SIMULTANEOUS REMOVAL OF CADMIUM AND TURBIDITY IN CONTAMINATED SOIL-WASHING WATER BY ELECTROFLOTATION

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Abstract
The removal of cadmium and turbidity from contaminated soil-washing water was studied by Electroflotation (EF) at the laboratory scale by using sodium lauryl sulfate (SLS) as an anionic surfactant, and calcium hydroxide (Ca(OH)₂) as a coagulant. The stoichiometric cadmium to collector (SLS) and coagulant (Ca(OH)₂) ratio was 1:4.5. Significant removal of cadmium (100 %, not detected in the residual) and turbidity (95.7 %) was obtained by EF without any coagulant additions. As a consequence, EF is considered an effective method to separate cadmium and turbidity from contaminated soil-washing water. The EF process may have practical applications for the removal of other hazardous metals from contaminated soil-washing water.

Keywords
Cadmium; electroflotation; soil-washing water; turbidity

INTRODUCTION
Cadmium (Cd) is a highly toxic metal that is rather ubiquitous in its distribution around the world. With the increasing use of cadmium for electroplating, batteries, alloys, pigments, stabilizers for catalysts and in semiconductors and TV tube phosphors, it represents a great potential hazard to humans and the environment (Kefala et al., 1999). Cadmium contamination in soil occurs mostly near cadmium mines and industrial sites. Although cadmium contaminated soil can be treated by various means, the commonly used treatment system is physical soil washing. Following soil washing, separation of dissolved cadmium and colloidal particles from the process and effluent water is required. One of the methods frequently used for cadmium separation from solutions is chemical precipitation as the hydroxide, sulfide, or other insoluble salts combined with flocculation. This process presents a difficult task with respect to the disposal of the sludge that is generated (Zouboulis et al., 1995; Scorzelli et al., 1999).

Other methods of metal removal, which include ion exchange, reverse osmosis, evaporation and activated carbon adsorption, can each do a specific job effectively but have high capital and operating costs. In addition, these technologies require more skilful operation and maintenance (Poon, 1997) and the concentration of residual toxic metals in solutions greatly influences the removal efficiency of the heavy metals (Kefala et al., 1999). Because industrial wastewater is a complex mixture, this drawback is the main deterrent to the wider application of these methods (Scorzelli et al., 1999; Hun et al., 1995). The purpose of the experiments described in this paper is to develop other effective methods for cadmium and turbidity removal in solutions and to determine an optimum operation parameter for EF.
MATERIALS AND METHODS

Materials
The cadmium-contaminated soil washing water that was used in the experiments was prepared as follows. Sand was enmeshed by two sieves between 0.15~0.85 mm. Cadmium chloride (2.073 g CdCl₂·2.5H₂O) was dissolved in distilled water in a 1L volumetric flask, to give a stock solution of 1000 ppm cadmium. A volume of 100 mL of this solution was transferred into a jar, which contained the 500 g of enmeshed sand. The sand was subsequently immersed in the 100 mL cadmium solution and was then rinsed with potable water in a 10 L volume tube, followed by stirring for an hour. The cadmium-contaminated soil washing water prepared in this way is termed “raw water” in this paper.

An anionic surfactant (Sodium Lauryl Sulfate, CH₃(CH₂)₁₀CH₂OSO₃Na) and an anionic coagulant (Ca(OH)₂ with a purity of 95 %) were used for cadmium removal. Both chemicals were used at a ratio of coagulant to cadmium of 4.5:1.

EF experiments
In this study, a bench-scale EF system was used to remove turbidity and Cd²⁺. It consisted of four 2 x 4 cm aluminum metal plates (or metal electrodes) that were placed on the bottom of the reactor. The total area of the electrodes was 32 cm². The position of the four electrodes was adjustable to within 0.6 cm (Song et al., 2001). A DC power supply provided 420 mA at 24 V. An effluent port was located 3.5 cm above the bottom of the reactor, or 1.5 cm above the upper edge of the metal electrodes. The dimensions of the cylinder were 45 cm in height and 6 cm in diameter, as shown in Figure 1.

Fig. 1. Schematic diagram of EF

The whole samples were collected from the effluent port at 5, 10 and 20 minutes from the start of each run. Measurement of pH, particle size, turbidity and concentration of Cd²⁺ were performed for each experiment. Additionally, ICP-AES (ICP-Atomic Emission Spectrometer, SHIMADZU, Japan) was performed to measure Cd²⁺.
RESULTS AND DISCUSSION

The characteristics of raw water
The raw water used for the EF experiments is as shown in Table 1.

Table 1. Characteristics of raw water

<table>
<thead>
<tr>
<th></th>
<th>Turbidity (ntu)</th>
<th>pH</th>
<th>Temperature (°C)</th>
<th>Cd²⁺ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw water</td>
<td>93.8</td>
<td>6.93</td>
<td>18.5</td>
<td>2.30</td>
</tr>
</tbody>
</table>

Turbidity and cadmium removal by EF
The EF experiment was carried out at first without SLS and calcium hydroxide. The following EF experiments were performed using SLS or calcium hydroxide. A stoichiometric ratio between Cd²⁺ and the collectors (SLS and Ca(OH)₂) was needed to remove cadmium from the raw water. The association of the metal ion, M²⁺, and the lauryl sulfate, RSO₄⁻, or hydroxide, 2OH⁻ can be represented by the following reactions:

\[
\begin{align*}
M^{2+} + 2RSO_4^- & \rightarrow M(RSO_4)_2 \\
M^{2+} + 2OH^- & \rightarrow M(OH)_2
\end{align*}
\]

(1)

Figure 2 and Figure 3 show turbidity and cadmium removal rates during EF. As shown in Figure 2, the EF experiments gave a very good turbidity removal rate. Turbidity removal by EF was 95.7% after 20 minutes, while pH increased from 6.93 to 8.12. EF did not require the addition of aluminum sulfate, because dissolution of the metal electrode produced Al³⁺ ions. The result of the addition of Ca(OH)₂ was similar to the simple EF in turbidity removal, and the pH was increased to 8.7 due to the addition of hydroxide ions.

Figure 3 represents cadmium removal rates measured during EF. The calcium hydroxide without coagulants showed a better cadmium removal rate after 10 minutes than the simple EF, because the hydroxides helped to remove cadmium. Therefore, Ca(OH)₂ could be used to achieve more rapid cadmium removal within 10 minutes. However, EF alone is also a very effective process as it does not need any additional chemicals for turbidity and cadmium removal. Use of SLS also showed a good cadmium removal rate at 20 minutes, but SLS did not have a good turbidity removal effect, because it caused turbidity by itself when it was dissolved in raw water.

The mechanism of cadmium removal by EF tests can be explained by the following reactions:
Anode : \( \text{Al} \rightarrow \text{Al}^{3+} + 3 \text{e}^- \)  
Cathode : \( 2\text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{H}_2 \text{(gas)} + 2\text{OH}^- \)  

In raw water : 
- \( \text{Cd}^{2+} + 2\text{OH}^- \rightarrow \text{Cd(OH)}_2 \cdot \text{precipitates} \)  
- \( \text{Al}^{3+} + 3\text{OH}^- \rightarrow \text{Al(OH)}_3 \cdot \text{precipitates} \)  
- Cationic ions (\( \text{Cd}^{2+} \) and \( \text{Al}^{3+} \)) + anionic particles \( \rightarrow \) precipitates as flocs

The cathode produces two hydroxides when \( 2\text{H}_2\text{O} \) receives two electrons from the anode, at which aluminum loses three electrons. However, this electron exchange reaction was not enough to describe very competitive interactions among negatively charged particles, cationic cadmium ions, \( \text{Al}^{3+} \) from the anode electrode and \( 2\text{OH}^- \) from the cathode electrode, as well as other components of raw water. An explanation of this complex reaction can be established by the fact that when a trivalent aluminum ion is produced, at least three hydroxide ions should be produced at the cathode to satisfy the turbidity removal and cadmium removal as well as the pH increase. In addition, insoluble \( \text{Al(OH)}_3 \) is formed between pH 5 and pH 9 and \( \text{Al(OH)}_4^- \) is formed over the pH value of 10 as an alkalinity zone. When EF is performed between pH 8–10, \( \text{Al}^{3+} \) ions will be removed as \( \text{Al(OH)}_3 \) forms. The hydroxides also formed cadmium precipitates by raising the pH value of the contaminated water (see reaction 3). These precipitates were removed from the raw water by rising gas (\( \text{H}_2 \)) bubbles generated by the cathode, in accordance with the concept of coflotation.

**Particle Size Distribution by EF**

![Particle Size Distribution by EF](image)

Figure 4 shows the particle size distribution by EF. When EF was performed, turbid particles were removed within 5 min. However, the fine particles between 1.2 µm and 3.3 µm increased as shown in Figure 4. It was observed that \( \text{Al}^{3+} \) ions from the anode electrodes reacted with \( \text{OH}^- \) from the cathode electrodes and formed \( \text{Al(OH)}_3 \) as mentioned regarding reaction 3. Due to the formation of \( \text{Al(OH)}_3 \), pH did not increase more than 9. These precipitates of \( \text{Al(OH)}_3 \) increased as the fine particles as operation time increased.

**CONCLUSIONS**

The best removal rate, of 100% cadmium and 95.7% turbidity, was obtained without any
coagulants at 20 minutes in EF. By adding calcium hydroxide, the reaction time could be reduced. This result shows that cadmium and turbidity can be removed without injecting SLS and calcium hydroxide or any other chemicals when EF is adopted. Additionally, EF shows great promise by way of cost reduction, as chemicals are not required.

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REFERENCES