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A comparative study of chemical precipitation and electrocoagulation for treatment of coal acid drainage wastewater

M.S. Oncel [a], A. Muhcu [a], E. Demirbas [b], M. Kobya [a,*]

[a] *Gebze Institute of Technology, Department of Environmental Engineering, 41400 Gebze, Turkey*
[b] *Gebze Institute of Technology, Department of Chemistry, 41400 Gebze, Turkey*

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ABSTRACT

The present study provided a quantitative comparison between chemical precipitation and electrocoagulation (EC) for removal of heavy metals such as Fe, Al, Ca, Mg, Mn, Zn, Si, Sr, B, Pb, Cr and As from coal mine drainage wastewater (CMDW) at a laboratory scale. The optimum pH for removal of most of heavy metals from CMDW by the chemical precipitation using sodium hydroxide was 8 except for Ca, Sr and B (pH 10 or higher). The removal efficiencies at the optimum pH were varied from 28.4% to 99.96%. Influence of current density and operating time in the EC process was explored on the removal efficiency and operating cost. Results from the EC process showed that the removal of metals present in CMDW increased with increasing current density and operating time. The EC process was able to achieve higher removal efficiencies (>99.9%) at an electrocoagulation time of 40 min, a current density of 500 A/m^2 and pH of 2.5 as compared to the results obtained with the chemical precipitation at pH 8. The operating costs at the optimum operating conditions were also determined to be 1.98 €/m^3 for the EC and 4.53 €/m^3 for the chemical precipitation. The EC process was more effective than the chemical precipitation with respect to the removal efficiency, amount of sludge generated and operating cost. Electrocoagulation has the potential to extensively eliminate disadvantages of the classical treatment techniques to achieve a sustainable and economic treatment of polluted wastewater.

Introduction

Acid mine drainage (AMD) generated from active and abandoned mining is a serious environmental problem with the potential of severe contamination of surface and groundwater [1–3]. AMD most commonly initiates from coal mining as materials exposed to water and atmospheric oxygen during the mining process and contains high concentration of FeS_2 [4]. In general, drainage from coal mines is not only of low pH but also includes high levels of sulphate and heavy metals such as Fe, Al, Mn, Ca and Zn [5,6]. High content of toxic metals and high acidity in AMD adversely affects surface water, groundwater and soil. These properties of mine drainage disrupt stream ecosystems and further aggravate the problem by creating yellow or white sediments [7]. Moreover, AMD is a highly acidic aqueous solution and formed through the chemical reaction of surface and shallow subsurface water with rocks containing sulphur-bearing minerals to give sulphuric acid. Heavy metals are not biodegradable and tend to accumulate in living organisms and many heavy metal ions are known to be toxic or carcinogenic. Toxic heavy metals for the treatment of industrial wastewaters include zinc, copper, nickel, mercury, cadmium, lead and chromium [8]. Therefore, these wastewaters must be treated before being discharged into the environment.

Passive and active treatment methods have been applied for the treatment of AMD [5,9]. Passive systems include using anoxic limestone drains, aerobic wetlands, compost reactors, permeable reactive barriers and packed bed iron-oxidation bioreactors [10]. Bioreactors represent a passive-treatment option for removal of sulphate and metals from AMD. However, their treatment performance can be quite variable depending on a number of factors including organic substrate sources and their degradation, mine-water chemistry, microbiological diversity and activities, reactor configuration and hydraulics [11]. Wetlands also are ineffective in areas with rocky soils and steep slopes [12]. Close proximity to floods and large land requirements negatively impact wetland use. The most widely used active treatment process for AMD is based on chemical neutralization and hydroxide precipitation of metals [13,14]. Most active treatment involves pH adjustment and removal by precipitation as a result of the formation of oxy/hydroxides. pH adjustment is needed for treatment of large quantities of AMD. Active treatment enhances the treatment efficiency with using of chemicals but causes a large economic burden owing to the high cost of maintenance and chemicals, and this process requires continuous operation [5]. The disadvantages of the traditional chemical treatment are high cost

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[*] Corresponding author. Tel.: +90 262 6053214; fax: +90 262 6538490.
E-mail address: kobya@gyte.edu.tr (M. Kobya).

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of the chemical reagents, inefficient removal of sulphate and production of a bulky sludge needed to be disposed of. Passive systems are economical as compared with the active treatment but require longer retention times and greater space. Therefore, they are not appropriate for treatment of large-scale mine drainage. Although the passive treatment has been implemented on full-scale sites in several countries, treatment efficiency can be uncertain because of seasonal changes in flow rate and temperature, and the systems are apt to fail during long-term operation.

Current AMD treatment technologies are either inadequate or too expensive. Thus high cost of conventional treatment technologies has produced economic pressure and has caused engineers to search for cost effective and environmental friendly technologies to treat AMD. In the past decades, research efforts have been directed towards advanced techniques for removal of heavy metals from AMD as well as industrial wastewater. Several techniques such as chemical precipitation, oxidation, reduction, coagulation, solvent extraction and adsorption have been commonly employed for the removal of heavy metal ions [8,15].

Currently, there are a number of studies about hydroxide precipitation process using lime, $Ca(OH)_2$ and NaOH for removal of heavy metals in the literature. Cu(II) and Cr(VI) ions from wastewater were evaluated. Maximum precipitation of Cr(III) occurred at pH 8.7 with the addition of $Ca(OH)_2$ and the concentration of chromate was reduced from 30 to 0.01 mg/L. The optimum pH for maximum copper precipitation was 12.0 for both $Ca(OH)_2$ and NaOH and the concentration of copper was reduced from 48.51 to 0.694 mg/L [16]. Fly ash was used as a seed material to enhance lime precipitation. The fly ash-lime carbonation treatment increased the particle size of the precipitate and significantly improved the efficiency of chromium, copper, lead and zinc removals. The concentrations of chromium, copper, lead and zinc in effluents were reduced from initial concentration of 100.0 mg/L to 0.08, 0.14, 0.03 and 0.45 mg/L [17]. Chemical coagulation and precipitation by lime were employed to treat synthetic wastewater consisting of Zn, Cd, Mn and Mg at the concentration of 450, 150, 1085 and 3154 mg/L. It was found that the optimum pH was greater than 9.5 for treatment of the wastewater to meet the Wastewater Standard of the Ministry of Industry [18]. Hydroxide precipitation may have some limitations: (i) hydroxide precipitation produces secondary wastes such as metal hydroxide sludge and gypsum which are highly regulated and have costly disposal requirements; (ii) some metal hydroxides are amphoteric, and the mixed metals create a problem using hydroxide precipitation since the ideal pH for one metal may put another metal back into solution; (iii) when complexing agents are in the wastewater, they inhibit metal hydroxide precipitation [19].

Removal efficiencies of Cu, Cr and Ni from metal plating wastewater using an Fe–Al electrode pair at a current density of 10 mA/cm^2, pH 3.0 and an EC time of 20 min with energy and electrode consumptions of 10.07 kWh/m^3 and 1.08 kg/m^3 were achieved with electrocoagulation (EC) process as 100% [20]. Optimum conditions for removal of Cr(VI) with a concentration of 1470 mg/L were determined to be 7.4 A, pH 1.84 and 70 min and the removal efficiency by the EC process was 100% [21]. The performance of simultaneous removal of Cu, Ni, Zn and Mn from a model wastewater was investigated with the EC using iron electrodes and removal efficiency of more than 96% was obtained for all metals with a total energy consumption of 49 kWh/m^3 at 25 mA/cm^2 [22]. Treatment of spent final rinse water of zinc phosphate from an automotive assembly plant was performed in an electrochemical cell equipped with aluminium or iron plate electrodes. The highest phosphate and zinc removal efficiencies at optimum conditions were 97.7% and 97.8% for Fe electrode (60.0 A/m^2, pH 3.0 and operating time of 15.0 min), and 99.8% and 96.7% for Al electrode (60.0 A/m^2, pH 5.0 and operating time of 25.0 min) [23]. Removal efficiencies of arsenic in a batch EC reactor using Al and Fe electrodes with monopolar parallel electrode connection mode were 93.5% for Fe electrode at 12.5 min and pH 6.5 and 95.7% for Al electrode at 15 min, pH 7 and at 2.5 A/m^2 [24]. Ni and Zn removals from Ni and Zn plating processes by the EC using stainless steel electrodes were achieved with 100% at 9 mA/cm^2 and pH 6 [25]. Separation of some heavy metal ions such as Fe, Ni, Cu, Zn, Pb and Cd with different initial concentrations in the range of 50–600 mg/L and initial pH between 7.5 and 7.8 was studied with electrocoagulation–electroflotation process. The removal rate was 95% at 15 min [26]. The removal efficiency of Mn^{2+} from synthetic wastewater containing 100 mgMn^{2+}/L by the EC was obtained for 78.2% at 6.25 mA/cm^2 and pH 7 [27].

There has been no direct report as yet being published for the treatment of coal mine drainage wastewater (CMDW) by the EC process, despite the considerable success of this process for the treatment of industrial wastewater, groundwater and surface water containing dissolved metal ions in the literature [21–26,28,29,31]. Therefore, the present study was aimed to focus on treatment of CMDW by the EC process using iron plate electrodes. Effects of current density and operating time for the removal of Fe, Al, Mn, Mg, Pb, Zn, Cr, As and Sr from CMDW at a laboratory scale were investigated to determine the optimum operating conditions in the EC process. The chemical precipitation by sodium hydroxide (NaOH) was used to treat CMDW. The operating costs for the EC and chemical precipitation processes at the optimum operating conditions were calculated.

Electrocoagulation and chemical precipitation processes

Electrocoagulation process

EC involves the generation of coagulants in situ by dissolving sacrificial anodes such as aluminium or iron upon application of a direct current. Iron is oxidized in an EC reactor at anodic sites to Fe^{2+} ions which dissolve to Fe^{3+}. The wastewater solution becomes green and bubbles of gas at cathode are observed during the EC process. The effluent becomes clear and then a green and yellow sludge are formed which are attributed to Fe^{2+} and Fe^{3+} hydroxides. The following major reactions take place in the EC process [28–30]:

$$Fe^{o} \rightarrow Fe^{2+} + 2e^{-} \tag{1}$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-} \tag{2}$$

$$Fe^{o} \rightarrow Fe^{3+} + 3e^{-} \tag{3}$$

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^{+} + 4e^{-} \tag{4}$$

The metal ions can form wide ranges of coagulated species and metal hydroxides, or precipitate and adsorb dissolved contaminants at an appropriate pH value. When CMDW contains high concentrations of different metals such as Fe, Al, Ca, Mg, Mn, Zn, several competitive reactions occur either at the cathode (metals deposition on the cathode electrodes) or in solution (precipitation and co-precipitation of metals with ferrous hydroxides). An amount of metal(s) is removed by cathodic reduction (metal is formed and deposited on the cathodes electrodes) according to the following reaction (5) [31]:

$$Me^{n+} + ne^{-} \rightarrow Me^{o} \tag{5}$$

$$2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-} \tag{6}$$

Several metals can be simultaneously or successively reduced on cathode electrodes. According the electrochemical motive force series the order of metals deposition should be as follows: Sr > Ca > Mg > Al > Mn > Zn > Cr > Fe > Pb. Furthermore, the

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hydroxide ions formed at the cathode increase the pH of the wastewater thereby inducing the precipitation of metal ions as corresponding hydroxides and co-precipitation with iron hydroxides [29]:

$$\mathrm{Me}^{n+} + n\mathrm{OH}^- \rightarrow \mathrm{Me(OH)}_{n(s)} \tag{7}$$

$$4\mathrm{Fe}^{2+} + \mathrm{O}_2 + 4\mathrm{H}^+ \rightarrow 4\mathrm{Fe}^{3+} + 2\mathrm{H}_2\mathrm{O} \tag{8}$$

$$\mathrm{Fe}^{3+} + 3\mathrm{H}_2\mathrm{O} \rightarrow \mathrm{Fe(OH)}_3 + 2\mathrm{H}^+ \tag{9}$$

M^{n+} and OH^- ions generated by electrode reactions (5) and (6) react to form various hydroxo monomeric and polymeric species, depending on pH range, which transform finally into $M(OH)_{n(s)}$ according to complex precipitation kinetics. Freshly formed amorphous $M(OH)_{n(s)}$ (sweep flocs) have large surface areas which are beneficial for a rapid adsorption of soluble organic compounds and trapping of colloidal particles. These flocs polymerize further as $M(OH)_{n(s)}$ and are removed easily from aqueous medium by sedimentation and flotation [32].

One of the operational issues with the EC process is electrode passivation. During the EC process using Fe electrodes, an oxide layer is formed at the anode because the anode surfaces are oxidized to a coarse, rusty, brownish-red appearance with increase usage and the electrode passivation causes Fe generation to decrease. Eliminating the oxide formation at the anode may reduce this effect. Various methods were reported for preventing and/or reducing the passivation problem of the electrodes in the literature [28,33–35] which were mechanical cleaning, adding chloride salt to the solution and using electrodes with reversible polarity. Mechanical cleaning and adding chloride salt to the solution (i.e., limits the formation of the passivation layer and to increase the conductivity as to decrease the energy consumption) were practiced in this study. For this reason, the electrodes are rinsed in the diluted HCl solution after the each experiment. Moreover, Cl^- is discharged at the anode to generate Cl_2, which is dissolved immediately in the solution, chemically converted to ClO^-. Then ClO^- oxidizes the pollutants effectively and increases removal efficiencies of metal ions (Eqs. (10)–(12)) [36]

$$2\mathrm{Cl}^- \rightleftharpoons \mathrm{Cl}_2 + 2\mathrm{e} \tag{10}$$

$$\mathrm{Cl}_2 + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{HClO} + \mathrm{H}^+ + \mathrm{Cl}^- \tag{11}$$

$$\mathrm{HClO} \rightleftharpoons \mathrm{ClO}^- + \mathrm{H}^+ \tag{12}$$

Chemical precipitation process

The chemical precipitation is a widely used for an effective treatment process for removal of dissolved metals from wastewater solution containing toxic metals. Effectiveness of the chemical precipitation process is dependent on several factors, including concentration of ionic metals present in the solution, the precipitant used and the presence of other constituents that may inhibit the precipitation reaction. The chemical precipitation in water treatment involves the addition of chemical to alter the physical state of dissolved and suspended solids and to facilitate their removal by sedimentation or filtration. A commonly used chemical as the reagent in the precipitation process is sodium hydroxide or calcium hydroxide to create solid metal hydroxides. The hydroxide ions react with metals to form insoluble metal hydroxides (Eqs. (13) and (14))

$$\mathrm{Me}^{2+} + 2\mathrm{OH}^- \rightarrow \mathrm{Me(OH)}_{2(s)} \tag{13}$$

$$\mathrm{Me}^{3+} + 3\mathrm{OH}^- \rightarrow \mathrm{Me(OH)}_{3(s)} \tag{14}$$

The insoluble metal hydroxides such as $Me(OH)_{2(s)}$ and $Me(OH)_{3(s)}$ are precipitated. The treated water is then decanted and appropriately discharged or reused [19,37].

When solution pH becomes acidic, the oxidation of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}) diminishes and therefore the metal removal decreases. Alkaline pH, however, tends to favours Fe^{2+} to Fe^{3+} oxidation as well as complex polymerization. The formation of the metal hydroxides with increase in pH accompanied by coprecipitation and/or adsorption of metal hydroxides for the majority of cases gives a mixed precipitate [38].

Materials and methods

Characterizations of CMDW

CMDW was collected from different parts of an abandoned coal mine disposal area in Turkey and stored in high-density polyethylene containers. The main contaminants of CMDW and coal mine drainage (CMD) in literature were presented in Table 1.

Chemical precipitation studies

CMDW was treated with 1 N NaOH (Merck). The chemical precipitation was carried out in a 1 L Pyrex glass containing 0.5 L of wastewater which was mixed by a magnetic stirrer (Heidolp MR 3000D). NaOH was added into CMDW until a desired pH value was reached. After the pH adjustment, the mixture was mixed for 20 min at 400 rpm and allowed to settle for 30 min. Each sample was filtered through 0.45 μm Millipore membrane filter and concentrations of samples were determined from an inductively coupled plasma atomic emission spectrometry (ICP-OES, PerkinElmer Optima 7000 DV model). The operating conditions for ICP-OES were shown in Table 2.

Electrocoagulation studies

The EC study was performed in a batch mode using vertically positioned iron electrodes with dimensions of 50 mm × 73 mm × 3 mm in a 1 L Plexiglas reactor (120 mm × 110 mm × 110 mm) at a constant temperature of 20 °C. The experimental setup was shown in Fig. 1. Two iron plate anodes and two iron plate cathodes (>99.5% purity) were connected to a digital DC power supply (Agilent 6675A; 120 V and 18 A) in a monopolar parallel connection mode and equipped with galvanostatic operational option. Total effective electrode area was

Table 1
Characterizations of CMDW sample and typical CMD.

Parameters	Units	Values for CMDW (this study)	Values for CMD[a]
pH	–	2.43	2.71–3.85
Eh	mV	420	372–493
Conductivity	mS/cm	2.35	1.69–3.96
Total Fe	mg/L	743.5	1297–1703
Fe^{2+}	mg/L	501.7	654–986
Fe^{3+}	mg/L	241.8	206–875
Ca	mg/L	259.6	165–242
Al	mg/L	64.1	60–82
Mg	mg/L	73.7	53–97
Mn	mg/L	40.6	30–42
Zn	mg/L	19.3	9–18
Si	mg/L	17.3	3–14
Na	mg/L	34.2	3–10
Sr	mg/L	9.1	2–5
B	mg/L	15.3	0.7–1.4
Cr	mg/L	0.20	0.1–0.5
As	μg/L	0.015	90–215
Pb	μg/L	27.6	11–36
SO_4^{2-}	mg/L	2650.8	2100–3240
NO_3^-	mg/L	32.2	21–86
Cl^-	mg/L	201	175–236

[a] Values taken from [1].

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Table 2
Operating conditions for ICP-OES.

ICP-OES	
Rf power (W)	1450
Plasma Ar flow (L/min)	15
Auxiliary Ar flow (L/min)	0.2
Nebuliser Ar flow (L/min)	0.7
Delay time (s)	60
Integration time	Automatic (15 s)
Measurement mode	Axial (Al, Cr, Pb, B, Zn, Sr, As) and radial (Fe, Ca, Mg, Mn)
Analytical lines (nm)	267.22 (Cr), 257.61 (Mn), 249.68 (B), 220.35 (Zn), 285.21 (Mg), 206.20 (Zn), 407.77 (Sr), 193.70 (As)[a], 238.20 (Fe), 396.15 (Al), 317.93 (Ca)

[a] Concentrations were determined with hydride generation.

219 cm^2 and the electrodes were spaced by 10 mm. Organic impurities and oxide layer on the electrode surfaces were removed by dipping in a solution freshly prepared by mixing HCl solution (35%) and hexamethylenetetramine aqueous solution (2.80%) for 2 min [39].

0.85 L of CMDW was placed into the batch EC reactor for each experimental run. The reactor was mixed at 400 rpm to reduce the mass transport over potential of the EC reactor. Current and voltage were held constant at desired values for each run and the experiment was started. The samples taken at pre-determined intervals from the EC reactor were filtered using a 0.45 μm Millipore membrane filter. At the end of the run, the electrodes were washed thoroughly with water to remove any solid residues on the surfaces, dried and reweighed.

Analytical method

The chemical analysis of CMDW was carried out according to standard methods [40]. pH and conductivity of solutions before and after the EC process were measured by a pH meter (Mettler Toledo 2050e) and a conductivity meter (Mettler Toledo 7100e). The total concentrations of metals were determined by ICP-OES. Ferrous ions were determined colorimetrically using 1,10-phenanthroline with a UV-spectrophotometer (PerkinElmer, Lambda 35) according to procedure in the standard methods (3500-Fe.B). The experiments were repeated twice. The experimental error was below 2% and the average data were reported.

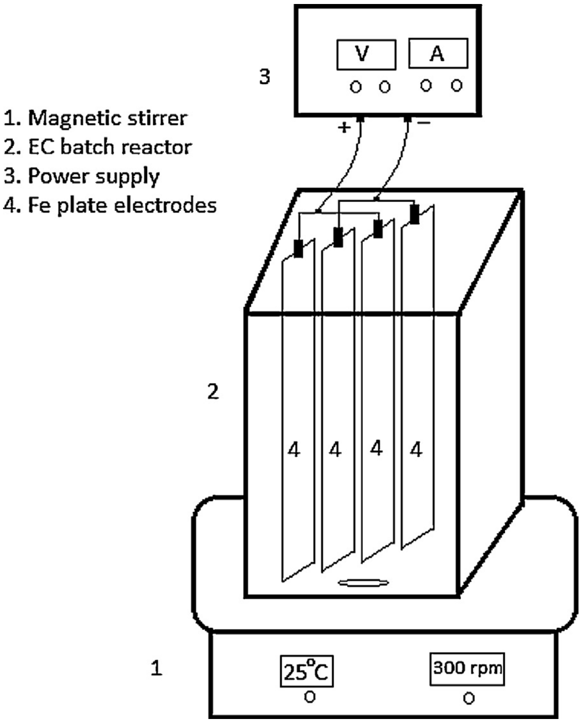

Fig. 1. Experimental setup used in the EC process.

Results and discussion

Chemical precipitation of CMDW

The removal of the metal ions from CMDW depended primarily on the solubility of the various complexes formed in water. For example, heavy metals formed hydroxide solid forms which had low solubility limits in water. Thus, the metals were precipitated out of solution as a result of the formation of insoluble hydroxides, i.e. the values of the concentration of cations and anions were such that their product exceeded the solubility product, K_{sp} (Table 3). The solubility of the metal compounds thus formed was pH dependent; most tended to be least soluble in alkaline solutions since the optimal pH for precipitation depended both on the metal to be removed and the counter ion used. Solubility of metal hydroxides as a function of pH for several metal hydroxides was shown in Fig. 2. As seen in this figure, the total residual concentration of Zn(II), as an example, increased when the pH value increased above 9 by adding NaOH because of an increase in the concentration of the negatively charged hydroxide metal complex [41].

Chemical precipitation experiment was conducted at pH values between 4 and 10. The optimum pH for maximum Fe, Al, Zn, Si, Pb, Cr and As precipitations was 8 and removal efficiencies at the optimum pH were 99.96% for Fe, 99.66% for Al, 99.59% for Zn, 96.99% for Si, 99.96% for Pb, 99.50% for Cr and 99.87% for As, respectively (Table 4). Maximum precipitation of Ca, Sr and B occurred at pH 10 and the concentrations were reduced from

Table 3
Solubility product constants for metal hydroxides at room temperature [38].

Substance	Formula	pK_s
Aluminium hydroxide	$Al(OH)_3$	33.5
Calcium hydroxide	$Ca(OH)_2$	5.3
Chromium(III) hydroxide	$Cr(OH)_3$	30.2
Iron(II) hydroxide	$Fe(OH)_2$	15.1
Iron(III) hydroxide	$Fe(OH)_3$	37.4
Manganese(II) hydroxide	$Mn(OH)_2$	12.7
Magnesium hydroxide	$Mg(OH)_2$	10.8
Lead hydroxide	$Pb(OH)_2$	16.1
Zinc hydroxide	$Zn(OH)_2$	15.7
Strontium hydroxide	$Sr(OH)_2$	2.64

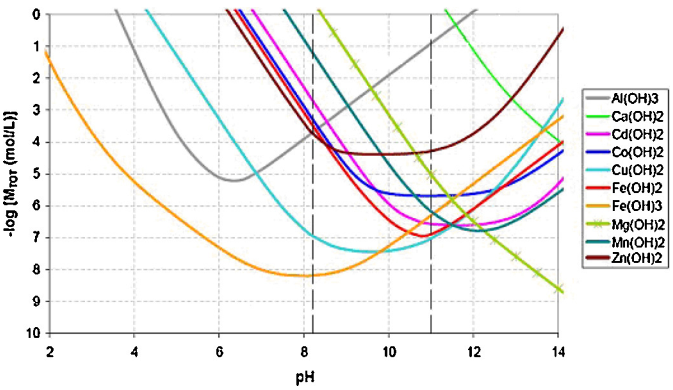

Fig. 2. Solubilities of metal hydroxides as a function of pH.

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Table 4
The dissolved metal concentrations of effluent at different pHs by the chemical precipitation.

Metal	Initial CMDW (mg/L)	pH						
		4	5	6	7	8	9	10
Total Fe	743.5	373.30	349.20	264.40	39.98	0.28	0.29	2.93
Ca	259.6	217.80	219.10	214.10	202.70	198.70	187.80	172.60
Al	64.1	23.30	0.65	0.47	0.23	0.22	0.30	1.18
Mg	73.7	57.97	58.10	55.38	52.68	49.87	39.32	13.08
Mn	40.6	34.31	34.21	32.32	25.60	7.54	1.02	0.25
Zn	19.3	12.86	10.09	2.84	0.42	0.08	0.04	0.02
Si	17.3	7.30	4.30	1.73	0.99	0.52	0.31	0.37
Sr	9.1	8.23	8.28	8.17	7.79	7.26	7.01	6.42
B	15.3	11.56	11.62	11.73	12.01	11.19	10.95	10.95
Pb	27.6	4.02	0.42	0.07	0.02	0.01	0.008	0.02
Cr	0.20	0.01	0.01	0.006	0.001	0.001	0.001	0.002
As	0.15	0.01	0.005	0.0001	0.0005	0.0002	0.0001	0.0001

259.60 to 172.60 mg/L for Ca (removal rate of 33.5%), 9.10 to 6.42 mg/L for Sr (removal rate of 37.8%) and 15.30 to 10.95 mg/L for B (removal rate of 28.4%). Moreover, concentrations of Mn and Mg were reduced from 40.6 to 0.25 mg/L (99.38%) and from 73.7 to 13.08 mg/L (82.20%) at pH 10. A major disadvantage of the chemical precipitation was the requirement of large doses of NaOH to increase and maintain pH values typically from 4.0 to 10.0 for removal efficiencies of the metal ions. The metal concentrations were reduced with increasing pH values from 4 to 10 but the concentrations of calcium, magnesium, strontium and boron cations did not seem to change substantially with change in pH. As can be seen from Table 4, the hydroxide precipitation had some limitation owing to the high solubilities and amphoteric properties of the metal hydroxides [30].

It was found that pH 8 was the optimum pH value for removal of most of the heavy metals from CMDW. Volumes of NaOH used for the pH adjustment of metal precipitations as a function of pH and costs were presented in Table 5. The costs of the chemical precipitation was varied from 1.04 to 6.62 €/m^3 at pH 4–10 (Table 5). Cost and amount of sludge generated for the process at the optimum operating condition were 4.53 €/m^3 and 5.06 kg/m^3.

Electrocoagulation of CMDW

In the electrochemical process, current density (j) and operating time (t_{EC}) are important parameter for controlling the reaction rate within the electrochemical reactor. The applied current density determines not only the coagulant dosage rate, but also the bubble production rate and the floc growth such as $Fe(OH)_{2(s)}$, $Fe(OH)_{3(s)}$, etc. coagulate particles) in the EC process, which can influence the treatment efficiency of the electrocoagulation [23,28,31].

Effect of current density on the removal of metal ions from CMDW in the batch EC process was studied with different current densities (200–500 A/m^2) at constant operating conditions (2.5 of initial pH and an operating time of 40 min). The residual metals in the CMDW as a function of the current density were illustrated in Table 6. Dramatic changes of metal concentrations in CMDW were observed for 0.001 mg/L for Al (decrease of 64.099 mg/L), 0.001 mg/L for Fe (decrease of 743.499 mg/L), 0.104 mg/L for Ca (decrease of 259.496 mg/L), 0.01 mg/L for Mg (decrease of 73.69 mg/L), 0.001 mg/L for Mn (decrease of 40.599 mg/L), 0.011 mg/L for B (decrease of 15.289 mg/L), 0.003 μg/L for Pb (decrease of 27.597 μg//L), 0.005 mg/L for Si (decrease of 17.295 mg/L), 0.002 mg/L for Sr (decrease of 9.098 mg/L), 0.001 mg/L for Zn (decrease of 19.299 mg/L), 0.0001 mg/L for Cr (decrease of 0.1999 mg/L), and 0.00001 mg/L for As (decrease of 0.14999 mg/L), respectively when the current density is at 500 A/m^2 and 40 min (Table 6). The corresponding removal efficiencies of >99.9% at 500 A/m^2 and 40 min were achieved with the EC process. Operating cost for the EC process at the optimum operating conditions was determined to be 1.98 €/m^3. The efficiency of ion production on the anode and cathode increased since the current density increased. This could be attributed at high current densities; the extent of anodic dissolution increased the metal-hydroxide cationic complexes which resulted in an improvement in the removal efficiency or reducing the residual concentrations in CMDW.

Table 5
Volume of NaOH used for pH adjustment and operating cost for the chemical precipitation in the sample solution.

pH	Volume of NaOH used for the pH adjustment (mL)	OC (€/m^3)
4	0.4	1.0364
5	0.7	1.8120
6	1.0	2.7416
7	1.4	3.7815
8	1.7	4.5294
9	2.1	5.5776
10	2.5	6.6177

When Faraday of charge passed through the circuit, 28 g of iron was dissolved at each anode in the EC process. Using this equation, the amount of coagulant delivered to the solution may be calculated. According to Faraday's law (Eq. (15)), the charge passed to the solution was directly proportional to amount of iron electrode dissolved. To achieve lower residual concentrations of metal ions in the wastewater, the current density was increased up to 500 A/m^2 and the highest removal efficiency was obtained as >99.9%.

$$C_{\text{electrode}} = \frac{i\,t_{EC}\,M_{Fe}}{z\,F\,v} \qquad (15)$$

Table 6
Effect of current density on the removal of metal ions from CMDW by the EC process (t_{EC} = 40 min and pH$_i$ = 2.5).

Metal	Initial CMDW (mg/L)	Current density (A/m^2)			
		200	300	400	500
Al	64.1	14.3	0.7	0.53	0.001
B	15.3	8.6	8.8	8.5	0.011
Ca	259.6	226.9	234.1	226.5	0.104
Fe	743.5	812.9	851.0	670.1	0.001
Mg	73.7	55.7	55.3	55.0	0.010
Mn	40.6	30.5	32.6	30.7	0.001
Pb	27.6	2.1	0.1	0.13	0.003
Si	17.3	5.2	2.7	2.8	0.005
Sr	9.1	8.5	8.7	8.4	0.002
Zn	19.3	8.4	3.1	2.1	0.001
Cr	0.20	0.004	0.0001	0.0001	0.0001
As	0.15	0.005	0.0001	0.00001	0.00001

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Table 7
Effect of operating time on the removal of metal ions from CMDW by the EC process ($j = 500\ \mathrm{A/m^2}$ and $\mathrm{pH_i} = 2.5$).

Metal (mg/L)	Operating time (min)								
	0	5	10	15	20	25	30	35	40
Al	64.10	48.40	44.10	10.40	2.20	1.70	0.35	0.05	0.001
B	15.30	10.75	9.60	9.08	8.45	6.30	4.52	0.85	0.011
Ca	259.60	244.54	238.73	228.90	210.45	153.70	114.25	0.28	0.104
Fe	743.12	695.60	753.25	841.90	868.30	841.23	790.41	0.45	0.001
Mg	73.70	65.55	62.10	61.50	60.85	57.92	55.58	0.39	0.010
Mn	40.60	37.29	36.31	34.70	31.85	25.83	21.83	0.36	0.001
Pb	27.10	7.02	6.04	2.85	0.121	0.109	0.072	0.035	0.003
Si	17.30	8.40	7.85	7.10	4.25	3.64	2.78	0.014	0.005
Sr	9.10	8.82	8.60	8.23	7.70	7.41	7.10	0.024	0.002
Zn	19.35	13.69	12.80	10.73	6.30	3.35	2.12	0.016	0.001
Cr	0.20	0.10	0.03	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
As	0.15	0.05	0.001	0.0002	0.0001	0.0001	0.0001	0.0001	0.00001

where $C_{electrode}$ is electrode consumption ($\mathrm{kg/m^3}$), i is the current (A), t_{EC} is the operating time (min), M_{Fe} is the molecular weight of Fe (55.86 g/mol), F is the Faraday's constant (96,487 C/mol), z is the number of electrons involved in the oxidation/reduction reaction and v is the volume of the treated solution ($\mathrm{m^3}$).

Effect of operating time (0–40 min) on the removal of metal ions from CMDW at 500 $\mathrm{A/m^2}$ and $\mathrm{pH_i}$ 2.5 was shown in Table 7. The removal of metal ions from CMDW was increased gradually, and no further removal of metals was observed after 40 min. Therefore, the optimum contact time for the maximum removal was considered to be 40 min. The lowest residual concentrations of metals present in CMDW were achieved at the optimum operating conditions as 0.001 mg/L for Al, 0.011 mg/L for B, 0.104 mg/L for Ca, 0.001 mg/L for Fe, 0.01 mg/L for Mg, 0.001 mg/L for Mn, 0.003 mg/L for Pb, 0.005 mg/L for Si, 0.002 mg/L for Sr, 0.001 mg/L for Zn, 0.0001 mg/L for Cr and 0.00001 mg/L for As, respectively (Table 7).

Final effluent $\mathrm{pH_f}$ of the treated CMDW at 40 min in the EC process was varied with the increasing current density as 4.65 at 200 $\mathrm{A/m^2}$, 5.83 at 300 $\mathrm{A/m^2}$, 6.37 at 400 $\mathrm{A/m^2}$ and 6.96 at 500 $\mathrm{A/m^2}$, respectively. Value of the $\mathrm{pH_f}$ in the EC process (6.96) at the optimum current density fell into the limit values set by discharge standards of water pollution control regulations (i.e., $\mathrm{pH_f}$ 6–9). The electrolytic cell was capable of producing enough hydroxyl ions (the product of electrolysis of water at the cathode electrodes) to compensate the acid-buffer and make the solution alkaline. It was the reason for the pH increased from 2.5 to around 7.0 during the EC process.

The operating cost

One of the most important parameters affecting the application of the EC process for the treatment of wastewater was the operating cost (OC). The OC of the EC process was calculated by including the material cost (mainly electrodes), utility cost (mainly electrical energy), chemicals, as well as labour, maintenance and other fixed costs. The energy (C_{energy}, $\mathrm{kWh/m^3}$) consumption in the EC process was calculated from the following equation

$$C_{energy} = \frac{U\, i\, t_{EC}}{v} \tag{16}$$

In this study, costs of the energy, electrode material and chemicals were taken into account as major cost items in the calculation of the OC as €/m^3 for the treatment of CMDW [42]:

$$\mathrm{OC} = aC_{energy} + bC_{electrode} + cC_{chemicals} \tag{17}$$

where $C_{chemicals}$ is consumption quantities of chemicals ($\mathrm{kg/m^3}$) of the wastewater treated. a, b and c constants in Eq. (17) provided by the Turkish market in December 2012 were values of electrical energy price (0.095 €/kWh), electrode price (0.85 €/kg) and chemical cost (0.60 €/kg for NaOH), respectively. The energy and electrode consumptions for the EC process were 1.32–5.64 $\mathrm{kWh/m^3}$ and 0.92–1.70 $\mathrm{kg/m^3}$ when the current density was in the range of 200–500 $\mathrm{A/m^2}$. Values of the operating cost and amounts of sludge produced at 200–500 $\mathrm{A/m^2}$ and 40 min were 0.91–1.98 €/m^3 and 0.85–3.58 $\mathrm{kg/m^3}$ (Table 8). The removal of metal ions from CMDW in the EC process was found to be very effective in terms of the removal efficiency and operating cost.

Table 8
Effect of current density on the operating cost and amount of sludge produced by the EC process.

j ($\mathrm{A/m^2}$)	i (A)	U (V)	t_{EC} (min)	C_{energy} ($\mathrm{kWh/m^3}$)	$C_{electrode}$ ($\mathrm{kg/m^3}$)	W_{sludge} ($\mathrm{kg/m^3}$)	OC (€/m^3)
200	0.8	2.0	40	1.32	0.92	0.85	0.91
300	1.1	2.7	40	2.47	1.19	1.11	1.25
400	1.4	3.3	40	3.79	1.28	2.12	1.45
500	1.8	3.8	40	5.64	1.70	3.58	1.98

Conclusions

This study dealt with removal of metal ions from CMDW by the chemical precipitation and electrocoagulation processes. The chemical precipitation was performed with NaOH, whereas the EC process was evaluated via an electrolytic cell using iron plate electrodes. In the chemical precipitation, the residual metal concentrations from CMDW were reduced with increasing pH values between 4 and 10 but not for Ca, Mg, Sr and B. The optimum pH value for majority of metal ions presents in CMDW was determined to be 8. Effects of current density (200–500 $\mathrm{A/m^2}$) and operating time (0–40 min) at $\mathrm{pH_i}$ 2.5 on the removal of metal ions from CMDW were investigated for the first time by the EC process. The residual metal ion concentrations varied from 0.00001 to 0.104 mg/L in the EC process were below the limiting value for CMDW discharge. The final effluent $\mathrm{pH_f}$ for the EC process was 6.96 at 500 $\mathrm{A/m^2}$ and 40 min and fell into the discharge limit values. The operating cost for removal of metal ions from CMDW by the chemical precipitation was 2.29 €/m^3 times higher than that of the EC process. Therefore, it can be concluded that the EC process has the potential to be utilized for cost-effective removal of heavy metals from water and wastewater.

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