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Removal of heavy metals from mining impacted water by an electrocoagulation-ultrafiltration hybrid process

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ABSTRACT

In this study, the use of an electrocoagulation-ultrafiltration (EC-UF) hybrid system for the treatment of mining impacted wastewater was investigated. A model wastewater solution containing copper, lead, cadmium and other constituents representative of mining impacted wastewater was used in this investigation. The effects of key operational parameters including electrolysis time, current density, and solution pH on the performance of the EC and EC-UF systems were systematically investigated. The removal rates of copper and lead by the EC process were consistently higher than that of cadmium. It is probable that the removal mechanism of cadmium was different from that of the base metal copper and lead. Results reported here indicate that an EC-UF hybrid system could be very effective in removing heavy metals at high solution pH. At an acidic condition, the removal efficiency of heavy metal by both EC and UF reduced dramatically. However, the overall removal efficiency by the hybrid EC-UF system remained quite high. Results reported here suggest that EC and UF can complement each other very well for optimum removal efficiency.

Keywords: Electrocoagulation; Heavy metals; Mining wastewater; Ultrafiltration

1. Introduction

Increased demand for minerals and other resources from the mining sector has resulted in the opening of new mines and the expansion of existing ones. However, mining activities often result in unintended environmental consequence. As a result, the mining sector is subjected to increasing environmental regulations [1]. One area of concern is the mining tailings that are left after the valuable materials has been extracted [1,2]. These tailings usually consist of crushed rock, sands and clays mixed together in a slurry or 'slime'. Tailing dumps where tailings are disposed often contaminate the underlying water tables due to leaching of trace elements such as heavy metals from the slime [2].

Tailing liquids are typically acidic and saline. Depending on the mine site, tailing liquids can have a high content of particulate matter, process chemicals and heavy metals [2]. While a variety of technologies including neutralisation and precipitation, ion exchange, reverse osmosis, bioremediation, and wetland treatment can be utilised to remove the contaminants present in mine waters, the effectiveness of these processes has not been well demonstrated [2]. Amongst these, neutralisation and precipitation are probably the most common treatment option. This technique involves a traditional chemical coagulation-flocculation step to remove the solids and heavy metals from the water. Salts of either trivalent aluminium or iron are often used as the coagulant. An alternative to this conventional approach is the use of electrocoagulation, which has recently received much scientific attention [3]. Successful treatment of various types of wastewater has been widely demonstrated in the literature [4–9].

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The basic premise of electrocoagulation is the production of a coagulant in wastewater through electrolysis. This is achieved by applying a current to a pair of cathode and anode. The anode is often made of either aluminium or iron, which can release the aluminium or iron metallic ions into the solution and react with the wastewater as a chemically induced coagulant would [3]. When aluminium electrodes are used, the Al^{3+} ions formed can efficiently remove heavy metal molecules through precipitation, the precipitate is then captured by the $Al(OH)_3$ flocs and floated into a gel state. An electrocoagulation system can be of relatively low cost while still achieving a high-removal efficiency of fine particulates in polluted water. The treatment equipment can be very compact and almost completely automated, and with the addition of sustainable technologies such as solar power, completely self-sufficient [3]. Coagulation using an electrochemical method can be effective although the fine particulates in the sludge can make precipitation quite difficult. Consequently, the use of a membrane filtration step which effectively removes the flocs produced can greatly enhance the electrocoagulation process [8].

Membrane systems are increasingly being used due to their advantages in regard to selectivity, high-surface area per unit volume, and their potential to control the contact and mixing of two phases. Two commonly used membrane technologies are ultrafiltration and microfiltration which recover macromolecules and retain suspended particles and colloids. In any membrane filtration applications, fouling is found to be a major problem. Fouling of microfiltration membranes was found to be negligible when a flotation pretreatment was included in the system, which also has the advantage of low operating costs [10]. In a preliminary study, Mavrov *et al*. demonstrated that a membrane process placed downstream of an electrocoagulation cell has been proven to be effective for selenium removal [8], which creates a very fine sludge when iron plates are used in the electrocoagulation step. The fine sludge produced is completely removed from the water with a microfiltration membrane placed downstream. As a result, these two systems can work together to create an efficient process that creates less solid waste, and uses less chemicals than other traditional treatment methods, such as a conventional lime neutralisation/ferric coagulation/filtration process [8].

The concept of combining electrocoagulation and ultrafiltration in a hybrid system for the treatment of mining impacted water remains relatively new. Since electrocoagulation is a rather complex process, sound understanding of major factors governing the performance of a hybrid EC-UF system is of paramount important. This study aims to investigate the effects of key operational parameters including electrolysis time, current density, and solution pH on the removal of three selected heavy metals – namely copper, lead, and cadmium – by laboratory scale EC and EC-UF systems. The synergy when electrocoagulation is used in combination with an ultrafiltration process is also examined.

2. Materials and methods

2.1. Model wastewater characteristics

The model wastewater was prepared by dissolving the required amount of copper sulphate, lead nitrate, cadmium nitrate, calcium chloride and sodium sulphate into deionised water. Sigma Aldrich humic acids were also used at a concentration of 20 mg/L (equivalent to 6 mg/L as TOC) to simulate a typical organic content of the mining impacted wastewater. The final solution contained approximately 200 mg/L Na^+, 500 mg/L Ca^{2+}, 150 mg/L Cl^-, 15 mg/L NO^-_3, and 500 mg/L SO_4^{2-}. Other characteristics of the model wastewater solution are shown in Table 1. The composition of this synthetic wastewater is similar to that of mine water retrieved from Ranger Uranium Mine in the Northern Territory and Mary Kathleen Mine in Queensland. With the exception of the humic acids, all chemical used in this study were of analytical grade and were supplied by Sigma Aldrich (Castle Hill, NSW, Australia). When it was desirable to maintain a constant pH throughout the EC experiment, buffer solutions were used. These included citric-phosphate buffer for pH 4, pH 5 and pH 6, and boric buffer for pH 7 and pH 8.

2.2. Electrocoagulation experiments

Electrocoagulation (EC) experiments were conducted in batch mode. The EC set up consisted of two

Table 1
Characteristics of the model wastewater.

pH	Conductivity (mS/cm)	Turbidity (NTU)	Organic matter (mg/L as TOC)	Cu (mg/L)	Pb (mg/L)	Cd (mg/L)
6.0–6.5	12	10	6	5	10	20

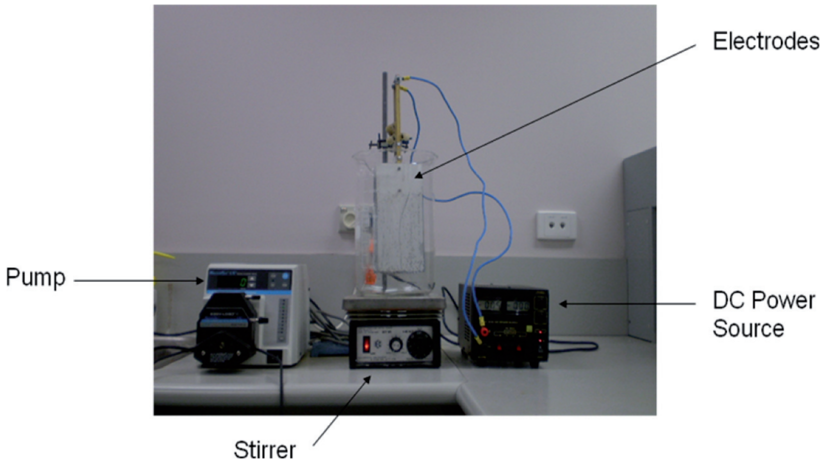

Fig. 1. The electrocoagulation apparatus.

vertical aluminium electrodes submerged in a 2500 mL beaker, a stirring plate, and a DC power converter (Q1770, Dick Smith Electronics, Australia) (Fig. 1). The aluminium electrodes had a dimension of 250 mm × 100 mm × 3 mm (purity of 95%–97%) and were supplied by Ullrich Aluminium Company Ltd., (Sydney, Australia). The distance between the two electrodes was fixed at 20 mm using a pair of Perspex spacer. Prior to each experiment, the electrodes were thoroughly cleaned using 1 N nitric acid and steel wool. When not in used, the electrodes were preserved in an acid bath (1 N nitric acid) to prevent oxidation of the surface.

Volume of the model wastewater used for each EC experiment was 2000 mL. The solution was gently agitated by a magnetic stirring bar. The applied current was adjusted using the DC power converter and the voltage across the two electrodes was also recorded. At the conclusion of each EC experiment, the solution was allowed to settle for 90 minutes and 1500 mL of clear supernatant was carefully extracted from the beaker using a peristaltic pump for analysis and subsequent membrane filtration experiments. The inlet of the pump was suspended to the middle of the beaker to avoid extracting sludge at the bottom as well as at the top of the beaker.

2.3. Membrane filtration

A commercially available ultrafiltration membrane was used in this investigation. According to the manufacturer, this is a polyamide thin-film composite membrane with a microporous polysulfone supporting layer. The membranes were received as flat sheet samples and were stored dry at 4°C. Filtration experiments were conducted using a bench scale dead-end filtration system. The stirred cell was made of stainless steel with an inner diameter of 56.6 mm resulting in a membrane surface area of 21.2 cm^2. This cell was connected to a 1 gal Millipore stainless steel reservoir. An Amicon magnetic stirrer was used and the stirrer speed was set at 400 rpm to minimize polarization concentration effects. Instrument grade air was used to pressurize the system. The permeate flux was measured by a Sartorius digital balance which was connected to a personal computer. A new membrane sample was used for each experiment. Each experiment was conducted in two steps. The membrane was compacted for 1 hour using MilliQ water at 6 bars. In the second step, the reservoir and cell were emptied and 1 liter of the test solution was introduced to the reservoir. The pressure was set to 4 bars and 6 permeate samples of 100 mL each were collected for analysis.

2.4. Analytical methods

A Hach 2100 N turbidity meter was used for turbidity measurement while conductivity and pH were measured using a Metrom 781 m. A Varian AA – 300 Plus Atomic Absorption Spectrometer (AAS) was used to measure heavy metal concentration in the samples. Prior to analysis, the samples were diluted, acidified with nitric acid, and digested to ensure that the target metals in the sample were completely converted into a soluble form.

3. Results and discussions

3.1. Optimising the electrocoagulation process

Electrocoagulation is a complex process and its efficiency regarding contaminant removal can be governed by several factors. Some of the most important factors include electrolysis time, characteristics of the influent, electrode material, and current density. It is therefore essential to elucidate the influence of such factors on the removal efficiency of heavy metals and to optimize the

EC process. In the current study, this was accomplished by isolating and investigating the effects of a single parameter on performance of the EC system while maintaining all other parameters constant. Parameters investigated in this study include electrolysis time, current density and pH of the EC reactor. The influence of these parameters on the heavy metal removal is delineated in the next section.

3.1.1. *Effects of electrocoagulation time*

During an ideal EC process, the amount of coagulant dosed into the solution is proportional to the reaction time and the current. In fact, for a particular electrical current flow in an electrolytic cell, the mass of aluminium theoretically dissolved from the sacrificial anode can be quantified by Faraday's law:

$$m = \frac{ItM}{zF} \tag{1}$$

where *m* is the amount of anode material dissolved (g), *I* is the current (A), *t* is the electrolysis time (s), *M* is the specific molecular weight (g mol^{-1}), *z* is the number of electrons involved in the reaction and *F* is the Faraday's constant (96,485 As mol^{-1}). As can be seen in Fig. 2(A), when a current density (100 A/m^2) was applied, the EC process was very effective for the removal of heavy metals. Removal efficiency in excess of 90% was achieved after 30 minutes reaction time. In addition, at a high-current density, removal rates of the three selected heavy metals were quite similar. No further increase in removal could be observed as the EC process continued beyond 30 minutes.

It is interesting to note that due to the electrolytic process, the solution pH in the EC reactor increased within the first 30 minutes running time and beyond this point the solution pH decreased to approximately pH 6.5 after 90 minutes running time. This evolution of pH as a function of reaction time is in fact consistent with the electrolysis reactions occurring in an EC system. The electrode reactions when using aluminium are:

$$\text{Anode:} \quad Al_{(s)} \rightarrow Al^{3+} + 3^{e-} \tag{2}$$

$$\text{Cathode:} \quad 2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^- \tag{3}$$

A further reaction occurs where the Al^{3+} ions precipitate to solid Al(OH)$_3$:

$$Al^{3+} + 3H_2O \leftrightarrow Al(OH)_{3(s)} + 3H^+ \tag{4}$$

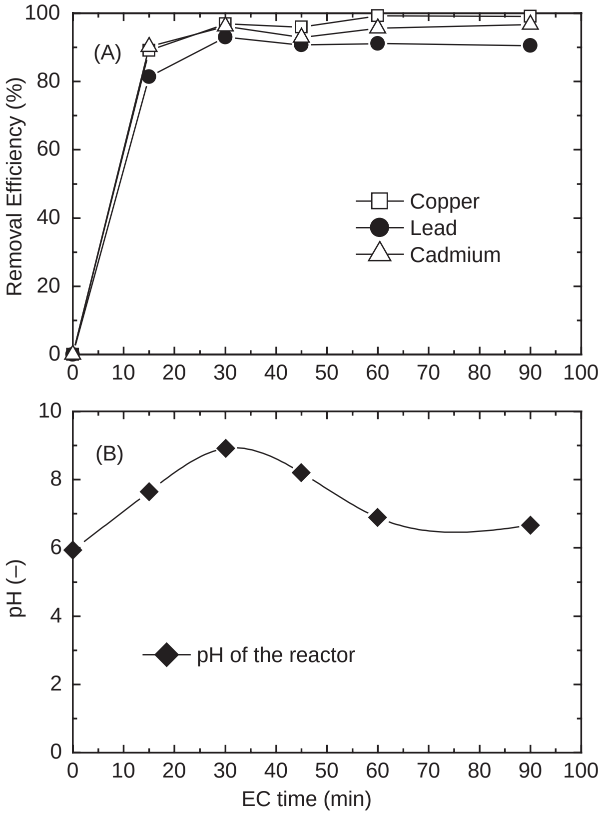

Fig. 2. (A) Removal of copper, lead, and cadmium by EC as a function of electrolysis time. (B) Evolution of the pH of the EC reactor as a function of electrolysis time. The applied current was 2.7 Amp at 30 V, corresponding to a current density of 100 A/m^2.

According to Eqs. 2 and 3, in the first stage electrolytic reactions at the anode and cathode produced one mole of Al^{3+} for every two moles of OH$^-$, leading to an increase in pH of in the EC reactor. However, as excess Al^{3+} was being generated, it was hydrolysed to produce three moles of H$^+$ for every mole of Al^{3+} being generated. As a result, once Al(OH)$_{3(s)}$ was formed, further electrolytic reaction could lead to a decrease in solution pH [Fig. 2(B)]. Such a decrease in solution pH could attribute to an increase in solubility of the heavy metals and amongst other factors, reduce the removal performance efficiency. Consequently, 30 minutes could be considered as the optimum reaction time of the EC system at 100 A/m^2.

3.1.2. *Effects of current density*

The supply of current to the EC system determines the amount of Al^{3+} released from the electrode to the treated solution [3]. The removal efficiency of both copper and lead increased dramatically as the current density increased (Fig. 3). It appears that EC was slightly more

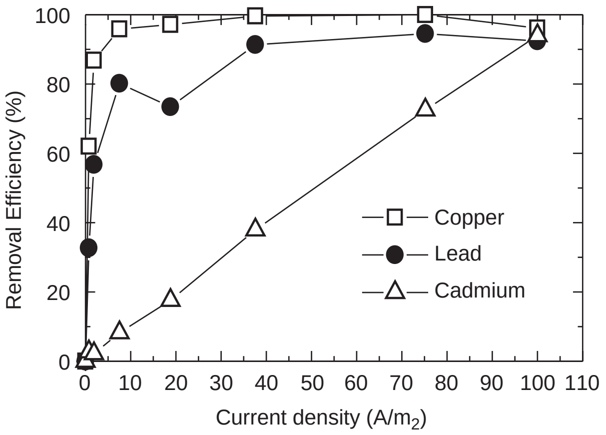

Fig. 3. Removal of copper, lead, and cadmium by EC as a function of current density. The electrolysis time was 30 minutes.

effective for the removal of copper than lead. At a current density of 40 A/m^2 complete removal of copper and approximately 90% removal of lead could be observed. It is striking to note that the EC behaviour of cadmium differed distinctively from those of copper and lead. The removal efficiency of cadmium increased linearly as the current density increased (Fig. 3). Such a relationship has not been well documented in the literature and may be due to more than just coagulant interactions like most of the base metals. Escobar *et al.*, [7] investigated the removal of copper, lead, and cadmium by an EC cell using iron electrodes and revealed a significantly lower removal of cadmium than that of copper and lead. Although the role of current density in governing heavy metal removal efficiency was not specifically studied, the authors reported a linear relationship between current density and the mass of sludge being generated [7]. In good agreement with the data presented here, Heidmann and Calmano [11] found that several base metals including copper, zinc and nickel have a uniform electrochemical behaviour and their removal rates by EC were very similar. In contrast, under the same experimental condition, the electrocoagulation behaviour of Cr(VI) was quite different and the removal rate was substantially lower than that of the base metals [11]. The authors suggested that Cr(VI) underwent a different removal mechanism that include reduction at the cathode before precipitating as hydroxide [11]. However, unlike Cr(VI) which can be reduced to Cr(III), cadmium cannot be further reduced in an aqueous solution. Additional investigation would be needed to systematically delineate the removal mechanism of cadmium by EC.

When a high current density was used, electrical energy can be wasted in heating up the solution and sometime can dramatically reduce the current efficiency [3]. Indeed a small but nevertheless discernible drop in the removal efficiency of copper and lead was observed when the current density increased beyond 75 A/m^2 (Fig. 3). In contrast, cadmium removal continued to increase as the current density increased from 75 to 100 A/m^2. Once again, the data suggests that the removal mechanism of cadmium by EC could be quite different from that of other base metals. Despite being a relatively high value, a current density of 100 A/m^2 is still considered the most appropriate to ensure an adequate removal efficiency of all three metals investigated in this study.

3.1.3. Effects of pH

The effects of the solution pH on EC are reflected by the current efficiency as well as the solubility of metal hydroxides. It is well established that the solution pH can vary dramatically during a typical EC experiment [3]. However, it is surprising to note that most if not all studies available to date have only examined the initial pH values and not the actual pH during the experiment. To evaluate the performance of the EC system at different pH, buffer solution was used to maintain a constant pH throughout the experiment. The effects of the solution pH on the removal rates of the three selected heavy metals were quite significant (Fig. 4). It can be seen that the removal efficiency of the heavy metals were lowest at pH 6, at which the removal rates were negligible for all three selected heavy metals. Higher removal efficiency could be obtained at either more acidic or more alkaline condition. In particular, at pH 7 and 8, copper and lead removal was well above 95% whereas the removal rate of cadmium also increased considerably. On the other hand, at an acidic condition (i.e.: pH 4 and 5), the removal rates of the three metals were considerably low.

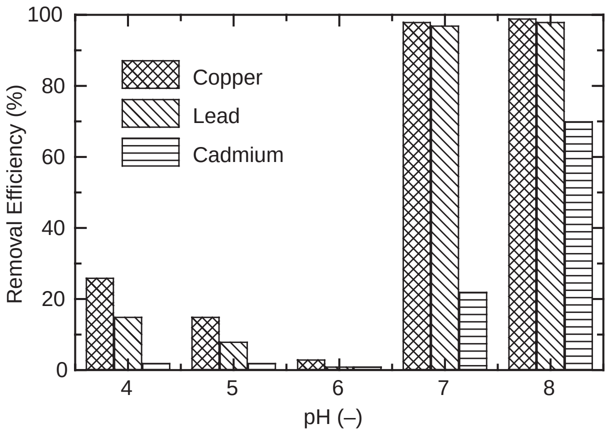

Fig. 4. Removal of copper, lead, and cadmium by EC as a function of the solution pH. The solution pH was kept constant by a buffer solution. The electrolysis time was 30 minutes. The applied current was 2.7 A at 30 V, corresponding to a current density of 100 A/m^2.

Low heavy metal removal efficiency at an acidic condition can probably be attributed to an increase in solubility of these metals and perhaps more importantly the unfavourable condition for metal hydroxide formation. It is possible that the buffers (citric, phosphate and boric) used in this study can interfere with the EC process and the extent of their influence on heavy metal removal efficiency remains unknown. Nevertheless, results reported in Fig. 4 are in good agreement with a consensus hypothesis in the literature that the aluminum current efficiencies are higher at either acidic or alkaline condition than at neutral [3].

3.2. Performance of a hybrid electrocoagulation coagulation – ultrafiltration system

Since mining impacted wastewater is usually acidic in nature [2], the relatively poor performance of EC at low pH seen here can present an important implication for the application of EC in a practical context unless pH of the wastewater can be adjusted to a higher value. It is noteworthy that the removal of heavy metals by membrane filtration (such as ultrafiltration and nanofiltration) can also be highly variable depending on the feed solution characteristic. For example, according to Mehiguene *et al.*, [12] cadmium rejection by the Nanomax nanofiltration membrane was as low as 35% in a chloride or nitrate matrix while copper rejection was considerably higher, ranging from 75%–95% under the same condition. In contrast, in a sulphate matrix, cadmium rejection of as high as 100% was reported. The authors suggested that cadmium rejection was strongly dependent on the presence of co-ions in the feed solution [12]. In a similar study, Ballet *et al.*, [13] reported that at pH 5 rejection of cadmium by the TFC-S nanofiltration membrane was lowest and that the rejection was approximately 50%. At either a higher and lower pH, cadmium rejection was considerably higher. The authors attributed this phenomenon to the variation of the membrane surface charge as a function of solution pH [13]. Interestingly, coagulation has commonly been used as a pretreatment process for membrane filtration. The objective of this section is therefore to examine the synergy when electrocoagualtion is used combination with an ultrafiltration process.

Figure 5 presents the removal rates of heavy metals by EC, UF, and the combination of EC-UF at three different pH. Once again, the solution pH was kept constant throughout the experiments by a buffer solution. Being consistent with the data reported above and the literature, at pH 8, the removal efficiency of all three metals by both EC and UF was quite high. At this pH, the hybrid EC-UF system was able to deliver a near complete removal of well above 97% of all three metals. Considerably lower removal efficiency was observed by the individual treatment process when the solution pH was reduced to pH 6.5 and 4. However, the combined removal efficiency for all three metals was remarkably higher than that of the individual process. Results reported in Fig. 5 clearly show that EC and UF can complement each other very well with regard to the removal of heavy metals. Even at pH 4, the removal rates of copper, lead, and cadmium by the hybrid EC-UF system was 86%, 74%, and 31% respectively (Fig. 5). It is also noteworthy that under all experimental conditions, turbidity of the effluent after EC-UF treatment was consistently below 0.5 NTU.

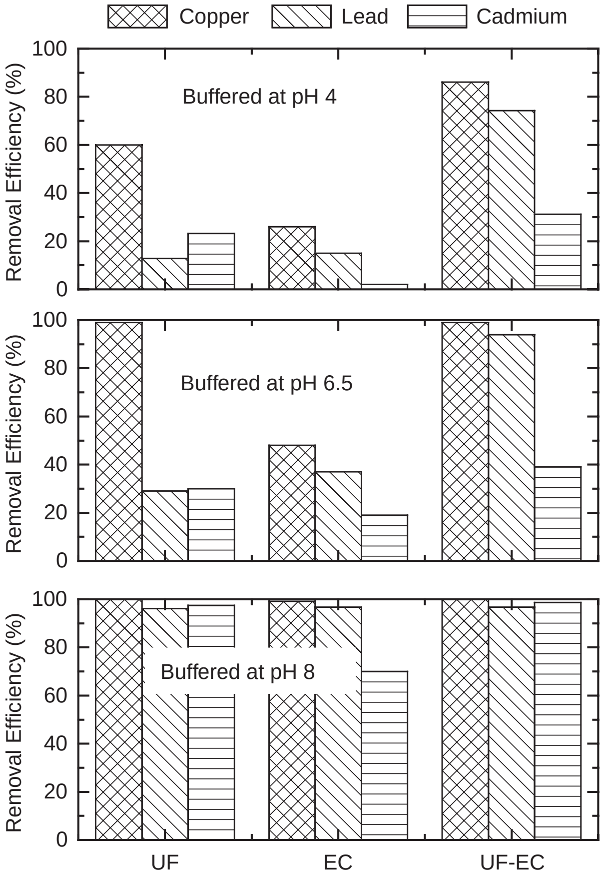

Fig. 5. Removal of copper, lead, and cadmium by the hybrid EC-UF system at pH 4, 6.5, 8. The solution pH was kept constant by a buffer solution. The electrolysis time was 30 minutes. The applied current was 2.7 A at 30 V, corresponding to a current density of 100 A/m^2.

4. Conclusion

This study examines the use of a novel EC-UF hybrid system for the treatment of mining impacted wastewater. Model wastewater containing copper, lead, cadmium and other constituents was prepared to represent a typical mining impacted wastewater solution.

The effects of key operational parameters including electrolysis time, current density, and solution pH on the performance of the EC and EC-UF systems were systematically investigated. The removal rates of copper and lead by the EC process were consistently higher than that of cadmium. It is probable that the removal mechanism of cadmium was different from that of the base metal copper and lead. Results reported here indicate that an EC-UF hybrid system could be very effective in removing heavy metals at high solution pH. At an acidic condition, the removal efficiency of heavy metal by both EC and UF reduced dramatically. However, the overall removal efficiency by the hybrid EC-UF system remained quite high. Results reported here suggest that EC and UF can complement each other very well for optimum removal efficiency.

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