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Removal of various pollutants from wastewater by electrocoagulation using iron and aluminium electrode

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ABSTRACT

The present study deals with removal of various pollutants from a real wastewater by electrocoagulation treatment. Combined wastewater from one of the Delhi industrial areas was collected and treated by electrocoagulation process using iron and aluminium electrodes. Removal of Cr, Zn, Ni and Cu were achieved up to 100, 98.71, 69.22 and 48.08% respectively using aluminium electrode while Cr, Cu, Zn and Ni were removed up to 100, 78.57, 75.48 and 58.68% respectively using iron electrode electrocoagulation. Chemical oxygen demand, total organic carbon, total dissolved solids and sulphate were removed up to 83.94, 46.92, 74.16 and 83.66%, respectively in aluminium electrode electrocoagulation while the same were removed up to 54.83, 77.39, 52.85 and 60.74% respectively in iron electrode electrocoagulation.

Keywords: Electrocoagulation; Iron electrode; Aluminium electrode; Combined wastewater

1. Introduction

Industrial wastewater containing heavy metal ions causes serious health hazards to all living creatures, when discharged untreated. These might damage nerves, liver, bones and block functional groups of vital enzymes [1,2]. Various industrial processes result in the production of metal bearing waste streams. Large scale use of heavy metal in different industries like metal plating, paints and pigments, leather tanning, textile dyeing, printing inks and wood preservation etc. release significant quantity of heavy metals into receiving water bodies [3]. Municipal wastewater also contains significant concentration of heavy metal which requires treatment before their final discharge [4]. The removal of toxic heavy metal and other pollutants from industrial wastewaters using conventional chemical approaches such as adsorption, oxidation– reduction and chemical precipitation are costly processes. These processes require large quantities of reagents and result in the production of considerable amount of toxic sludge and secondary pollutants. Besides this, operational costs of such treatment processes are high for treatment of complex wastewater [5]. Therefore conventional treatment methods are not very suitable in treating the industrial and municipal

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wastewater up to the required discharge standards at low cost [6]. Hence development of low-cost technologies to replace costly wastewater treatment methods is attracting the attention of researchers [7]. Beside this, in recent years, concern for treating the toxic metals from wastewater has also led the search for more effective and economically viable treatment processes for heavy metal.

These problems have encouraged many researchers to investigate the use of electrocoagulation for treating various industrial effluents [8]. It has been shown that electrocoagulation is able to eliminate a variety of pollutants from wastewaters, for example metals and fluoride [9-11], clay minerals [12,13], chemical oxygen demand (COD) [14-16], colour [17,18] organic pollutants [19] paper mill wastewater [20] and dairy effluents [21]. In electrocoagulation, coagulant and hydrogen are generated at sacrificial anode and cathode, respectively under the influence of applied current, which removes various pollutants by sorption, precipitation and co-precipitation, electrostatic attraction, flotation and coagulation. Moreover, there is a possibility of oxidation and reduction of polluting substances at the anode and cathode, respectively. Electrocoagulation can compete with the conventional chemical coagulation process for treating industrial and municipal wastewaters. In electrocoagulation, a range of coagulant species and hydroxides are formed which destabilize and coagulate the suspended particles and adsorb dissolved contaminants [17]. Electrocoagulation can overcome the drawbacks of the classical treatment techniques and emerge as a sustainable wastewater treatment system [22,23]. Electrocoagulation is an economical technique as it produces less sludge in comparison to conventional methods [24].

Numbers of industries in Delhi has grown up from 18,000 industries in 1961 to 120,000 industries. These industries are located in 28 industrial areas. Most of these industries are small-scale industries and only 200 are medium or large-scale industries [25,26]. Industries which have spent only one million Indian rupees on infrastructure fall into the small-scale industrial sector in India. In general they have less production individually and subsequently result in less waste generation. This is a reason which exempts them from following stringent rules for the treatment of waste. But altogether, collective volume of wastewater generated from small-scale industries in an industrial area has become huge. Thus, government is encouraging the combined wastewater treatment option for such industrial areas. These small-scale industries are engaged in various activities like garments, dyeing, battery manufacturing, manufacturing

of electrical appliances, electronics, printings and publishing, glass processing, electroplating, steel and metal processing etc. In this study, wastewater of one of the industrial areas of Delhi namely Wazirpur has been chosen as it contains high level of various heavy metals and very low pH. The main objective of the present work is to assess the electrocoagulation treatment potential for Wazirpur industrial area which is very complex in nature as it is a combination of wastewater of several hundreds of small-scale industries. In the said industrial area, various small-scale industries like automobile, chemical, agriculture process-based, electrical appliance manufacturing, iron and steel processing, leather, textile, paper and plastics manufacturing etc. are working and producing very complex combined wastewater. Because of this complexity, treatment of this wastewater by other biological or any single chemical method is not feasible.

2. Materials and methods

2.1. Wastewater characterization

Combined wastewater samples were collected from Wazirpur industrial area of Delhi. Wastewater were characterized for various pollutants according to the standard method [27]. The characteristics of Wazirpur industrial area wastewater is summarized in Table 1. Conductivity of the wastewater was adjusted by addition of sodium salt to 20 mS/cm in order to reduce the IR-drop or solution resistance potential η IR [11,12].

2.2. Experimental procedure

Batch experiments were carried out in a 2,000 mL beaker. Four electrodes were installed vertically with a spacer to ensure fixed distances of 5 mm in order to minimize the IR-drop [12,14]. Aluminium and iron plates of $78 \times 99 \times 2 \text{ mm}$ in dimension were used as electrodes. Each electrode was perforated with 28 holes, each 5 mm in diameter for better mixing of wastewater. The active anode surface was 0.031 m^2 . To remove the oxide and/or passivation layer from the electrodes, the electrode surfaces were ground with sandpaper before each experiment. The electrodes were operated in bipolar mode, so only the outer electrodes were connected to the power supply. DC current of 3.0 A was used for all experiments conducted using industrial wastewater. The electrical contacts were established with crocodile clips. During the experiments, the direction of the current was reversed every 10 min to limit the formation of passivation

Table 1 Combined wastewater characteristics of Wazirpur industrial area of Delhi

Parameters	Concentration (mg/L)
рН	2.2
COD	369
TDS	4,681
TOC	205
SO_4	8,714
Cr	29.33
Ni	16.72
Zn	8.20
Cu	18.71

layers [12]. Every electrocoagulation experiment was started with 1,500 mL of wastewater. Twenty milliliters samples were withdrawn from the wastewater in every 5 min for analysis. The pH and conductivity were monitored with WTW-Multi-Parameter 3500i kit. Heavy metal analysis was done on an atomic absorption spectrophotometer (Perkin Elmer, Analyst 200, USA).

3. Results and discussion

3.1. Removal of heavy metals from wastewater by electrocoagulation using aluminium electrode

Fig. 1 shows the results of heavy metal removal from wastewater by electrocoagulation using aluminium electrode. Results indicated that the initial pH of the industrial wastewater was 2.2, which increased up to 5.4 in treatment time of 80 min. Continuous rise in pH with increasing treatment time was observed. All the Cr were removed from the wastewater in treatment time of 40 min. The first 20 min of treatment time produced 88.4% of chromium removal. Zinc was removed up to 98.71% in treatment time of 80 min. Rest of the metals like Ni and Cu were removed up to 69.22, and 48.08%, respectively in treatment time of 80 min. Flocks formation was observed after few minutes of starting the treatment. This was caused by electro-dissolution of the anode and the reduction of water at the cathode which generates aluminium and hydroxide ions according to the following reactions [28,29]:

Anode:

$$\mathrm{Al} \to \mathrm{Al}^{3+} + 3e^{-} \tag{1}$$

Cathode:

$$3H_2O + 3e^- \rightarrow 3/2H_2 + 3OH^-$$
 (2)

At high pH, both anode and cathode may be attacked by OH⁻ ions according to the reaction below [30]:

$$2Al + 6H_2O + 2OH^- \rightarrow 2Al(OH)_4^- + 3H_2$$
 (3)

The Al³⁺ and OH⁻ ions produced at the electrodes, react to form monomeric and polymeric species which transform finally into Al(OH)₃ capable to bind Cr, Ni, Cu and Zn ions [12]. The aluminium hydroxide flocks act as adsorbents and/or traps for metal ions and so eliminate them from the solution. Furthermore, a direct electrochemical reduction of Cr(VI) in Cr(III) may occur at the cathode surface. Simultaneously, the hydroxyl ions which are produced at the cathode increase the pH in the electrolyte and may induce coprecipitation of Cu²⁺, Zn²⁺ and Cr(III) in the form of their corresponding hydroxides [8]. This acts synergistically to remove pollutants from water. As indicated in results, pH of the wastewater increased from 2.2 to 5.4. Other investigators also observed that treatment induced an increase in the pH [19,28]. This might be explained by the excess of hydroxyl ions produced at the cathode in sufficiently acidic conditions and by the liberation of OH⁻ due to the occurrence of a partial exchange of Cl^- with OH^- in $Al(OH)_3$ [28].

3.2. Removal of heavy metals from wastewater by electrocoagulation using iron electrode

Fig. 2 shows the results of heavy metals removal from wastewater by electrocoagulation using iron electrode. Initial pH of the wastewater was 2.2, which increased up to pH 5.7 in treatment time of 80 min. All the Cr removal was attained in treatment time of 40 min. In first 20 min, 75.28% of chromium was removed which reached to 100% in 40 min. In case of Ni, 58.68% removal was noted in treatment time of 80 min. Significant removal i.e. 78.57% of Cu and 75.48% of Zn was achieved in treatment time of 80 min. Iron upon oxidation in an electrolytic system produces iron hydroxide, Fe(OH) *n*, where n = 2 or 3. Fe²⁺ is the common ion generated during the electrolysis of iron, and in the presence of dissolved oxygen in water, it can be easily oxidized into Fe3+. Two mechanisms have been proposed to explain the production of iron hydroxides [30].

Mechanism 1: Anode:

$$4\mathrm{Fe} \to 4\mathrm{Fe}^{2+} + 8e^{-} \tag{4}$$

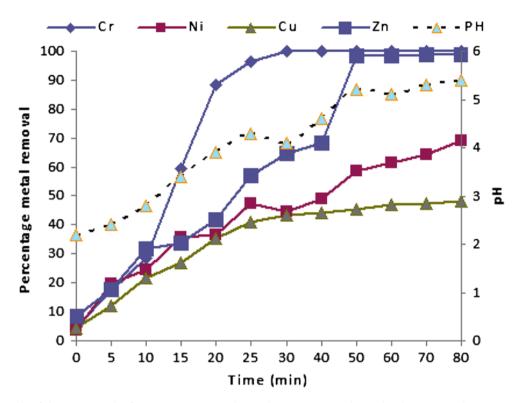


Fig. 1. Removal of heavy metals from Wazirpur industrial wastewater through electrocoagulation using aluminium electrodes.

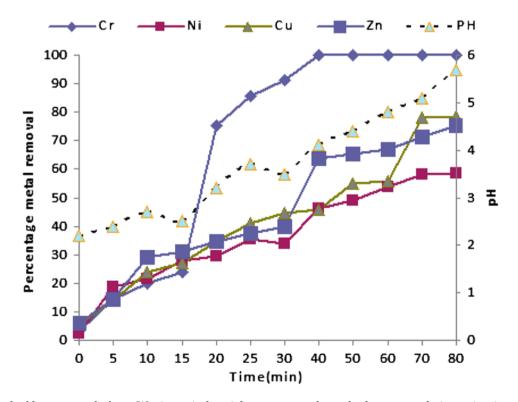


Fig. 2. Removal of heavy metals from Wazirpur industrial wastewater through electrocoagulation using iron electrodes.

(5)

 $4Fe^{2+} + 10H_2O + O_2 \rightarrow 4Fe(OH)_3 + 8H^+$

Cathode:

$$8\mathrm{H}^{+} + 8e^{-} \to 4\mathrm{H}_{2} \tag{6}$$

Overall reaction:

$$4Fe + 10H_2O + O_2 \rightarrow 4Fe(OH)_3 + 4H_2 \tag{7}$$

Mechanism 2: Anode:

$$Fe \to Fe^{2+} + 2e^{-} \tag{8}$$

$$Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_{2} \tag{9}$$

Cathode:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2$$
 (10)

Overall equation:

$$Fe + 2H_2O \rightarrow Fe(OH)_2 + H_2 \tag{11}$$

The Fe(OH)_{*n*} formed remains in the aqueous stream as a gelatinous suspension, which can remove the pollutants like heavy metals from wastewater either by complexation or by electrostatic attraction, followed by coagulation [31,32].

3.3. Removal of COD, TOC, TDS and sulphate from wastewater by electrocoagulation using aluminium electrode

Fig. 3 shows the results of COD, total organic carbon (TOC), total dissolved solids (TDS) and sulphate removal from wastewater by electrocoagulation using aluminium electrode. Forty-seven per cent of TOC removal was achieved in treatment time of 80 min. Removal of TOC by electrocoagulation could be due to the removal of solids and precipitation of dissolved organic molecules [31]. The TOC removal process may also involve electrochemical oxidation and adsorption by electrostatic attraction and physical entrapment [16]. In case of COD, 83.94% removal was achieved in treatment time of 80 min using aluminium electrode. High COD removal may be due to factors such as low COD of the wastewater and aluminium has only one oxidation state. Due to this, organic compound could react with aluminium to form an insoluble compound. Solubility of aluminium hydroxide Al(OH)₃ is minimum at a lower pH close to 4. This is also one of the reasons for higher COD removal. Beside, at lower pH, oxygen evolution at the cathode is possible which might also help in lower oxygen demand [33-35]. Removal of sulphate in treatment time of 80 min was found to be 83.66%. Removal of suphate may be attributed to the precipitation of sulphate salts at the bottom of the electrocoagulation cell, which was formed by the reaction of aluminium hydroxide with the sulphate ions in the wastewater. Lower solubility of aluminium sulphate is also a reason for higher

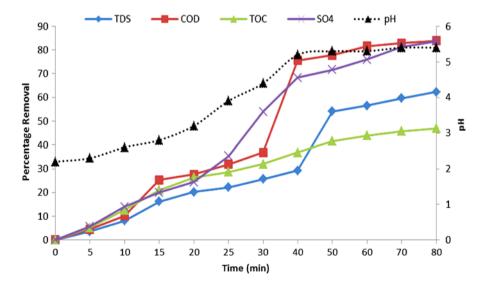


Fig. 3. Removal of TDS, TOC, COD and sulphate from Wazirpur wastewater through electrocoagulation using Al electrodes.

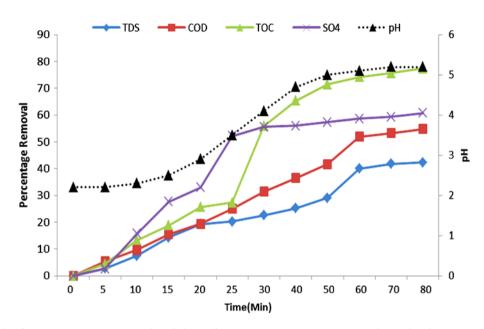


Fig. 4. Removal of TDS, TOC, COD and sulphate from Wazirpur wastewater through electrocoagulation using Fe electrodes.

removal of sulphate [36]. 62.33% of TDS removal was achieved in treatment time of 80 min.

3.4. Removal of COD, TOC, TDS and sulphate from wastewater by electrocoagulation using iron electrode

Fig. 4 shows the results of COD, TOC, TDS and sulphate removal from wastewater by electrocoagulation using iron electrode. 54.83% removal of COD was achieved in treatment time of 80 min which is low as compared to aluminium electrode electrocoagulation. It can be expected that only compounds that react with both Fe(II) and Fe(III) to form insoluble compounds will be removed. In case of sulphate, 60.74% removal was achieved in treatment time of 80 min which is also low as compared to aluminium electrode electrocoagulation. It may be due to higher solubility of ferrous sulphate as compared to aluminium sulphate [36]. 77.39% of TOC removal was achieved in treatment time of 80 min which may be due to electrochemical oxidation and adsorption by electrostatic attraction and physical entrapment of solids and precipitation of dissolved organic molecules [16]. 42.28% of TDS was removed in treatment time of 80 min. Similar results were obtained (50% from initial value of 19,644 mg/l) for removal of TDS in iron electrode electrocoagulation by Kongjao et al. [37].

4. Conclusions

This study proved that removal of various pollutants from combined wastewater of Wazirpur

industrial area by electrocoagulation is possible. Removal of Cr, Zn, Ni and Cu were achieved up to 100, 98.71, 69.22 and 48.08% respectively using aluminium electrode while Cr, Cu, Zn and Ni were removed up to 100, 78.57, 75.48 and 58.68% respectively using iron electrode electrocoagulation. COD, TOC, TDS and sulphate were removed up to 83.94, 46.92, 74.16 and 83.66%, respectively in aluminium electrode electrocoagulation while same were removed up to 54.83, 77.39, 52.85 and 60.74% respectively in iron electrode electrocoagulation. Electrocoagulation can raise the pH of wastewater from highly acidic to slightly acidic. In this study, aluminium electrodes were found to be good as compared to iron electrodes. Further work on electrocoagulation for optimization of process and operational parameters can lead to development of low-cost, efficient, and feasible methods for wastewater treatment, especially for small-scale industries of Delhi. Cost-benefit analysis of the electrocoagulation process should also be attempted in future work.

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