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Research article

Simultaneous removal of cadmium, zinc and manganese using electrocoagulation: Influence of operating parameters and electrolyte nature

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A B S T R A C T

In the present study, the influence of operating parameters and electrolyte nature on the simultaneous removal of toxic metals (cadmium, zinc and manganese) from synthetic smelting wastewater by batch electrocoagulation was investigated. This wastewater contained high concentrations of anion–cation electrolytes. Results indicated that the efficiency of heavy metals removal can be enhanced by increasing the solution pH and current density. The Fe–Fe electrode combination is more effective than the other combinations (Al–Al, Al–Fe and Fe–Al). The interaction of heavy metal ions showed that the increase of initial Zn^{2+} concentration adversely affects on Cd^{2+} removal. In addition, the single chloride system exhibits the optimum removal efficiency on Mn^{2+}. Single sulfate and binary anion systems exert a more positive effect on Cd^{2+} and Zn^{2+} removal because of the stronger charge neutralization and destabilization of iron hydroxide flocs. Increases of Ca^{2+} and Mg^{2+} ions exert a significant negative effect on metal removal. However, the addition of a small amount of sodium chloride into a high sulfate and hardness solution can accelerate the removal of heavy metals. Finally, the sludge samples generated from electrocoagulation were characterized by XRD and SEM–EDS analyses.

1. Introduction

Smelting wastewater contains various toxic heavy metals such as copper, lead, zinc, cadmium, and manganese. Whether discharged directly or indirectly, these toxic metals can lead to serious environmental problems. Cadmium, one of the most toxic nonessential elements, can severely damage to our kidneys, metabolism, and nerves even in trace amounts. Excess zinc and manganese can also cause harm to hunman health, though both metals are essential mineral for the hunman body. Concentrations of lower than 0.003 and 0.5 mg/L (WHO, 2011) in drinking water are essential to human health, respectively (Vasudevan and Lakshmi, 2011; Wang et al., 2017). In addition, these toxic metals can be easily absorbed and accumulated in the living organisms because they are highly water-soluble and non-biodegradable in the natural ecosystem (Colantonio and Kim, 2016). Thus, smelting wastewater should be treated and regulated carefully to meet environmental regulations.

Electrocoagulation (EC) inherits the advantages of classic chemical coagulation and overcomes many key problems in its practical application such as large sludge production, high operating cost, and secondary pollution (Aoudj et al., 2015; Semerjian et al., 2015). In EC, as presented in Eq. (4), an amount of hydroxide ions is released from the cathode and then spontaneously diffuses to the solution, thereby increasing the solution pH. Meanwhile, free iron ions (usually Fe^{2+}) are produced from the anode plate (Eqs. (1)–(2)) because electrochemical oxidization can immediately spontaneously convert into corresponding monomeric and polymeric hydroxides (Eqs. (5)–(6)) in a suitable pH range (Eiband et al., 2014; Kuokkanen et al., 2015; Linares-Hernández et al., 2009). These freshly generated iron hydroxides exhibit a strong adsorption capacity for pollutants, owing to their large surface areas and electrified characteristics (Bazrafshan et al., 2015; Lu et al., 2015). In addition, according to Eq. (7), heavy metals hydroxides are produced by similar chemical reaction. These metals

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species eventually settled to the bottom of the reactor via flocculation, adsorption and co-precipitation by iron hydroxides flocs.

$$\text{Anode reactions:} \quad Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^{-} \quad E^0 = -0.44V \tag{1}$$

$$Fe_{(s)} \rightarrow Fe^{3+}_{(aq)} + 3e^{-} \quad E^0 = +0.04V \tag{2}$$

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^{+}_{(aq)} + 4e^{-} \quad E^0 = +1.229V \tag{3}$$

$$\text{Cathode reactions in alkaline pH:} 2H_2O_{(l)} + 2e^{-} \rightarrow H_{2(g)} + 2OH^{-}_{(aq)} E^0 = -0.828V \tag{4}$$

$$\text{Other reactions:} \quad Fe^{2+}_{(aq)} + 2OH^{-}_{(aq)} \rightarrow Fe(OH)_{2(s)} \tag{5}$$

$$Fe^{2+}_{(aq)} + 3OH^{-}_{(aq)} + \frac{1}{4}O_{2(g)} \rightarrow Fe(OH)_{3(s)} \tag{6}$$

$$M^{n+}_{(aq)} + nOH^{-}_{(aq)} \rightarrow M(OH)_{n(s)} \tag{7}$$

In recent decades, EC has been successfully employed to treat various types of industrial wastewaters, such as landfill leachate (Shu et al., 2016a), municipal (Al-Shannag et al., 2013), slaughterhouse (Bazrafshan et al., 2012a), restaurant (Chen et al., 2000), carwash (Bazrafshan et al., 2012b), pharmaceutical (Parsa et al., 2016), potable water (Heffron et al., 2016), textile (Cherifi et al., 2015; Kobya et al., 2016), tannery (Elabbas et al., 2016; Sirajuddin et al., 2007), smelting (Ahmed et al., 2008), and petroleum refinery (Gousmi et al., 2016) wastewaters. Previous studies mainly focused on single or binary electrolytes at low concentrations. Those wastewater does not agree with the characteristics of actual industrial wastewater. In practical smelting, large amount of sodium sulfate and sodium chloride are added to improve the conductivity of solution, not to mention that the raw material itself is also rich in sodium, potassium, calcium and magnesium. Thereby caused the wastewater discharged from smelting process contain high concentrations of inorganic salt and hardness. In addition, these coexisting anions and cations exert highly complex effects on pollutant removal during EC process. However, the increase in hardness facilitates the coagulation in trace amounts (Hu et al., 2006a). Excessive Ca^{2+} and Mg^{2+} might accelerate the deposition of their hydroxides and carbonate on the surface of flocs and electrode according to the dynamic dissolution equilibrium, particularly in the presence of SO_4^{2-} (Sahu et al., 2014; Zhao et al., 2010). It probably is the dominant reason for the generation of passivation in EC. In general, the passivation of electrodes could cause a series of issues, such as reduction in current efficiency, prevention of iron plate dissolution and increase in energy consumption (Yang et al., 2015).

Chloride is often used as a "passivation inhibitor" for improving the EC performance. Aoudj (Aoudj et al., 2015) and Huang (Huang et al., 2009) demonstrated that a certain amount of SO_4^{2-}, in the absence of Ca^{2+} and Mg^{2+}, exhibit a significantly negative effect on metals removal, whereas the same dosage of Cl^- can improve pollutant removal. However, it remains undetermined whether chloride, sulfate, and binary anions also perform well for heavy metal wastewater treatment in the presence of high hardness? Thus, multi metals and high hardness should be considered in evaluating the effect of coexisting electrolytes on EC performance, particularly anions. These aspects contributes to resolving practical problems for the application of electrocoagulation in real industrial wastewater.

In the present study, batch EC experiments have been carried out to investigate the effect of various parameter on the removal of heavy metals from synthetic wastewater. In consideration of the complexity of real smelting wastewater that contains not only high concentration of Zn^{2+}, Cd^{2+}, and Mn^{2+} ions but high levels of Cl^-, SO_4^{2-}, Ca^{2+} and Mg^{2+} ions, the effects of several factors on metal removal were evaluated. These factors included the following: electrode combinations, initial pH (pH_i), current density (j), initial Zn^{2+} concentration ($[Zn^{2+}]_0$), concentration of co-anions (nature and ratio ($R_{Cl:SO4}$) of anions) and hardness. Finally, the sludge samples generated from EC were characterized by XRD and SEM–EDS.

2. Experiment

2.1. Synthetic wastewater

The synthetic wastewater of cadmium (15 mg/L), zinc (92 mg/L) and manganese (320 mg/L) were prepared by mixing suitable stoichiometric amounts of $CdCl_2$, $ZnCl_2$, and $MnCl_2 \cdot 4H_2O$ in ultra-pure water, respectively. Specific amounts of NaCl (50 mmol/L) and Na_2SO_4 (10 mmol/L) were added as supporting electrolytes. The wastewater hardness was simulated by calcium salt ($CaCl_2 \cdot 2H_2O$, $CaSO_4 \cdot 2H_2O$) and magnesium salt ($MgCl_2 \cdot 6H_2O$, $MgSO_4 \cdot 7H_2O$). All reagents used were of analytical grade and supplied by Sinopharm Chemical Reagent Co., Ltd., China.

2.2. Electrocoagulation system

EC experiments were conducted using a 700 mL cuboid reactor (effective volume was 500 mL) measuring 100 mm × 70 mm × 100 mm and fabricated from polymethyl methacrylate (PMMA). A schematic of the EC system is shown in Fig. 1. A pair of parallel plates operated in the monopolar mode was vertically positioned in the reactor with a submerged surface area of 50 cm^2. The separation distance was fixed at 20 mm, and the purity of iron and aluminum plates were greater than 99.0%. During EC, the wastewater was agitated using a magnetic stirrer (ES-307, China) at a rotational speed of 150 rpm. A of 0–5 A and 0–30 V precision DC power supply (PS-305DM, China) was used to control the desired current. All experiments were conducted at a steady room temperature of 25 ± 0.5 °C.

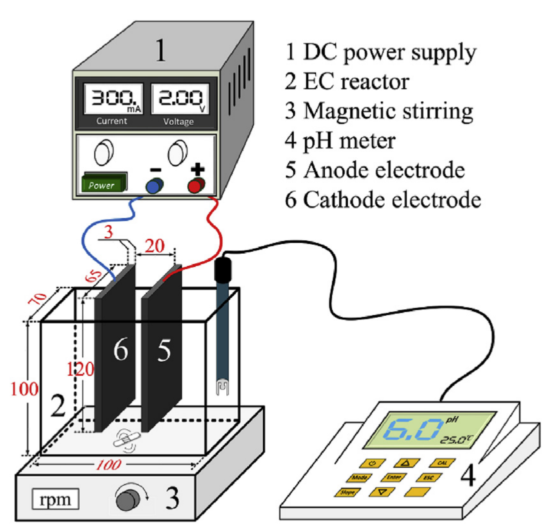

Fig. 1. Schematic of the electrocoagulation system.