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Adsorbing Colloid Flotation of As(V)--Feasibility of Utilizing Streaming Current Detector

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Adsorbing Colloid Flotation of As(V)—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 flotation processes. The adsorbing colloid flotation (ACF) of As(V) with iron oxide and sodium dodecylsulfate (SDS) was investigated. Both zeta potential and streaming current (SC) reading of each colloidal systems were measured. Results show SC changed with pH values and can be well correlated to zeta potential. The optimum pH range for As(V) removal was found to be ca. 4–5. Removal of As(V) as affected by SDS concentration, colloidal concentration, and gas flow rate were investigated. It is proposed that both free arsenic oxyanions and iron-arsenate complex were involved in the process. Preliminary results show it feasible for SCD to be utilized in adsorbing colloid flotation.

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

INTRODUCTION

Consumption of groundwater containing As has caused Blackfoot disease in certain parts of Taiwan (1). There has been great concern about arsenate pollution. Some epidemiological studies and engineering control

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measures have been investigated. Extensive literature shows that As can be removed from water by utilizing various separation processes such as adsorption (2–4) and foam separation (5, 6). Some local researchers have studied coagulation/flocculation reactions for the removal of As(V) (7). Although foam separation processes have been widely utilized for other purposes, they have never been tested in Taiwan for the removal of As(V) from contaminated groundwater. Various applications of foam separation, such as minerals enrichment, preconcentration of biochemicals, and pollution control have been reviewed (8). Important parameters, such as pH, activators, surfactant, and gas flow rate, are well known to affect significantly flotation processes. Among all of these variables, the surface charge of a colloidal system plays a key role in determining the optimum conditions for separation. The zeta potentials of colloidal systems are commonly measured to determine how solution pH, colloid, surfactant, and contaminants in the aqueous phase are interacting, and consequently how they affect the removal efficiency. Recent developments in on-line detection of the surface charge of a colloidal system, such as the streaming current detector (SCD), has facilitated the automatic control of the coagulation reaction (9–11). The major objective of the current work is to study the feasibility of utilizing SCD in the adsorbing colloid flotation of As(V). In addition to zeta potential measurement, streaming current readings (SC) will be detected and compared with the zeta potential. To remove As(V) from aqueous solution, $FeSO_4$ was used to form colloid, and sodium dodecylsulfate (SDS) was used as the collector. Experimental results will be compared with theoretical predictions. In case SCD proves to be applicable, better on-line control of flotation processes will be achieved.

EXPERIMENTAL

Streaming Current and Zeta Potential Measurement

Before each zeta potential measurement, the cell of the zeta meter (Photal ELS-600) was first immersed in aqua regia and then rinsed with pure water. A Blank experiment was conducted to ensure the absence of any impurity. The pH values of colloidal systems were adjusted with 0.1 N HNO_3 and 0.1 N NaOH. Temperature was kept at 27°C. For the measurement of streaming current, a streaming current detector (Chemtrac 2000-XR) was used. The sensor was thoroughly cleaned by a cleanser (Alconox detergent 8) several times and rinsed with pure water. The cell and accessory parts, such as syringe and tube, were placed under an ultrasonic vibrator (CTI SK-20) for at least 12 hours. Through repeated operation using pure water as the blank test, it was found that the streaming current of a pure water system should yield a reading of -5.20. This blank offset has been reported (12, 13). Before each set of experiments, perchloric acid solution (5 M) was used to clean the sensor until this background reading was reached. Readings of pH and streaming current were not recorded until the system was stabilized.

Adsorbing Colloid Flotation Experiment

The cell utilized in the flotation experiment was based on a developed technique (14). The flotation column is made of acrylic with the overflow height at 45 cm and an inside diameter of 3.5 cm. Nitrogen gas flows through a flask filled with distilled water to get it saturated before it is charged into the column. Stock solutions of 2 g/L $FeSO_4$ (Nacalai Tesque), 1 g/L SDS (J.T. Baker), 1 M $NaNO_3$ (Merck), and 100 mg/L Na_2HAsO_4 (Nacalai Tesque) were prepared. Each time a 500 mL solution of a different concentration was utilized. After the pH value was adjusted by 1 M NaOH and 1 M HNO_3, the solution was poured into the flotation column for the removal of As(V). Samples were taken at certain time interval. They were filtered through a 0.45-μm membrane filter (MFS) before the residual As(V) 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

Zeta potentials of colloidal systems as affected by pH are shown in Fig. 1. Amorphous iron oxides started to form when the pH value was higher than ca. 3.0 for the simple $FeSO_4$ system. The iron oxides were positively charged under acidic conditions. The isoelectric point (IEP) was found at 8.0. This is consistent with a reported value (15). When 20 mg/L SDS was added to the $FeSO_4$ system, the zeta potential shifted to the acidic range as a result of the adsorption of SDS (16). In the presence of 10 mg/L Na_2HAsO_4, the zeta potential was also shifted, to a greater extent, to the acidic range. The IEP became 4.0. This change of surface charge and the subsequent shift of IEP are caused by the specific adsorption of $H_xAsO_4^{x-3}$ ions (17). The zeta potential of the $FeSO_4$ system in the presence of SDS and Na_2HAsO_4 under acidic conditions was almost identical to that of the $FeSO_4$ and Na_2HAsO_4 system. The IEP was 4.0. The arsenic oxyanions $H_xAsO_4^{x-3}$ affect the surface charge of iron oxides more significantly than does SDS. This also implies that the specific adsorption of $H_xAsO_4^{x-3}$ onto iron oxide surfaces is stronger than that of SDS.

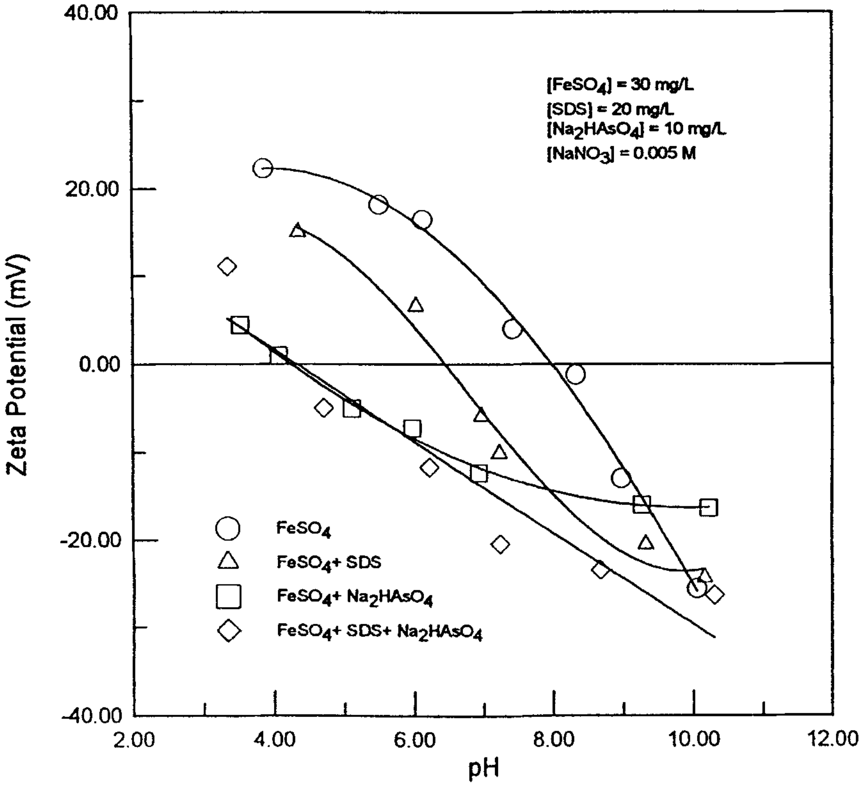

FIG. 1 Zeta potential of systems as functions of pH.

The streaming current (SC) detector reading of colloidal systems as affected by pH value are shown in Fig. 2. Generally speaking, patterns of SC are similar to those of zeta potential among the four colloidal systems. For the colloidal system $FeSO_4$, SDS, and Na_2HAsO_4 that was to be examined in the flotation experiment, SC decreased with increasing pH value and exerted an IEP at ca. 4.0. It is notable that the SC can be linearly correlated to the zeta potential (ZP) (Figs. 3A and 3B) and can be written as

$$SC = 0.0303 \cdot ZP + 0.00997 \qquad (R^2 = 0.969)$$

$$SC = 0.0192 \cdot ZP - 0.128 \qquad (R^2 = 0.944)$$

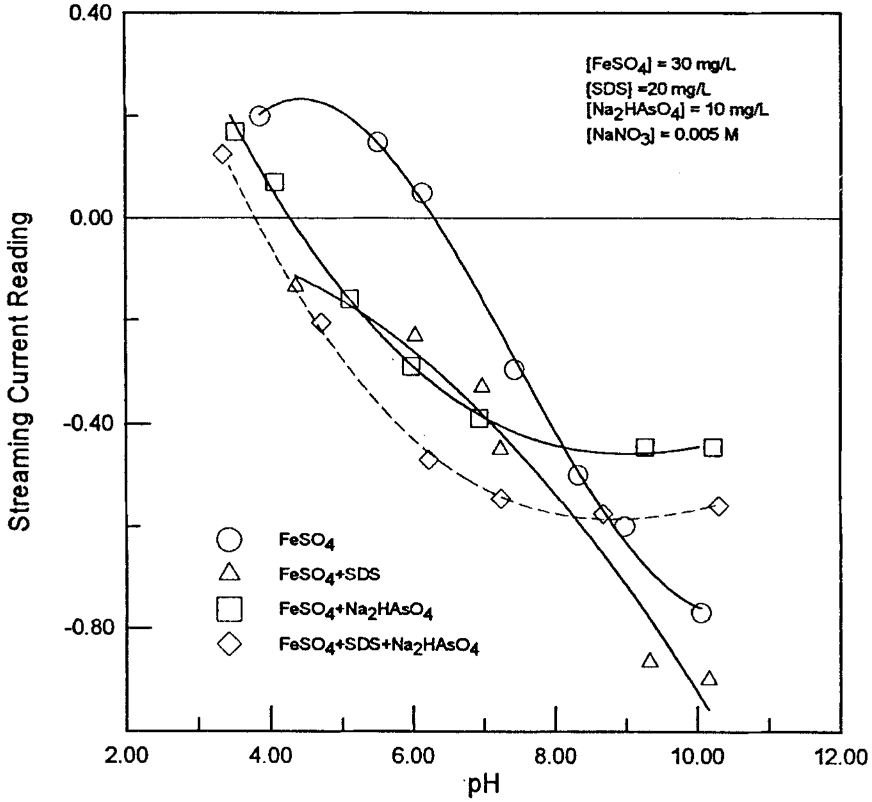

FIG. 2 Streaming current reading of systems as functions of pH.

An instrument showing increasing application for the in-situ monitoring of colloidal systems and the theoretical background of SCD has been elaborated by some investigators. Some theoretical relationships have been proposed between streaming current and zeta potential. It is basically assumed that colloids to be characterized are adsorbed uniformly on the inside surfaces of the SCD's sensor, and possess a diffuse layer of counterions. The reciprocating movement of a piston inside the dead-ended cylindrical bore makes counterions move and produces electrical current which can be measured by electrodes in the surrounding cylinder. An equation based upon several simplified assumptions was first proposed to relate streaming current with zeta potential (12). The equation was further modi-

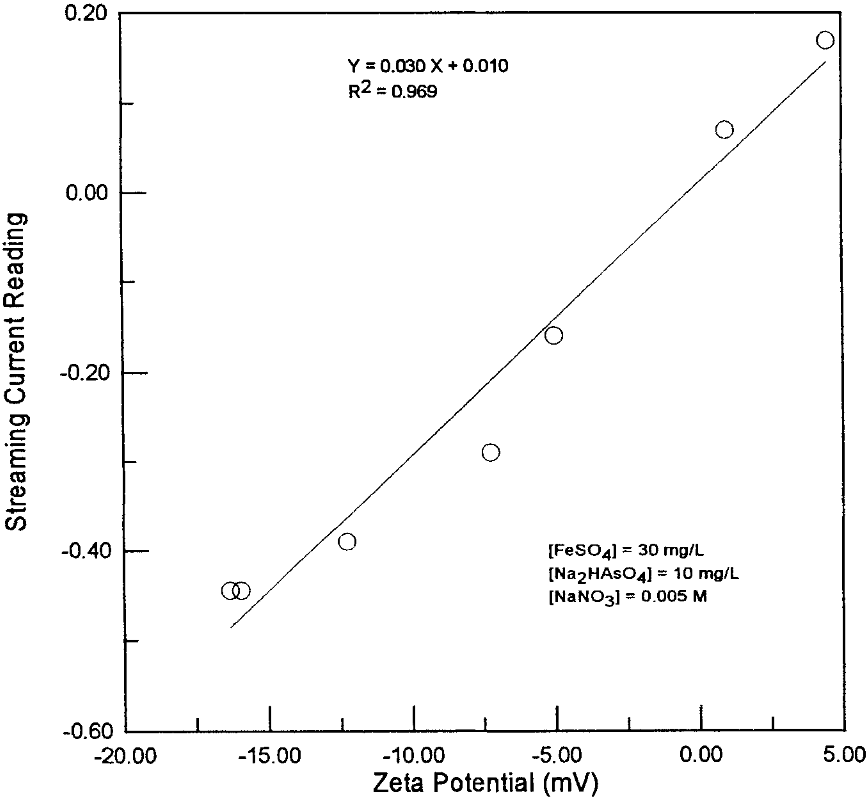

FIG. 3A Correlation between streaming current and zeta potential of colloidal systems.

fied based upon different assumptions about the velocity profile within the SCD sensor and electrical double layer structure (18). It has been indicated that the theoretical correlation between streaming current and zeta potential could be more complex, and there still exist certain shortcomings in theory (13). Nevertheless, the SCD functions satisfactorily as an instrument to monitor the electrical properties of colloids. It is acknowledged that many parameters are involved in the adsorbing colloid flotation process, and the on-line detection of the electrokinetics of a colloidal system would certainly facilitate a better understanding and possibly automatic control of the process. What has been observed in the current work shows that SCD could replace the zeta meter and possibly be applied in the automatic control of adsorbing colloid flotation processes. Complex

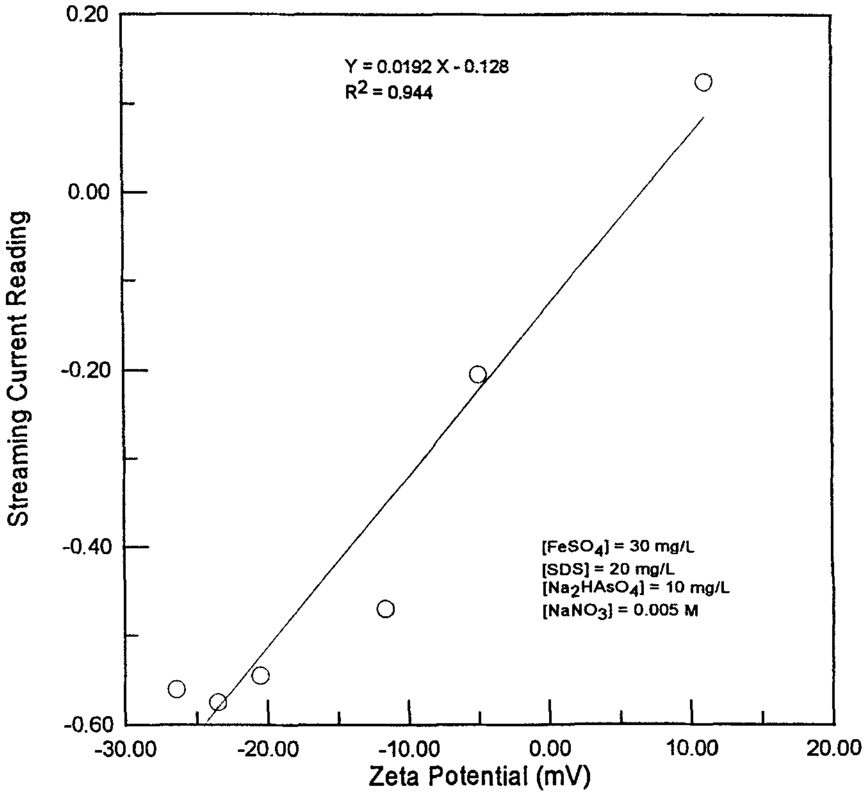

FIG. 3B Correlation between streaming current and zeta potential of colloidal systems.

colloidal systems are commonly encountered in the adsorbing colloid flotation process. Once the optimum conditions for separation are determined, on-line monitoring of both pH and SC could ensure control of the colloidal systems involved.

Adsorbing Colloid Flotation of As(V)

The effect of pH on the removal of As(V) is shown in Fig. 4. There are three segments in the removal curve: an increase of removal efficiency in the 2 to 4 pH range, a maximum removal of As(V) (over 65%) in the 4 to 5 pH range, and a decrease in As(V) removal above pH 5. This is consistent with previous findings (5, 6).

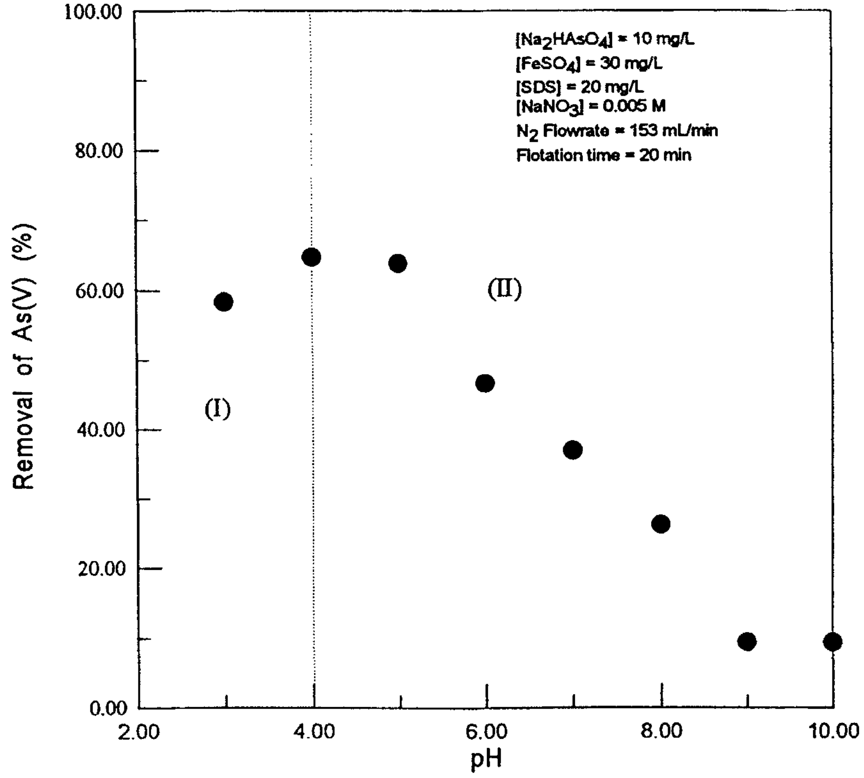

FIG. 4 Removal of As(V) as affected by pH.

The effect of SDS concentration on the removal of As(V) at pH 4.0 is shown in Fig. 5. In the absence of SDS, the removal of As(V) was ca. 40%, mostly via adsorption onto iron oxide surfaces. When the SDS concentration was 20 mg/L, stable foam was produced and a maximum removal efficiency of 62% was achieved. Any further increase of SDS concentration would reduce the removal efficiency slightly. This inhibitory effect of an excessive amount of SDS has been discussed (5, 6).

In order to investigate the effect coprecipitant concentrations on the removal of As(V), experiments were conducted with various concentrations of $FeSO_4$ at pH 4.0. Figure 6 shows the removal of As(V) as affected by $FeSO_4$ concentration. The removal efficiency increased with an increasing concentration of $FeSO_4$. Only 15% of As(V) was removed if no $FeSO_4$ was added. This removal could be attributed to homogeneous

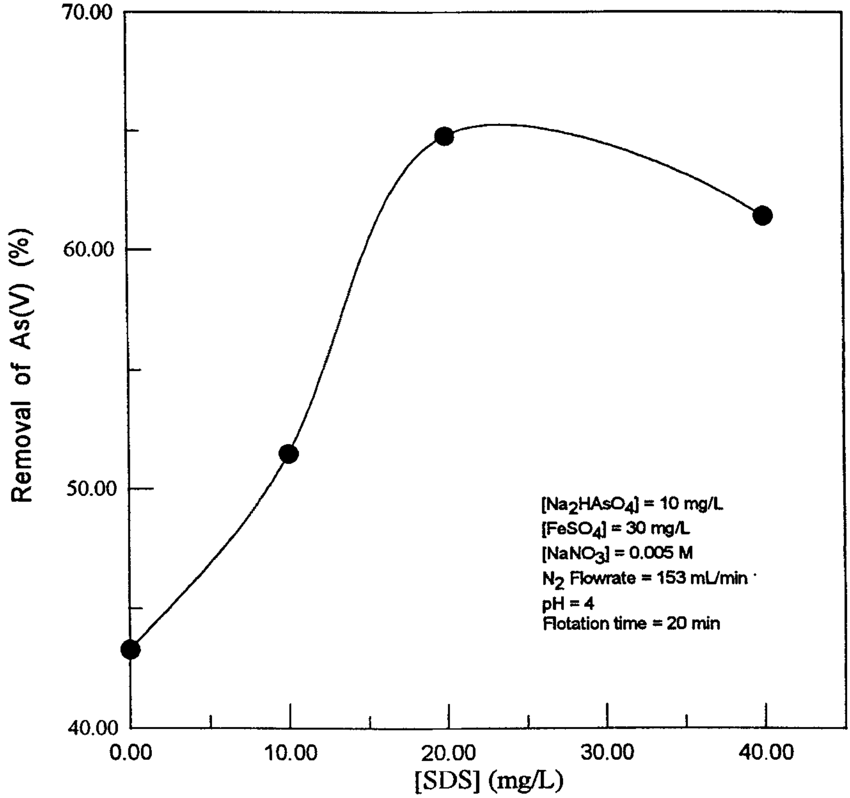

FIG. 5 Removal of As(V) as affected by SDS concentration.

phase foam fractionation. At a $FeSO_4$ concentration of 10 mg/L, the removal percentage increased to 25%. When the $FeSO_4$ concentration was increased to 60 mg/L, 80% of As(V) was removed. It is believed that a higher As(V) removal efficiency will be achieved if a larger amount of $FeSO_4$ is utilized.

In the flotation process, the gas flow rate affects the bubble size and flow patterns in the column, therefore, neither too fast nor too slow a flow rate is advisable (6, 8). In the current work, the effect of N_2 flow rate was examined. The results are shown in Fig. 7. When the N_2 flow rate was increased from 59 to 153 mL/min, As(V) removal was increased from 40 to 65%. However, the maximum removal achievable by increasing the N_2 flow rate was limited to ca. 75%. Any further increase of the gas

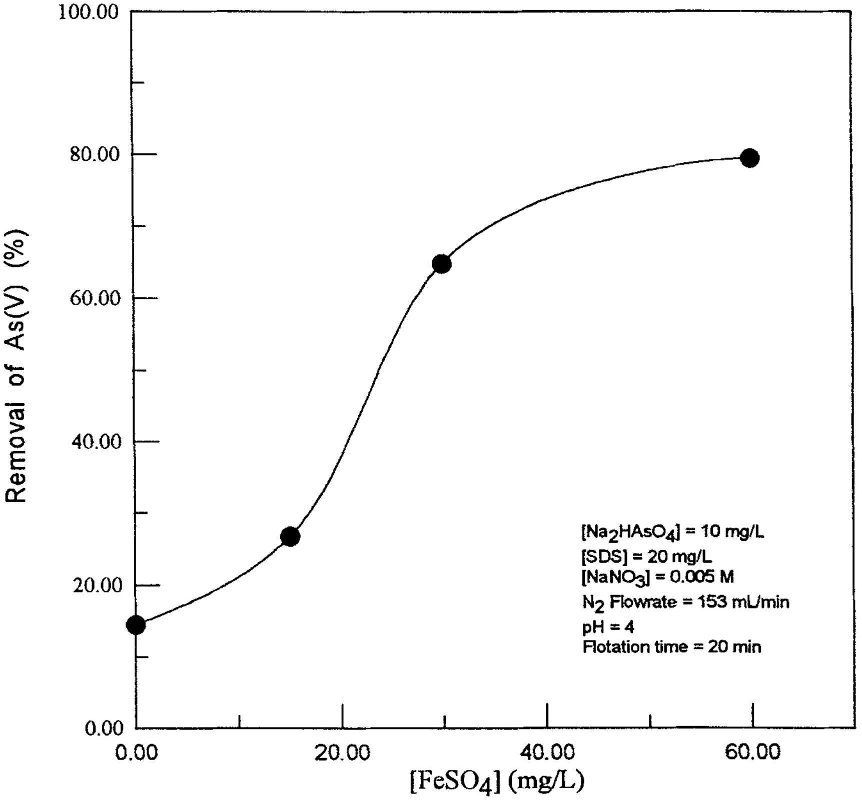

FIG. 6 Removal of As(V) as affected by [$FeSO_4$] concentration.

flow rate above 153 mL/min had only an insignificant enhancement effect on As(V) removal.

In order to elaborate on the mechanism of adsorbing colloid flotation of As(V), chemical speciation was further evaluated. The deprotonation constants (pK_{a1}, pK_{a2}, pK_{a3}) of arsenate are 2.22, 6.98, and 11.50, respectively (19). The dominant species is H_3AsO_4 when the pH is lower than 2.22. In the pH range from 2.22 to 6.98, arsenate exists mainly as $H_2AsO_4^-$. When the pH is between 6.98 to 11.50, $HAsO_4^{2-}$ is the dominant species. A computer software, GEOCHEM (20), was utilized to calculate thermodynamic equilibria, including precipitation of Fe(II) and the complexation reaction between Fe(II) and soluble arsenate species. The predicted results are shown in Fig. 8. At 25°C and 1 atm, the majority of

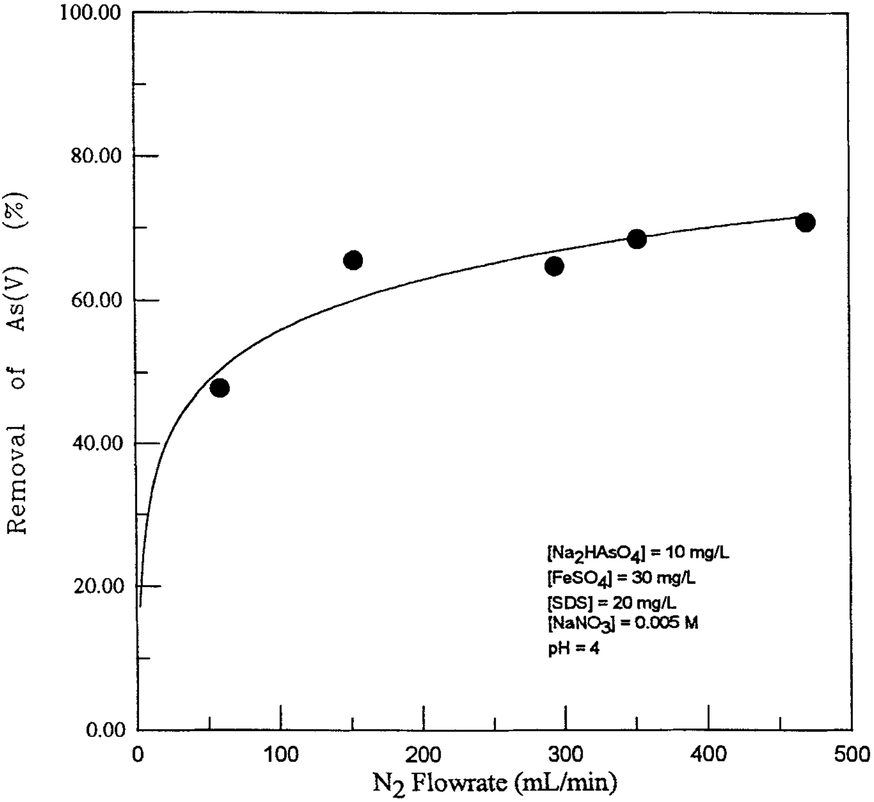

FIG. 7 Removal of As(V) as affected by N_2 flow rate.

As(V) exists as a chemical complex with iron, Fe–AsO_4(aq), in the pH range from 2.2 to 3.0. When the pH was higher than 3.0, iron oxide starts to form and soluble Fe(II) decreases to ca. 60%. When the pH is higher than 4.0, only a small amount of soluble Fe(II) exists. Amorphous iron oxide forms the dominant fraction of Fe(II). Based on the zeta potential and streaming current measurements, it is clear that at a pH lower than 3.0 the removal of As is primarily the foam fractionation of $H_2AsO_4^-$ and Fe–AsO_4 complex. When iron oxide colloid starts to form, adsorption of $H_2AsO_4^-$ and Fe–AsO_4 complex onto the positively charged surface (iron oxide) becomes significant. Therefore, the As(V) can either be removed through foam fractionation in the form of $H_2AsO_4^-$ and Fe–AsO_4 complex, or through adsorbing colloid flotation of the soluble As(V) species, such

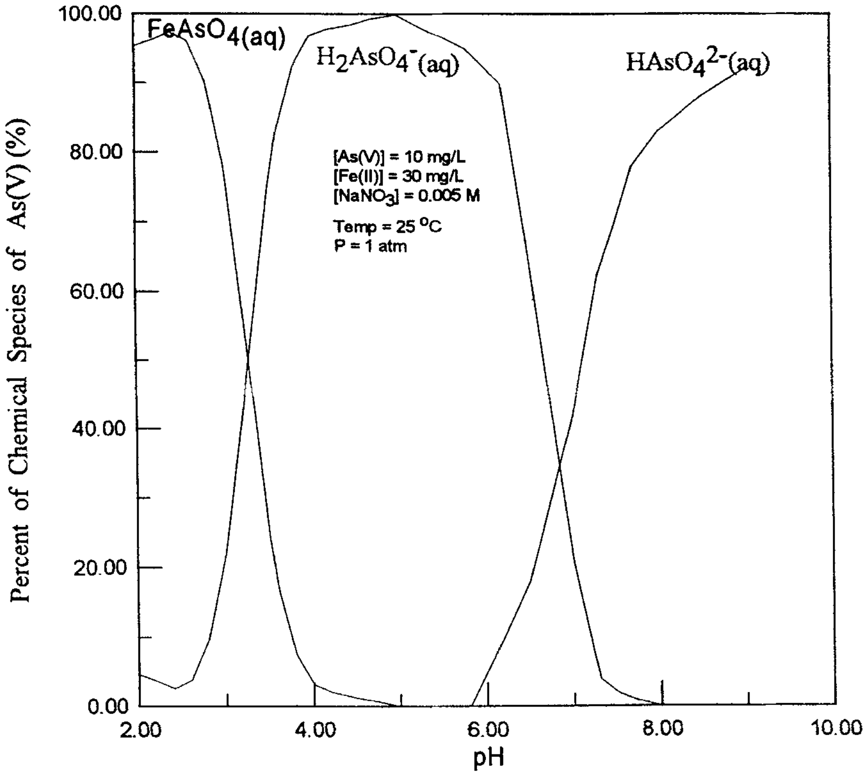

FIG. 8 Chemical speciation of arsenate predicted by GEOCHEM.

as $H_2AsO_4^-$, $HAsO_4^{2-}$, and Fe–AsO_4 complex. This proposed mechanism is supported by the fact that most As(V) is strongly adsorbed onto amorphous iron oxide under acidic condition, and a smaller amount is adsorbed under alkaline condition (2, 17).

CONCLUSION

A 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 processes. In addition, removal of As(V) by adsorbing colloid flotation was examined. Effects of pH, coprecipitant concentrations, SDS concentrations, and gas flow rate were investigated. It is proposed that As(V), depending on pH, can either be removed through foam fractionation in the form of $H_2AsO_4^-$ and Fe–AsO_4 complex, or through adsorbing colloid flotation of soluble As(V) species and Fe–AsO_4 complex.

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