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Removal of Ni (II) and Co (II) Mixtures from Synthetic Drinking Water by Electrocoagulation Technique Using Alternating Current

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ABSTRACT

Drinking water polluted with trace heavy metals cause serious problems in water supply system in many parts of the world. The heavy metals, nickel (II) and cobalt (II) mixtures are among the important contaminants in drinking water, the removal of which can be achieved by Electrocoagulation (EC). Electrocoagulation (with aluminum as electrode) to remove nickel and cobalt from aqueous medium was studied in the present study. Different concentration of nickel (Ni) and cobalt (Co) solution in tap water was considered for the experiment. During EC process, various amorphous aluminum hydroxides complexes with high sorption capacity were formed. It was observed that the removal of Ni (II) and Co (II) increases with current densities. Inter electrode distance was varied from 0.005 to 0.025 m and was found that least inter-electrode distance is suitable in order to achieve higher mixture removal. Other parameters such as conductivity, pH and salt concentration were kept constant as per tap water quality. Satisfactory mixture removal of around 99% was obtained at the end of 35 min of operation from initial concentration of 25 mg L⁻¹ of Ni (II) and Co (II). Mixture of nickel and cobalt concentration in the solution was determined using Atomic absorption Spectrophotometer. The values of resistances, equivalent conductance and viscosity at under current density 0.04 A m⁻² using AC of 50 Hz and 50 volt were calculated. The results from the kinetic studies showed, that the kinetic data fit the second-order kinetic model. The standards for drinking water are met for a very large relative volume of treated water.

Key words: Electrocoagulation, nickel, cobalt, kinetic studies, water quality

INTRODUCTION

The removal of toxic heavy metals such as cadmium, copper, lead, nickel, mercury and zinc from aqueous environments has been received considerable attention in recent years due to their toxicity and carcinogenicity. These are all naturally occurring substances which are often present in the environment at low levels. Though small amounts of these elements are actually essential for human health, in larger amounts, they can be dangerous (Al-Ghouti *et al.*, 2004; Kim and Keane, 2002; Rengaraj and Moon, 2002). Generally, humans are exposed to these metals by ingestion or inhalation. Exposure to high levels of these metals can severely damage the blood composition, the brain, lungs, kidneys and liver and ultimately may cause death.

The Maximum Contaminant Level Goal (MCLG) for nickel (Ni) and cobalt (Co) have been set by United States Environmental Protection Agency (USEPA) at 0.1 and 0.107 parts per million, respectively, as this level of protection would not cause any potential health problems (USEPA,

2003; WHO, 2006; EC, 1998). In drinking water, higher concentrations Ni may cause health problems like cancer of lungs, nose and bone if found in amounts greater than the health standard set by the USEPA. Dermatitis (Ni itch) is another most frequent problem due to constant exposure to Ni. The other problems include headache, dizziness, nausea and vomiting, chest pain, tightness of chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness (Meena *et al.*, 2005).

The electrocoagulation/floatation process provides an alternative technique for removing pollutants from water and waste water. This process involves applying an electric current to sacrificial electrodes inside a reactor tank. The electrodes generate the positive and negative ions which combine to form metal hydroxides flocs. These metal hydroxide flocs combine with the destabilized contaminants creating metal oxides and hydroxides which precipitate. Along with ions generation, hydrogen gas bubbles are also generated from the cathode. These gas bubbles stick to the pollutant particles and float them to surface of the water. The EC treatment technology offers an alternative to the use of metal salts or polymers and polyelectrolyte addition for breaking stable emulsions and suspensions and allow for easier removal of pollutants by sedimentation and flotation.

In essence, an electrocoagulation reactor is an electrochemical cell wherein a sacrificial metal anode, usually aluminum but occasionally iron, is used to dose polluted water with a coagulating agent (Ghosh *et al.*, 2008; Holt *et al.*, 2005). There are several methods for removal of cobalt and nickel mixture from drinking water like ion exchange and water softening (Vaaramaa and Lehto, 2003), activated carbon and other filtration materials (Munter *et al.*, 2005), supercritical fluid extraction (Andersen and Bruno, 2003), bioremediation (Berbenni *et al.*, 2000) limestone treatment (Aziz *et al.*, 2004), oxidation by aeration, chlorination and ozonation followed by filtration (Ellis *et al.*, 2000), by ash (Das *et al.*, 2007), by aerated granular filter (Cho, 2005) and by adsorption (Tahir and Rauf, 2004).

On the other hand, electrocoagulation has been found to be a promising technique in treating urban waste water (Pouet and Grasmick, 1995), treatment of restaurant waste water (Chen *et al.*, 2000), treatment of potable water (Vik *et al.*, 1984), potato chips waste water (Kobyas *et al.*, 2006), arsenic removal (Kumar *et al.*, 2004), fluorine removal from underground and waste water (Drondina and Drake, 1994), treatment of poultry slaughter house waste water (Bayramoglu *et al.*, 2006), treatment of copper, lead and cadmium in natural water and simulated waste waters (Escobar *et al.*, 2006), treatment of laundry waste water (Ge *et al.*, 2004), boron removal (Yilmaz *et al.*, 2007), olive mill waste waters (Un *et al.*, 2006) and alcohol distillery waste water (Yavruz, 2007). In this work, electrocoagulation was tested as an alternative method for treating the mixture metal ion (II) ranging in concentration up to 25 mg L⁻¹. Effects of different parameters such as applied current density, initial concentration of metal ion and inter electrode-distance over the extent of Co (II) and Ni (II) mixture removal were studied under 50 volt at 50 Hz in detail.

MATERIALS AND METHODS

Chemicals: NiCl₂ and CoCl₂ used in this study for preparing the solution mixture of Ni (II) and Co (II), were of analytical grade (Aldrich) and tap water was used in all preparations. The conductivity and pH of tap water were 13 S.m⁻¹ and 7.5, respectively. The synthetic drinking water concentration was prepared from the stock solution by suitable dilution.

Apparatus: A laboratory model DC power supply apparatus (PHYWE System GmbH and Co. KG., Germany) was used to maintain constant DC current. Voltage and current were measured by a

digital voltameter (max2) and digital ammeter (DT9201A). Conductivity was measured by means of Philips digital conductometer (PW 9526). The pH and the temperature were measured using an inoLab 740 pH meter (WTW GmbH, Germany) connected to a combined electrode comprising a temperature sensor (HI1217D). The concentration changes of metal ions were measured by atomic absorption spectrophotometry (Du 800, Beckman Coulter, Inc., USA).

Experimental setup: Electro-coagulation (EC) was carried out in a lab-scale batch reactor, which was composed of an electrolysis cell with two aluminum plates acting as electrodes, a power supply and a magnetic stirrer. The electrolysis cell was made of perspex (W 0.18 × L 0.18 m × H 0.18 m) with working volume of about 1 L. Sizes of the electrodes were 0.004 m (thick) × 0.15 m (width) × 0.15 m (height).

Experimental method: For each experiment, 1 L of the synthetic water, loaded with a freshly prepared metal ion mixture of Ni (II) and Co (II), was transferred into the electrochemical cell. The electrodes were connected to the respective anode and cathode lead of the AC rectifier and energized for a required duration at a fixed current. During the experiment, samples were collected at different time intervals, filtered using a grade HM2 filter paper of size 11 cm and analyzed for various parameters. After the experiment, the power was switched off and the electrodes were disconnected and interchanged for effective electrode utilization.

To remove the oxide from aluminum surface the electrodes were cleaned with sand paper and energized by dipping them in 5 M HCl solution for 2 min. The viscosity was measured by means of suspended Ubbelohde type viscometer thoroughly cleaned, dried and calibrated with triply distilled water and purified ethanol. After attainment of thermal equilibrium, the efflux times of flow of liquids were recorded with a stopwatch corrected to ±0.1 sec. In this study, the effects of the reaction time (up to 35 min), the applied current (0.01-0.04 A.m⁻²), initial Co (II) and Ni (II) concentrations (5-25 mg L⁻¹) and inter electrode distance (0.005-0.002 m) were investigated.

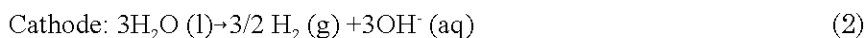
RESULTS AND DISCUSSION

An electro-coagulation process has been developed for water treatment. The design of the electro-coagulation unit greatly affects the operation and its efficiency. The main operating parameters of electrochemical treatment process generally addressed are: Geometry of unit, electrode material, pH, conductivity, TDS, voltage, current density and temperature. Electrocoagulation was used for wastewater treatment in previous works by numerous authors. Some of them have reported that the current density can influence the treatment efficiency (Pouet and Grasmick, 1995), while others have reported that it has no significant effect on effluent treatment (Chen *et al.*, 2000).

For drinking water treatment, the electrode material should be nontoxic for human health. In this study, aluminum was selected as the electrode material. Aluminum is usually preferred because of its low cost and easy availability non harmful and having comparatively less oxidation potential. The solution pH is a relevant factor that affects adsorbed amount of the ions, an increase in the adsorption capacities was generally found with rise in the pH. With the motivation of Ni (II) removal in slightly basic (pH > 7) range, electrocoagulation is believed to be a favorable technology due to the formation of more OH⁻ ions in the electrolysis of water (Sung and Morgan, 1980). In the electrocoagulation where Al electrode is used, it has been observed that at slightly basic ambience Al (OH)₃ precipitation occurs and the sweep-flock mechanism dominates (Gurses *et al.*, 2002). A

grey-pale sludge due to the formation of mixture Ni (OH)₂ and Co (OH)₂ was observed at the bottom of the cell shortly after the completion of the experiment.

This is according to the mechanism of electrocoagulation process. In the process of electrocoagulation, an applied potential generates the coagulant species in situ as the sacrificial metal anode (aluminum or ferric) dissolves, while hydrogen is simultaneously evolved at the cathode. The coagulant species is believed to be responsible in aggregation as well as precipitation of suspended particles and simultaneously adsorption of dissolved contaminants. Tiny bubbles of hydrogen and oxygen, which are formed during electrolysis of water collide with air bubbles and float the pollutant particles. Different electrodes have reported in the literature like carbon (Alvarez-Gallegos and Pletcher, 1999), mild steel (Golder *et al.*, 2005), graphite, titanium (Muruganathan *et al.*, 2004) iron (Yilmaz *et al.*, 2007) and aluminum (Linares-Hernandez *et al.*, 2007). But iron and aluminum have been reported to be very effective and successful in pollutant removal at favorable operating conditions. The electrode reactions are summarized as follows:



During the final stages, coagulated aggregates interact with bubbles and float to the surface or settle to the bottom of the EC reactor. Al (III) and OH⁻ ions generated by electrode reactions (1) and (2) react to form various monomeric species such as Al(OH)⁺², Al(OH)₂⁺, Al₂(OH)₂⁴⁺ and Al₂(OH)₄⁻ and polymeric species such as Al₆(OH)₁₅³⁺, Al₇(OH)₁₇⁴⁺, Al₈(OH)₂₀⁴⁺, Al₁₃O₄(OH)₂₄⁷⁺ and Al₁₃(OH)₃₄⁵⁺ which transform finally into Al(OH)_{3(s)} according to complex precipitation kinetics:



Presence of chloride ion may undergo the following reactions in bulk solution:



and at the anode:



Therefore, the formation of stable precipitate observed at the bottom of the reaction chamber may be interpreted due to the generation of more aluminum hydroxides which is an important factor that could affects the adsorbed amounts of Co (OH)₂ and Ni (OH)₂ from the solution. The

Table 1: Variation of percentage of metal ions (II) mixture removal with time at different current densities

Time (min)	Current density ($A\ m^{-2}$)			
	0.01	0.02	0.03	0.04
5	60.90	62.20	65.05	66.90
10	61.50	63.40	67.30	68.70
15	63.70	65.30	70.10	70.30
20	65.30	67.50	73.30	73.90
25	66.80	69.05	75.80	76.00
30	67.05	70.80	77.60	78.70
35	68.80	73.30	79.70	80.00
40	69.50	75.70	81.50	83.10
45	70.10	76.30	83.70	85.00
50	72.30	77.50	85.90	87.10
55	74.40	79.60	88.60	89.00
60	76.50	81.30	89.90	90.50
65	77.70	84.00	91.60	93.70
70	78.83	86.25	92.5	99.05

Inter-electrode distance: 0.005 m, initial Ni (II) and Co (II) concentration: 25 mg L⁻¹, pH: 7.9, conductivity: 12.7 S m⁻¹ at 50 Hz and 50 volt using AC

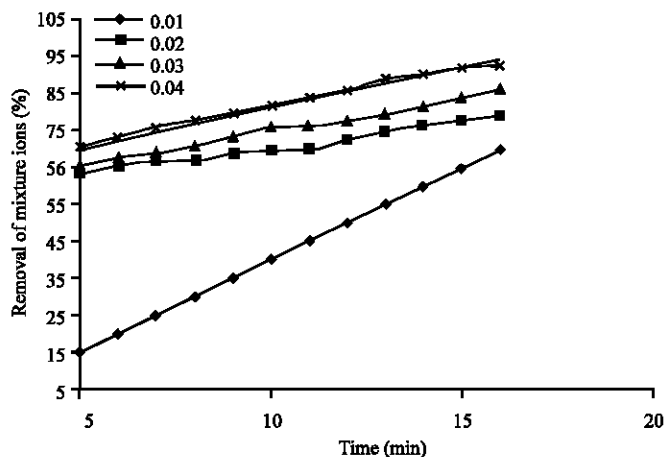


Fig. 1: Percentage removal of mixture ions versus time (min) at different current densities

effect of current density on the percentage removal of ion mixtures is shown in Table 1 and Fig. 1. It can be seen that Ni (II) and Co (II) mixtures removal as well as specific electrical energy consumption will increase as the time of the EC process is increased. This could be because more current density favors the formation of more number of aluminum complexes, which also gives an attribute to the enhanced removal of ion mixtures as expected. This also causes the higher weight loss of aluminum electrode and therefore, increases the specific electrical energy consumption.

Sludge Settled during the EC experiment was filtered out of the chamber, dried and weighed. From the results it is evident that as the initial Ni (II) and Co (II) and the current density are increased, the levels of sludge production are increased. However, sludge production is decreased as inter electrode distance is increased. In the case of using a current density of 0.04 A m⁻² and inter electrode distance of 0.005 m for tap water loaded with initial Ni (II) and Co (II) mixture concentrations of 5, 10 and 25 mg L⁻¹, the weight of sludge was estimated as 30,42 and 96 mg, respectively.

Table 2: Variation of pH of Ni (II) and Co (II) with time at different current densities

Time (min)	Current density ($A\ m^{-2}$)			
	0.01	0.02	0.03	0.04
5	7.67	7.69	7.71	7.73
10	7.69	7.70	7.72	7.74
15	7.71	7.72	7.74	7.76
20	7.73	7.74	7.76	7.77
25	7.75	7.76	7.78	7.80
30	7.77	7.78	7.79	7.82
35	7.79	7.80	7.81	7.83
40	7.81	7.82	7.83	7.85
45	7.82	7.83	7.85	7.88
50	7.83	7.84	7.87	7.89
55	7.84	7.85	7.89	7.92
60	7.85	7.86	7.91	7.95
65	7.86	7.87	7.93	7.99
70	7.87	7.89	7.94	8.03

Inter electrode distance: 0.005 m, initial Ni (II) and Co (II) concentration: 25 mg L⁻¹, pH: 7.9, conductivity: 12.7 S m⁻¹ at 50 Hz and 50 volt using AC

Table 3: Variation of extent mixture metal ions (II) removal with time at different current densities

Time (min)	Initial concentration of mixture metal ions (II) mg L ⁻¹				
	5	10	15	20	25
5	80.44	77.90	6.50	75.40	71.30
10	82.30	79.30	78.10	77.10	73.10
15	84.50	81.50	80.00	79.30	75.30
20	86.30	83.10	82.10	81.00	76.70
25	88.90	85.20	84.30	83.70	78.10
30	90.50	87.50	86.50	85.10	80.00
35	92.30	89.10	88.10	87.00	82.30
40	94.50	91.30	90.00	89.60	84.10
45	96.20	93.70	92.10	91.00	86.30
50	97.10	95.10	94.30	93.70	88.20
55	98.10	96.30	95.90	95.30	90.10
60	98.70	97.20	97.00	96.90	93.40
65	99.50	98.90	98.50	98.10	95.10
70	100.00	99.85	99.70	99.00	99.00

Inter electrode distance: 0.005 m, current density: 0.04 A m⁻², pH: 7.9, conductivity: 12.7 S m⁻¹ at 50 Hz and 50 volt using AC

As can be seen from Table 2, when the applied current density was 0.04 A m⁻² in a potential difference of 50 V at 50 Hz, the maximum value of pH 7.90 was obtained at the end of 35 min. Evidently the values of pH of the solution remained almost constant throughout the process. The results compiled in Table 3 show variations of adsorbed mixture of Co (II) and Ni (II) with different initial concentration of 5, 10, 15, 20 and 25 mg L⁻¹ using a current density of 0.04 A m⁻². From the results it is evident that the percentage of adsorbed mixture solution (II) increases with time. This process, with suitable oxidizing environment, is sufficient to remove the ions mixture within 10 min. However, the rate of generation of aluminum hydroxide complex alone are sufficient to remove

Table 4: Effects of inter electrode distance on mixture metal ions (II) removal

Inter Electrode Distance (10^3) m	Removal of mixture metal ions (II) %
0.5	99.02
1.0	94.90
1.5	91.80
2.0	88.30
2.5	86.00

Current density: 0.04 A m^{-2} , initial concentration of Ni (II): 25 mg L^{-1} , time: 35 min., pH: 7.9, conductivity: 12.7 S m^{-1} at 50 Hz and 50 volt using AC

Table 5: The value of resistances (Ω), equivalent conductance and viscosity

Time (min)	Resistance (Ω)	Equivalent conductance $\text{cm}^2/\Omega.\text{eq}$	Viscosity $10^{-3} \eta$ ($\text{Nm}^{-2} \text{ S}$)
5	25.28	46.82	1.005
10	24.64	51.25	1.003
15	24.20	55.25	1.002
20	21.98	75.83	1.001
25	20.82	95.80	0.999
30	19.67	116.88	0.997
35	18.42	134.00	0.995
40	18.00	158.85	0.993
45	17.46	173.33	0.991
50	17.35	192.00	0.990
55	17.05	234.80	0.987
60	16.95	295.00	0.970
65	16.42	382.67	0.950
70	16.34	574.00	0.930

Current density, 0.04 A m^{-2} using 50 HZ and 50 volt with AC

high Ni (II) and Co (II) concentration ($>15 \text{ mg L}^{-1}$) within ca. 35 min. of operation. It is found, for example, that 35 min is required for a complete removal of initial metal ions (II) mixture of 25 mg L^{-1} from solution. As it is seen, longer residence time is required for EC of higher concentration of metal ions (II) mixture. It is quite clear also, that under the present experimental conditions, and up to 10 mg L^{-1} of initial Ni (II) and Co (II) concentration, a complete removal of metal ions (II) mixture can be achieved within a time interval of 5 min.

To consider how effective the design of EC reactor can be, one must consider, among other variables, inter-electrode distances. Table 4 illustrates the removal efficiency as a function of the spacing between electrodes. It is clearly seen from Table 4 that under constant current density (0.04 A m^{-2}) at 50 Hz and 50 V, initial concentration of metal ions (25 mg L^{-1}), overall treatment time (35 min), pH(7.9) and conductivity (12.7 S m^{-1}), when the inter- electrode distance was increased from 0.005 to 0.025 m, the removal (%) of metal ions mixture was decreased from 99.02 to 86.00%.

The values of resistances, equivalent conductance and viscosity at current density 0.04 A m^{-2} using AC current of 50 Hz and 50 V are included in Table 5. As shown in Fig. 2 and Table 5, the equivalent conductance increases when the operating time of the EC is increased. In such conditions, the viscosity is decreased to reach the optimum conditions. In addition, the higher current density will generally cause a decrease in the cell resistance. Accordingly, the ohmic loss (IR resistance) will remain constant which, in turn, inhibits the rate of anodic oxidation. As the rate

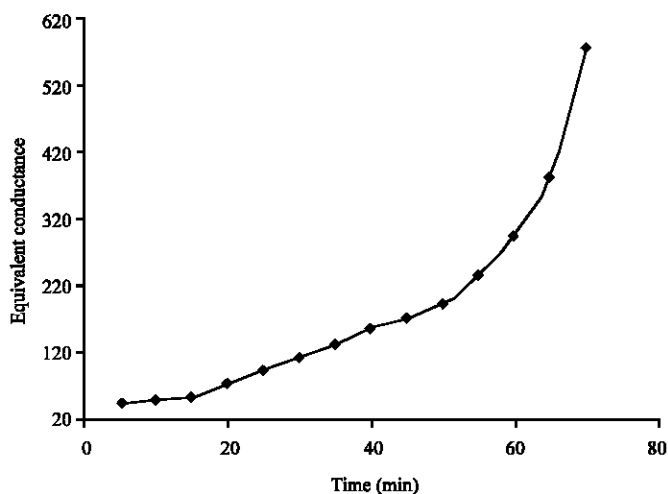


Fig. 2: The equivalent conductance of metal ion mixture at current density 0.04 A m^{-2} using AC current at 50 Hz and 50 volt

of anodic oxidation becomes lower, numbers of cations at anode also decreases. Since these cations are responsible for the formation of coagulant. Therefore, at higher inter-electrode distance, rate of aggregation of suspended particles as well as adsorption of contaminants would be low. This inhibitory effect may be the reason behind the lower removal efficiency at higher inter-electrode distance. At minimum inter- electrode distance the resistance for current flow in the solution will become lower and this, in turn, facilitates the electrolytic process for enhanced Ni and Co mixtures removal.

The variation in IR drop is governed by the following Eq.:

$$\eta_{\text{IR}} = I d/AK \quad (10)$$

where, I is the current (ampere), d is the distance between the electrodes (m), A is the active anode surface (m^2) and K is the specific conductivity (10^8 ms/m) (Vik *et al.*, 1984). The relationship between specific conductance (K) and equivalent conductance (Λ) is expressed as:

$$\Lambda = 10^3 K/C \quad (11)$$

The above equation infers that at constant anodic surface area and conductivity of solution, voltage drop (IR) increases with the increase of inter electrode distance. The increase in IR drop is not recommended for EC process in order to have acceptable energy consumptions as well as desired effective separation. In order to achieve 100% removal for the initial concentration of 25 mg L^{-1} of Ni (II) and Co (II) mixture, the optimum inter electrode distance is found to be 0.005 m.

Faraday's law may be used to relate the mass (m) of electrolytically generated aluminium released into the solution to the operating current (I) and the operating time (t):

$$M = I t M/ZF \quad (12)$$

where, M is the atomic mass of aluminium, Z is the number of electrons transferred in the anodic dissolution ($Z = 3$) and F is Faraday's constant (96486 C.mol^{-1}). By using this equation, the amount of coagulant delivered to the solution may be calculated.

Current efficiency Φ for different operating conditions are calculated as:

$$\Phi = \Delta m_{\text{exp}} / \Delta m_{\text{theo}} \quad (13)$$

This calculation is based on the comparison of the experimental weight loss of aluminum electrodes ΔM_{exp} during EC process with the theoretical amount of dissolution ΔM_{theo} according to Faraday's law. The specific electrical energy consumption (S_{eec}) is calculated as a function of aluminum electrodes weight consumption, in kW. h/kg Al, during EC (Sundstorm and Klei, 1979; Stumm and Lee, 1961):

$$S_{\text{eec}} = nFU / 3.6 \times 10^3 M \Phi \quad (14)$$

For EC process the operating cost includes material, mainly electrode and electrical energy costs. The latter costs items are largely independent of the type of electrode material (Escobar *et al.*, 2006; Gurses *et al.*, 2002). The operating cost is calculated according to equation (15).

$$\text{Operating cost} = aC_{\text{energy}} + bC_{\text{electrode}} \quad (15)$$

where, C_{energy} (kW. h/m³ of Ni (II) solution) and $C_{\text{electrode}}$ (kg Al/m³ of Fe (II) solution) are consumption quantities for the Ni (II) and Co (II) mixture removal, which are obtained experimentally. For Arabian market (2009), the electrical energy price (a) is 0.009 US \$/ kW.h and the electrode price (b) is 0.4 US \$/kg Al. The cost due to electrical energy (kWh/m³ Co (II) and Ni (II) solution) is calculated as:

$$C_{\text{energy}} = Uit_{\text{EC}} / V \quad (16)$$

where, U is cell voltage (V), I is current (A), t_{EC} is the time of electrolysis (s) and V is the volume (m³) of the mixture of Co (II) and Ni (II) solution. The cost of electrode in kg Al/m³ the mixture of Co (II) and Ni (II) solution is calculated by Faraday's law:

$$C_{\text{electrode}} = ItM_w / ZFV \quad (17)$$

where, I is current (A), t is the time of electrolysis (s), M_w is atomic mass of aluminum (26.98 g mol⁻¹), Z is the number of electron moles transferred (Z = 3), F is Faraday's constant (96487 C/mol) and V is volume (m³) of Fe (II) solution (Drondina and Drake, 1994).

The overall EC process in COD removal kinetics is described by a macro-kinetics model in which the rate constant depends on the pH and current density. This model provides preliminary data for evaluation of the kinetic constants. The kinetic rate law for describing the decrease in COD concentration from the PCW with time is best described with the second order kinetic model.

$$t/C_t = (1/k_2 C_o^2) + (t/C_o) \quad (18)$$

where, C_o is the initial concentration of metal ion mixture (mg/L) and C_t is the concentration after each run, t represents retention time and k_2 (L/mg min) is the rate constant of second order

Table 6: Kinetic rate constant and pK values for removal mixture metal ions (II) at conditions of different pH using AC

Time	pH	pK	C _t (10 ⁶)	t /C _t (10 ⁵)	k ₂ (10 ⁶)
5	7.73	8.32	15.2	0.33	138.60
10	7.74	8.48	6.9	1.43	64.00
15	7.76	8.72	7.5	25.00	37.50
20	7.77	8.76	6.0	40.00	18.00
25	7.80	8.83	5.0	55.56	10.00
30	7.82	8.88	4.5	75.00	6.75
35	7.83	8.93	4.0	100.00	4.57
40	7.85	8.97	3.5	133.33	2.72
45	7.88	8.99	3.3	150.00	2.00
50	7.89	9.01	3.0	185.16	1.45
55	7.92	9.08	2.7	220.00	1.32
60	7.95	9.11	2.5	240.00	0.67
65	7.99	9.18	2.4	270.00	0.39
70	8.03	9.24	2.3	300.00	0.014

adsorption. Table 6 shows the rate constants and pK values for removal of metal ions mixture obtained by using AC as a function of different pH values. These findings show that the experimental data could be well fitted by the linearized second order kinetic model for the adsorption process. Based on the conformity between the experimental data and the model values expressed by the correlation values (r^2) (r^2 values close to 1) indicates that the model can successfully be applied to the kinetics of EC system. The best fit value for the second-order rate constant k_2 is calculated as 2.0889×10^6 L/mg min.

The pK values of solution was estimated using the following Eq.:

$$\text{pH} = \text{pK} + \log C/C_0 \tag{19}$$

where, C is the concentration of each run and C_0 is the initial concentration of solution.

The viscosity of the solution η , is given by the following Eq.:

$$\eta = (Kt - l/t)/\rho \tag{20}$$

where, K and l are the viscometer constants and t and ρ are the efflux time of flow (in seconds) and density of the experimental liquid, respectively. The uncertainty in viscosity measurements is within ± 0.003 mpas.

The calculation of color removal efficiency after electrocoagulation treatment was performed using this Eq.:

$$\text{CR \%} = [C_0 - C/C_0] \times 100 \tag{21}$$

where, C_0 and C are the of Ni (II) and Co (II) mixture concentration before and after EC process in mgL^{-1} , respectively.

The heat of adsorption (ΔH°) and entropy changes ΔS° were calculated using Van't Hoff equation (Boonamnuyvitaya *et al.*, 2004):

$$\ln K_{\text{ads}} = -\Delta H^\circ /RT + \Delta S^\circ/R \tag{22}$$

Table 7: Thermodynamic parameters of adsorption of mixture Ni (II) and Co (II) in EC using AC

Temperature (K)	$-\Delta G^\circ$ (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J molk ⁻¹)	T ΔS°
303	39.18	-0.213	0.1286	38.97
313	40.46			40.25
323	41.75			41.54
333	43.03			42.82
343	45.59			44.11

Table 8: The values of C/C₀ of the mixture of Ni (II) and Co (II), transmittance and absorption with time in EC using AC

Time	C/C ₀	T (%)	Absorption at 390 nm
5	0.2570	15.90	0.8000
10	0.1832	26.00	0.5850
15	0.1094	51.00	0.2924
20	0.1018	76.00	0.1192
25	0.0942	81.00	0.0915
30	0.0869	85.10	0.0700
35	0.0795	87.10	0.0600
40	0.0783	89.10	0.0500
45	0.0770	91.20	0.0400
50	0.0750	93.30	0.0300
55	0.0730	94.40	0.0250
60	0.0690	95.50	0.0200
65	0.0650	96.60	0.0150
70	0.0610	97.50	0.0110

where, R is the universal gas constant (8.314 J/mol.K), T is the absolute temperature (K). Plotting $\ln K_{ads}$ against $1/T$ gives a straight line with slope and intercept equal to $-\Delta H^\circ/R$ and $\Delta S^\circ/R$, respectively. The values of ΔH° and ΔS° calculated from equation (22) were used to obtain the Gibbs free energy of adsorption (ΔG°) using:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (23)$$

The data given in Table 7 shows that $|\Delta H^\circ| < |T\Delta S^\circ|$ at all temperatures. This indicates that the adsorption process is dominated by entropic rather than enthalpic changes (Mpofu *et al.*, 2004). The negative value of ΔH° indicates an exothermic adsorption process. Whereas, the positive value of ΔS° indicates a more random state and that is mostly encountered in metal chelation due to the liberation of hydration ion. The increase of negative value of ΔG° with rising temperature implies the adsorption process becomes more favorable at higher temperature. It is evident from Table 8, that the values of C/C₀ and absorption decrease, but the values of transmittance increase with time.

CONCLUSION

Electrocoagulation technique was carried out to remove metal ions mixture from synthetic solution using tap water. Variation of percentage removal of metal ions mixture with different operating parameters such as current density, initial concentration of metal ions mixture and operating time were studied in detail.

The electrocoagulation was carried out for 35 min for initial concentrations as high as 25 mg L⁻¹ and satisfactory removal of 99.2% was obtained. The results showed that the removal efficiency

increases with the increase in current density from 0.01 to 0.04 A m⁻³. At the optimum current density of 0.04 A m⁻³ the electrolysis time was reduced to ca. 5 min for concentration range of 5-10 mg L⁻¹.

Thus electrocoagulation was found to be very fast and effective method for the water containing metal ions(II) mixture from low to very high concentrations. Operating costs for the treatment of the metal ions (II) mixture using EC were evaluated for 100% removal of different initial metal ions concentrations with optimum operating condition. Operating time and current density exhibit similar effects on the process performances and the operating cost.

Finally, it must be concluded that an EC process comprises also equipments other than the electrolysis unit and a detailed technical and economic analysis of the whole process is necessary. The simplified approach used in this study provides only preliminary data for detailed analysis.

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