Efficiency of Aluminum and Iron Electrodes for the Removal of Heavy Metals [(Ni (II), Pb (II), Cd (II)] by Electrocoagulation Method

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ABSTRACT. Electrocoagulation (EC) technique is applied for the treatment of wastewater containing heavy metals ions such as nickle (Ni), lead (Pb) and cadmium (Cd) by using sacrificial anodes corrode to release active coagulant flocs usually aluminium or iron cations into the solution. During electrolytic reactions hydrogen gas evolve at the cathode. All the experiments were carried out in Batch mode. The tank was filled with synthetic wastewater containing heavy metals and efficiency of electrocoagulation in combination with aluminum and iron electrodes were investigated for removal of such metals. Several parameters, such as contact time, pH, electro-coagulant concentration, and current density were optimized to achieve maximum removal efficiency (%). The concentrations of heavy metals were determined by using Atomic Absorption Spectroscopy (AAS). It is found that the electro-coagulation process has potential to be utilized for the cost-effective removal of heavy metals from wastewater specially using iron electrodes in terms of high removal efficiencies and operating cost.

Key words: Aluminum electrode, Iron electrode, Industrial wastewater, Heavy metals, Electrocoagulation

INTRODUCTION

Heavy metals are toxic in nature and these metals are released directly into the environment from a number of point sources and non-point sources such as electro-plating, metal processing, mining, dyeing and automobile manufacturing industries. High toxicity and non-biodegradability of heavy metals, such as copper, lead, chromium, cadmium, zinc and nickel, caused a number of environmental problems. For most countries, the concentration of toxic heavy metals in effluents should be controlled in order to meet the water quality standards. Different separation techniques for the treatment of industrial wastewater containing heavy metals include adsorption, filtration, precipitation, electrodialysis, reverse osmosis, solvent extraction and ion exchange are used but due to their selective separation efficiencies have limitations and they are also not cost effective techniques.² In UK in 1889, it was first proposed to use the electricity to treat wastewater. The process of electrocoagulation was first applied to drinking water on large scale in the US in 1946.³ Short wave electrolysis or radio Frequency Diathermy is the other names of electrocoagulation (EC). Different physical and biological processes are used for the treatment wastewater; these include electrooxidation (EO), electrocoagulation (EC) and electroflotation (EF).⁴ Electrocoagulation (EC) is becoming a popular process for the treatment of wastewater due to some advantages over chemical coagulation can be applied to a broad range of water and wastewater treatment systems and are most effective in removing inorganic contaminants and pathogens. Because of their broad applicability, they have been used for groundwater and surface water remediation at several sites. A combined process of electrocoagulation and electroflotation in a continuous flow reactor was used to treat wastewater from restaurants in Hong Kong with high oil and grease content. Several reports have been published in scientific journals on electrocoagulation combined with electroflotation for treating potablewater, 6-14 decolourisation of a strongly coloured solution containing reactive textile dyes. 15-19

In France an electrocoagulation and flotation system was joined to study the membrane process (microfiltration) on the flux of municipal wastewater treatment.^{20,21} The research studies showed that electrocoagulation is an efficient technology for treatment of industrial wastewaters. However, the capacity and efficiency of an electrocoagulation process depends on the nature of the effluents and initial pollutant concentrations. By electrocoagulation method suspended solids, hydrocarbons and heavy metals can be removed from wastewater by destabilization of finally dispersed particles.²² Aluminium or Iron electrodes are usually used as

sacrificial electrodes and by applying direct current; cations are generated by dissolution of sacrificial anodes and reacted with hydroxyl ions in the solution and hydrogen gas is produced at the cathode.²³

The metal hydroxide ions are produced by the hydrolysis of metal ions generated in the electrochemical cell according to reactions 1–6 and at pH in range of 6.0–7.0, the only neutral specie M(OH)₃ has a very low solubility. When metal species react with negatively charged particles flocs are generated in the water. The coagulants are generated in situ so no addition of any chemicals is required in electrocoagulation process. The production of gases during the electrolysis of water and dissolution of metal permit the resulting flocs to floated.24

$$Al \to Al^{3+}_{(aq)} + 3e^{-}$$
 (1)

Al
$$\rightarrow$$
 Al³⁺_(aq) + 3e⁻ (1)
3H₂O + 3e⁻ \rightarrow 3/2H_{2(g)} + 3OH⁻ (2)

$$Al^{3+}_{(aq)} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$$
 (3)

The floc of aluminum hydroxide mainly act as adsorbent for the metal ions. Therefore it can eliminate them from solution.

And for the iron electrodes

$$3H_2O + e^- \rightarrow 3/2H_{2(g)} + 3OH^-$$
 (4)

$$4Fe_{(s)} \rightarrow 4Fe^{2+} + 8e^{-}$$
 (5)

$$4Fe_{(s)} + 10H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 4H_{2(g)}$$

The main aim of this investigation is to present bench and field scale research studies for the EC and ECF technology to remove different pollutants from water and wastewater treatment plants. These processes are characterized by ease of operation, reduced production of sludge, and no need to handle chemicals. They have been applied efficiently to various water treatment problems. Therefore, if EC can replace conventional chemical coagulation, very little modification is required to make the present treatment plants more efficient and resolve the many problems caused by chemical coagulation.

MATERIALS AND METHODS

Self Synthetic wastewater samples were prepared in the laboratory. Different concentrations were prepared by dissolving appropriate amount of salts of Ni (II), Cd (II) and Pb (II) in distilled water.

EXPERIMENTAL SETUP

The experimental setup is shown in Fig. 1 which was used for the study of electrocoagulation consist of electro-

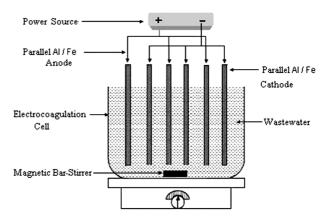


Figure 1. A schematic diagram of experimental setup.

lytic cell of 1.5 liter, having effective volume of 1000 cm³ to hold the sample. Baffles were attached to the inner phase of electrolytic cell which further facilitated the proper mixing of sample and created a turbulent flow. Three pairs of iron / aluminum electrodes were used separately that have an active surface area of 16 cm², serve as cathode and anode. These electrodes were arranged having space of 2.5 cm between them. Electrodes were connected to DC power source and to minimize the mass transfer during the course of reaction, a magnetic stirrer was used which facilitated the proper mixing of solution. A switch was used to change the polarity of electrodes which reduced the passivation phenomenon. Passivation phenomenon further disturbed oxidation and reduction processes during the course of reaction.²⁵

EXPERIMENTAL PROCEDURE

All the experiments were conducted in a bipolar batch reactor. A set of 6 aluminum electrodes or 6 iron electrodes were used respectively that was connected in parallel. A synthetic wastewater sample was prepared in each experimental run and then placed in an electrolytic cell. Potassium chloride (1N) was added to increase the conductivity of solution by reducing the phenomenon of passivation which occurred due to formation of oxide layer on anode. Aluminum and iron electrodes were dipped into the sample solution so that they had maximum surface area in sample solution. Proper mixing of solution was achieved by a magnetic stirrer while pH of the solution was adjusted by 1 M. sodium hydroxide / 1 M. sulphuric acid solution. At the end of each experiment, the mass loss of aluminum and iron electrodes were measured respectively. The current of 1.0 to 5.0 A were passed for contact time of 0, 2, 4, 6, 8, 10 minutes. Samples were extracted after every 10 min and after filtration of the solution through 0.45-µm mixed cellulose

acetate membrane, pH and conductance were measured by transferring solution into another beaker. The residual metal ions concentration was determined according to the standard method by using the Atomic Absorption method.²⁶ The amount of metal ions removal was measured at pH 1, 2, 3, 5, 7 and 9 and in electrical potential of 5, 9, and 12 V.

RESULTS AND DISCUSSION

The process of electrocoagulation is not so complex and can be examined by the optimization of several parameters like contact time, initial pH, electrocoagulant concentration and current density. In the present study, the process of electrocoagulation has been explored as a treatment technology for the removal of nickel, lead and cadmium from synthetic wastewater. After electrocoagulation process it was observed that the conductance values of the water samples were in permissible range. While color of the wastewater samples disappears as the contact time increased. Removal efficiency of these metal ions in different operating conditions such as pH, electro-coagulant concentration and current density at various intervals of time has been evaluated. After the treatment of wastewater by electrocoagulation process, the percent removal efficiency (RE%) calculated by following formula:

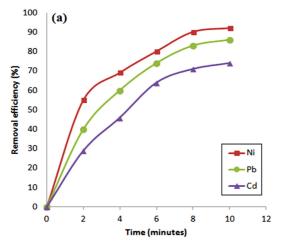
$$RE\% = (C_0 - C/C_0) \times 100$$

Where

 C_0 = Initial pollutant ions concentration

C = Final pollutant ions concentration

The mass of aluminum and iron electrodes decreased as the time of electrolysis increased. There is more consumption of mass in acidic media.



Effect of Contact Time

The effect of operating time on the removal of nickel, lead and cadmium by process of electrocoagulation is shown in Fig. 2(a and b). The maximum removal efficiency of nickel, lead and cadmium is 92, 86 and 74% respectively for aluminium electrodes. Similarly, the maximum removal efficiency for nickel is 99% while that of lead and cadmium is 90 and 89% respectively with same reaction time using iron electrodes. It was observed that a successive decreased in the initial metal ions concentration caused by increasing reaction time. The electrocoagulation efficiency for removing heavy metals from wastewater is high by using iron electrodes because there is the less consumption of electrode mass for the efficient removal of metal as the metal concentration in the solution increased. Due to excess amount of floc formation which ultimately sweeps away the metal from solution and the need for consumption of electrode mass was less.8 Thus, by electrocoagulation process, the discharge of the treated wastewater to the other water bodies or environment can be performed safely.²⁷

Effect of pH

Different hydroxide species formed during electrocoagulation are affected by pH. The surface charge of the particles can also be modified by a change in pH. Hydroxyaluminum species are generated on the hydrolysis of Al³⁺ ions. Predomination of aqueous complex $Al(H_2O)_6^{3+}$ at pH < 4 is observed. While hydrolysis products Al(OH)²⁺ and Al(OH)₂⁺ are formed between pH 5 and 6. The most prevalent specie between pH 5.2 and 8.8 is Al(OH)₃ and Al(OH)₄ is only predominant specie above pH 9.11 The effect of pH on the removal of nickel, lead and cadmium was studied at different pH ranged from of 1-9 using aluminum and iron

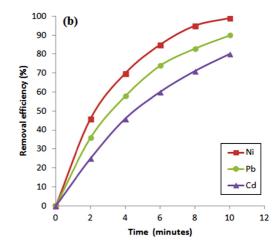


Figure 2. (a) Effect of Contact Time on removal of metals by using Aluminium electrodes (b) Effect of Contact Time on removal of metals by using Iron electrodes.

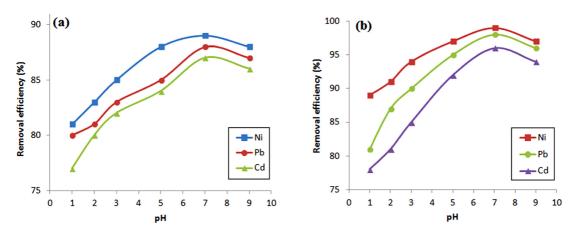


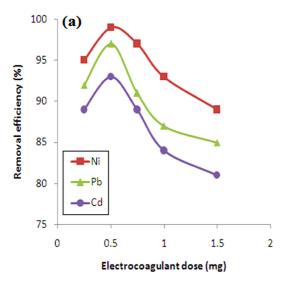
Figure 3. (a) Effect of pH on removal of metals by using Aluminium electrodes (b) Effect of pH on removal of metals by using Iron electrodes.

electrodes separately. The percent removal efficiencies of different metals as a function of pH presented in Fig. 3(a and b). The maximum removal efficiency observed at pH 7 for nickel which is about 87.8%. In case of lead and cadmium, the percent removal efficiency is 88.2 and 87.9% respectively. Similarly, at optimized time and pH, the maximum removal efficiency of nickel is 97.5% for iron electrode and removal of lead is 96.1 and cadmium removal is 94.8%. As discussed earlier, the process of electro-coagulation can act as pH buffer for the treatment of wastewater so the additional cost for adjusting the pH of solution can be avoided during treatment.²⁸

Effect of Electro-coagulant Doze

The conductivity of wastewater can influence the elec-

trochemical treatment because it facilitates the passage of current. To investigate the effect of the supporting electrolyte concentration on removal efficiency of nickel, lead and cadmium for aluminum and iron electrodes, different concentration of sodium sulphate (Na₂SO₄) were added to the electrolytic cell respectively. There is a direct relation between concentration of electrolyte and conductivity of solution. As the Na₂SO₄ concentration increases, the conductivity of the solution increases. The metal ion removal efficiency decreases from for 0.25 M to 0.125 M Na₂SO₄, because as the concentration increased the removal efficiency decreases. The maximum removal efficiency of different metals observed with 0.25 M Na₂SO₄²⁻ which is 95.5% in case of nickel as shown in Fig. 7 and 91.1% for lead and 93.2% for cadmium as presented in Fig. 4(a and b)



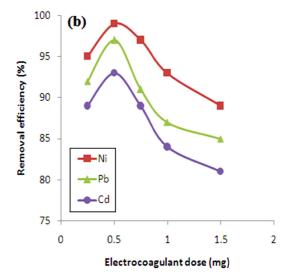


Figure 4. (a) Effect of electrocoagulant dose on removal of metals by using Iron electrodes (b) Effect of electrocoagulant dose on removal of metals by using Iron electrodes.

by using aluminum electrodes. While by using iron electrodes, the removal efficiency of nickel is 99.6%, lead removal is 99.7% and 98% cadmium removed. The reduction in metal ions removal efficiency with increasing supporting electrolyte concentration from 0.25 M to 1.25 M may be due to the excess of SO_4^{2-} ions, which interact with hydroxyl ions and hindered the corrosion of aluminum and iron electrodes.²⁹

Effect of Current Density

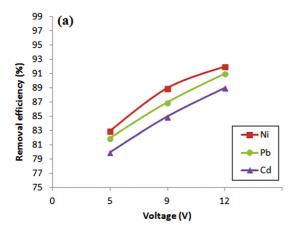
To determine the effect of applied voltage on the removal efficiency of nickel, lead and cadmium, Laboratory testing of the electrolysis cell involved. It is illustrious that the flocs growth, bubble production size and rate and coagulant dosage rate is determined by electrical current which can directly affect the treatment efficiency of the process of electrocoagulation.^{30–32} Consequently, it was investigated that the applied voltage has direct effect on the pollutants removal. As expected, the removal efficiency of metals increased by increasing applied voltage for a given period of time. At highest electrical voltage (12V), quickest reduction of metal ions occurred and the maximum removal efficiency of nickel is 92.3% while that of lead and cadmium is 91.5 and 89.4% respectively by using aluminum electrodes as represented in the Fig. 5(a and b). While by using iron electrodes, the maximum removal efficiency is 99.0% for nickel, 98.3% for lead and 96.8% for cadmium. Iron electrodes gives highest removal efficiency values as compared to aluminum. The lowest metal removal efficiency occurred in the lowest applied voltage (5 V). This is attributed to the fact that the amount of oxidized metal ions increased at higher voltage which favore the removal of the pollutants by forming greater amount of precipitates. It was observed that by increasing current density, the size of the bubbles decreased and their density increased which in turn resulting in a faster removal of metal ions and greater upwards flux. 33 The treatment efficiency of metal ions was mainly affected by charge loading phenomenon (Q = It). 34

CONCLUSION

Electrocoagulation (EC) is most efficient and cost-effective treatment method that has been applied for the treatment of industrial and synthetic wastewater.

A set of experiments was conducted in order to find the effects of different operational parameters on the removal efficiency of heavy metals and it was found that as the contact time increased, the percent removal also increased and high percent removal of metals by using aluminum and iron electrodes achieved at pH of 7 as the treatment efficiency was very poor either at low or high pH. Different concentrations of Na₂SO₄ were used to increase the ionic conductivity of the wastewater. It was revealed that the percent removal of metals decreased at higher concentration of Na₂SO₄. While in case of current density, it has been observed that by increasing current density, removal efficiencies increased for both aluminum and iron electrodes.

Higher efficiency is obtained by applying 12 V. The experimental results showed that iron electrodes are more efficient than iron electrodes. It may be because of high adsorption capacity of hydrous ferric oxides. Iron electrodes gives highest removal efficiency values 97.6, 99.3, and 98.8% for nickel, lead and cadmium as compared to aluminum 89.3, 89.5, and 91.4% at optimized parameters as discussed above.



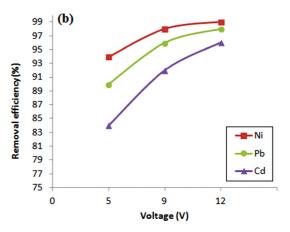


Figure 5. (a) Effect of Current density on removal of metals by using Aluminium electrodes (b) Effect of Current density on removal of metals by using Iron electrodes.

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