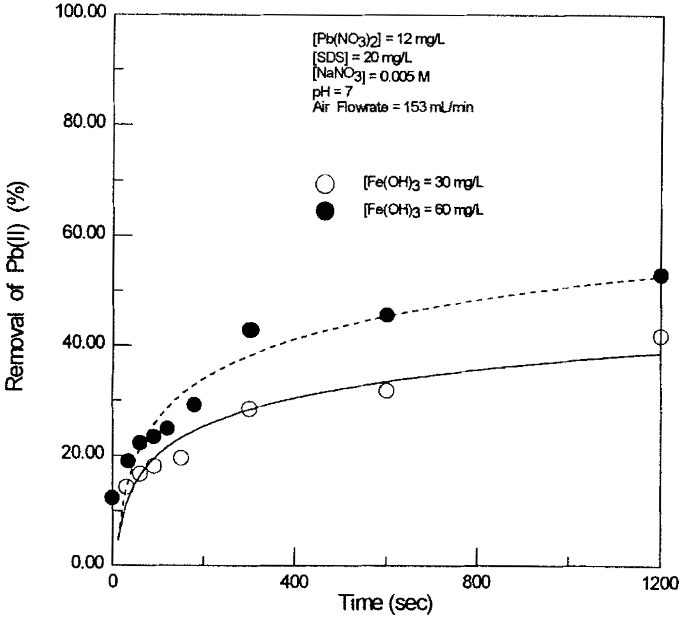

FIG. 7 Removal of Pb(II) as affected by [Fe(OH)$_3$] concentration. Experimental conditions: [Pb(NO$_3$)$_2$] = 12 mg/L, SDS = 20 mg/L, [NaNO$_3$] = 0.005 M, pH 7, air flow rate = 153 mL/min.

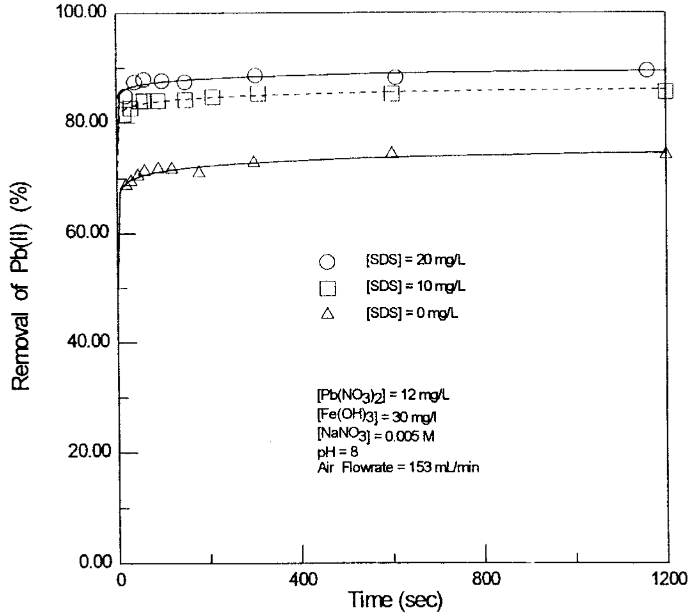

FIG. 8A Removal of Pb(II) as affected by SDS concentration. Experimental conditions: $[Pb(NO_3)_2]$ = 12 mg/L, $[Fe(OH)_3]$ = 30 mg/L, $[NaNO_3]$ = 0.005 M, pH 8, air flow rate = 153 mL/min.

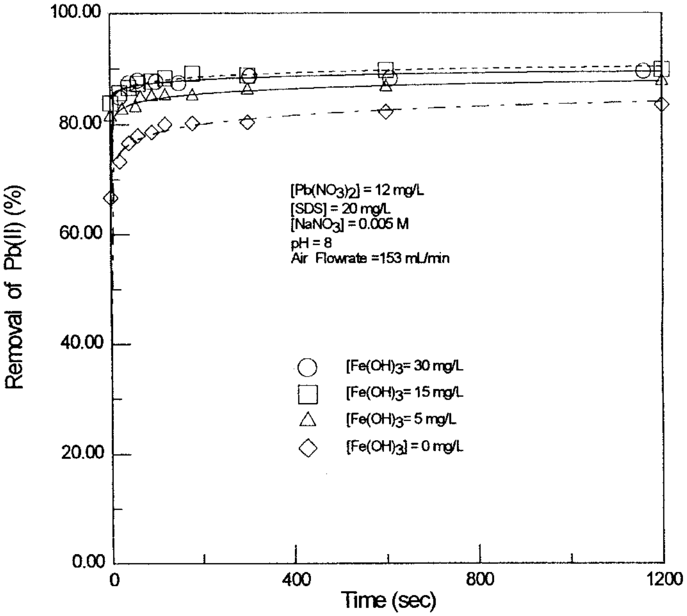

FIG. 8B Removal of Pb(II) as affected by $[Fe(OH)_3]$ concentration. Experimental conditions: $[Pb(NO_3)_2]$ = 12 mg/L, SDS = 20 mg/L, $[NaNO_3]$ = 0.005 M, pH 8, air flow rate = 153 mL/min.

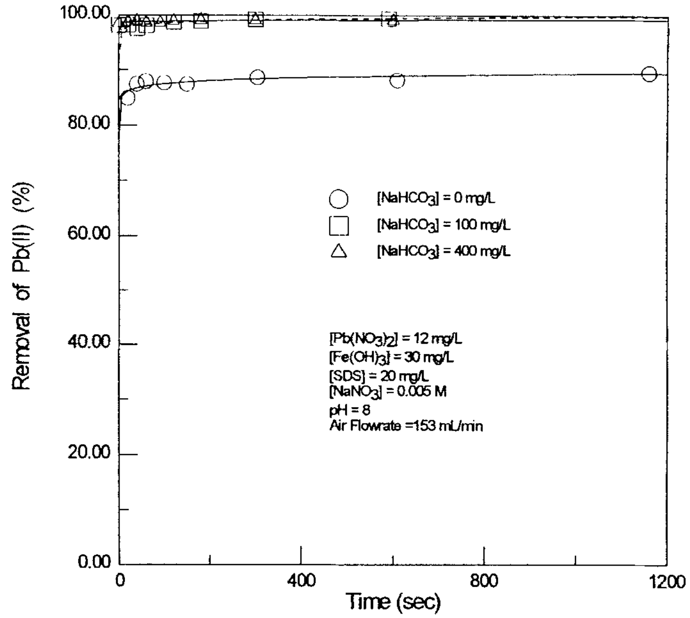

FIG. 8C Removal of Pb(II) as affected by alkalinity. Experimental conditions: $[Pb(NO_3)_2]$ = 12 mg/L, $[Fe(OH)_3]$ = 30 mg/L, SDS = 20 mg/L, $[NaNO_3]$ = 0.005 M, pH 8, air flow rate = 153 mL/min.

alkalinity were made. Figure 8C shows that higher alkalinity facilitates better precipitation of $Pb(OH)_2$ and better removal efficiency. This finding supports our proposed mechanism that precipitate flotation is determining at a pH of 8.0 or higher.

Flotation of Pb(II) when $FeSO_4$ was used to form an amorphous iron oxide colloid was also investigated. Experiments were conducted with a constant concentration of $FeSO_4$ at various pH values. Figure 9 shows the removal of Pb(II) as affected by pH. The removal efficiency increased with increasing pH. Less than 10% of Pb(II) was removed at pH 3.0. At pH 5.0, the removal percentage was raised to 44%. When the pH was 6.0, 63% of Pb(II) was removed. Almost all the Pb(II) was removed when the pH was higher than 7.0. Since amorphous iron oxide starts to precipitate when the pH is higher than 4.0 (1), Pb(II) removal under different pH values could likewise be divided into three regions. Under acidic conditions (region I), with pH values less than 3.0, Pb(II) removal can be solely attributed to homogeneous phase foam fractionation. In region II, where the pH ranges from 4.0 to 7.0, combined foam fractionation and adsorbing colloid flotation of Pb(II) are both important. When the pH values are

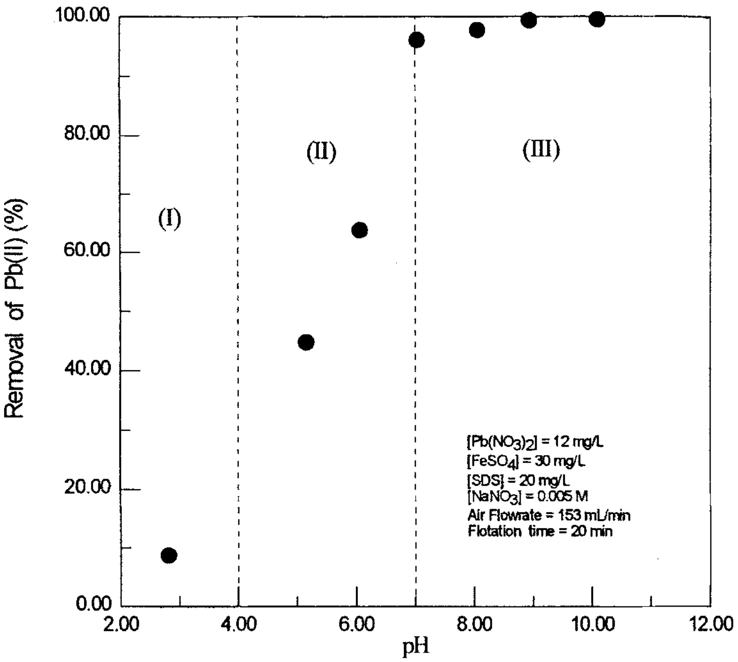

FIG. 9 Removal of Pb(II) as affected by pH. Experimental conditions: $[Pb(NO_3)_2]$ = 12 mg/L, $[FeSO_4]$ = 30 mg/L, [SDS] = 20 mg/L, $[NaNO_3]$ = 0.005 M, air flow rate = 153 mL/min, flotation time = 20 minutes.

higher than 7.0, Pb(II) is mostly removed through precipitate flotation in the form of $Pb(OH)_2(s)$ or a Pb–Fe coprecipitate (16).

CONCLUSION

In the flotation of Pb(II), the streaming current detector (SCD) was found to function well in determining the electrical properties of colloidal systems and to correlate satisfactorily with zeta potential measurements. Preliminary results show it is feasible for SCD to be utilized in adsorbing colloid flotation of Pb(II) and other heavy metals. In addition, removal of Pb(II) by adsorbing colloid flotation was examined. Effects of pH, colloidal concentrations, and SDS concentrations were investigated. It is proposed that Pb(II) can be removed through foam fractionation in the form of $Pb^{2+}(aq)$, or through adsorbing colloid flotation of the soluble species $Pb^{2+}(aq)$ and $PbOH^{+}(aq)$, or through precipitate flotation of $Pb(OH)_2(s)$ or a Pb–Fe coprecipitate, depending on the pH.

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