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Removal of Cobalt from Drinking Water by Alternating Current Electrocoagulation Technique

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Abstract: This research presents a preliminary study for the removal of cobalt from drinking water using Alternating Current Electrocoagulation (ACE) technology. The experiments were carried out using batch apparatus. Batch experiments with two monopolar aluminum plate anodes and cathodes were employed as electrodes. The effect of operational parameters such as initial pH, current density, reaction time, initial concentrations, solution conductivity and inter-electrode distance were studied in an attempt to reach higher Co (II) ion removal efficiency. Important operating parameters were optimized to attain higher (98.60%) Co(II) removal efficiency as follows: inter-electrode distance: 0.005 m, current density: 0.04 A m^{-2} , operating time: 35 min, pH: 7.5, conductivity: 13 S m^{-1} , frequency: 50 Hz and voltage: 50 V. The adsorption process followed first-order kinetics and the temperature studies showed that the adsorption was exothermic and spontaneous in nature.

Key words: Alternating current electrocoagulation, aluminum anode, electrochemical treatment, cobalt removal, drinking water

INTRODUCTION

Suspended and dissolved materials in water are produced by the natural weathering of minerals. Inorganic particles may consist of iron oxides, salts, sulfur, silts and clays. Depending on the concentration of these particles in raw water sources, human health effects can vary from beneficial to toxic. Dissolved cobalt compounds are naturally occurring substances that can impact human health. Cobalt is an essential oligoelement necessary for the formation of vitamin B12 (hydroxocobalamin). The total daily intake of cobalt is variable and may be as much as 1 mg. Investigations of health risk caused by the exposure to cobalt in drinking water at very low levels have revealed the unlikely potential for adverse health effects to humans (Karim, 2011). However, excessive administration of this trace element ($>5 \text{ mg day}^{-1}$) produces abnormal thyroid functions, polycythemia and overproduction of red blood cells (erythropoiesis) with increased production of the hormone erythropoietin from the kidneys (Lauwerys and Lison, 1994; Barceloux, 1999). Therefore, a main goal in supplying quality drinking water is the maximum removal of such element.

Direct Current Electrocoagulation (DCE) technology has proven to be effective in the removal of ionic species from wastewater, particularly heavy metals (Mollah *et al.*, 2004; Parga *et al.*, 2007). This process can eliminate over 99% of some heavy metal cations (Duffey, 1983). It is also

able to remove significant amounts of the destabilized suspended, emulsified, or dissolved contaminants from an aqueous medium (Benefield *et al.*, 1982). The fundamental operating principle is that cations produced electrolytically from the sacrificial iron and/or aluminum anodes provide continuous supply of polyvalent metal cations (coagulants) near the anode. These cations react with the OH^- ions generated at the cathode during the evolution of hydrogen, to produce various forms of gelatinous monomeric and polymeric hydroxo cationic species (Babu *et al.*, 2007). These activated intermediates can interact with the destabilized contaminants via several routes (Mollah *et al.*, 2001; Mollah *et al.*, 2004), creating metal oxides and hydroxides which agglomerate and settle out of suspension. The proposed EC mechanisms for the electrode reactions and the production of H_2 (g) and OH^- (at the cathode) and H^+ and O_2 (g) (at the anode) are discussed elsewhere (Moreno *et al.*, 2009).

However, The DCE technology is associated with the formation of the passivation layers on the cathode as well as corrosion of the anode due to oxidation. This prevents the effective current transfer between the electrodes and therefore, leads to the loss of efficiency of DCE processes. These drawbacks have been controlled by applying Alternating Current Electrocoagulation (ACE) in the removal processes (Vasudevan *et al.*, 2011; Mansour and Hasieb, 2012). Alternating current was used to prevent the passivity or polarization of electrodes. It is

also believed that the ac cyclic energization can retard electrophoretic transport of the charged particles and may induce dipole–dipole interactions in water containing non spherical charged species and thus disrupt the stability of balanced dipolar structures existing in such a system. The main objective of this study was to investigate the effects of alternating current on the removal of cobalt from drinking water using aluminum electrodes and to determine the effects of several parameters, namely initial pH, current density, initial Co(II) ion concentrations, inter-electrode distance, conductivity and electrolysis time, on the removal efficiency.

MATERIALS AND METHODS

ACE processes were conducted in a lab-scale batch system, which was composed of an electrolysis cell, ac power supply, a magnetic stirrer and pH meter. An electrolysis cell was made of rectangular glass tank of 2 L capacity in which a pair of commercially obtained aluminum plates of size 0.15×0.15×0.004 m were used as electrodes. The electrodes were immersed vertically in the bottom of the reactor to a 15 cm depth with an effective area of 225 cm² each. Currents (ranging 0.01-0.04 A m⁻²) were applied between the electrodes. One liter experimental solution of initial Co(II) concentration (ranging 5-25 mg L⁻¹) was placed in ACE reactor and slowly stirred with a magnetic bar at 200 rpm. The inter-electrode distances were varied from 0.005-0.02 m. During electrolysis, samples of 5 mL were taken every 5 min and filtered using Whatman filter paper (Grade 40) and analyzed for cobalt. The concentration changes of Co(II) ions were determined by UV-Spectrophotometer (Beckman, DU 800). The electrical conductivity and viscosity were measured using conductivity meter and suspended Ubbelohde type viscometer, respectively.

The calculation of % removal efficiency of Co(II) after ACE treatment was performed using the equation (Daneshvar *et al.*, 2006):

$$\%RE = [C_o - C/C_o] \times 100$$

where, C_o and C concentration of dissolved Co(II) ions before and after ACE process in mg L⁻¹, respectively.

RESULTS AND DISCUSSION

Applied current density plays significant role in electrolytic treatment as it is the only operational parameter that can be controlled directly. It determines the rate of electrochemical metal dosing and electrolytic bubble production and size and the floc growth resulting in a faster removal of pollutants (Khosla *et al.*, 1991; Holt *et al.*, 2002). Measurements were carried out at different current densities 0.01, 0.02, 0.03 and 0.04 A m⁻²

at fixed electrode spacing of 0.005 m, with the same concentration of 25 mg L⁻¹ of Co(II) solution of pH = 7.5. According to Fig. 1 the removal rates of the studied metal increased with increasing current density. Also with decrease of electrical current, the required time for achieving similar efficiencies increases. This was attributed due to the fact that at high current densities, the extent of anodic dissolution increased and in turn the amount of hydroxo-cationic complexes resulted in increase of cobalt removal. These findings are in line with the results of Cr⁶⁺ removal investigations (Kumar *et al.*, 2004; Bazrafshan *et al.*, 2007).

It is well known that pH is an important parameter influencing the efficiency of the EC process (Mollah *et al.*, 2004). As can be seen in Fig. 2 the ACE treatment using aluminum electrodes induces an increase in the pH when the initial pH value of the medium was 7.5. This solution

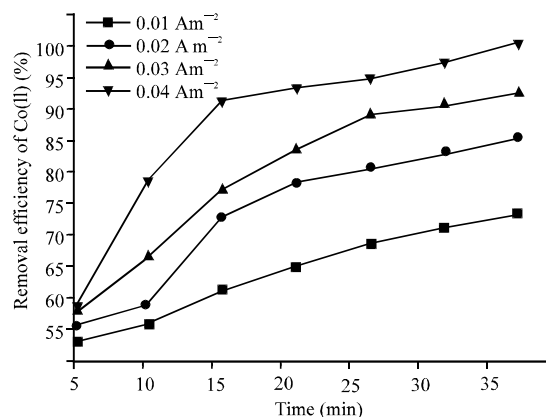


Fig. 1: Percentage removal efficiency of Co(II) ions vs. time at different current densities in solutions containing 25 mg L⁻¹ of the metal

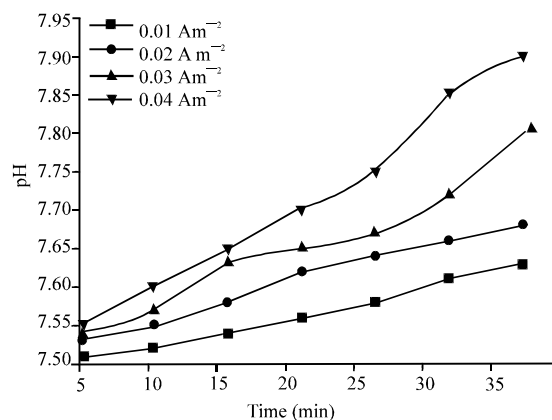


Fig. 2: Variation of pH of Co(II) solutions with time at different current densities. Inter-electrode distance: 0.005 m, Initial Co(II) concentration: 25 mg L⁻¹, Conductivity: 13 S m⁻¹, Current frequency: 50 Hz and Potential: 50 V

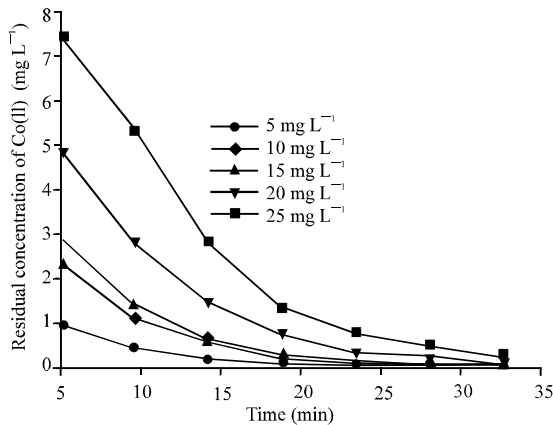


Fig. 3: Residual concentration of Co(II) vs. time. Inter-electrode distance: 0.005 m, Current density: 0.04 A m⁻², AC of frequency: 50 Hz and Potential: 50 V, pH: 7.5, Conductivity 13 S m⁻¹

pH stabilizes at nearly constant value around 8.7. It is also noticed (Fig. 3), that the removal efficiency of the studied metal after 35 min of electrolysis time at the constant current density of 0.04 A m⁻² reached very high values, 98.60% in the pH range 7.5-8. These results could be explained by the excess of hydroxyl ions produced at the cathode and by the intensification in Al(OH)₃ generated in solution during electrolysis time in neutral and slightly alkali conditions which produce more of aluminum hydroxides with a consequent removal of Co(II) (Daida, 2005; Ghernaout *et al.*, 2008). The stabilization of pH at nearly constant value around 8.7 may be ascribed to the buffering capacity of complex nature of aqua Al³⁺/Al(OH)₃ system (Kobya *et al.*, 2006).

To explain the effect of initial Co(II) concentration and the time required for its quantitative removal, a set of experiments were performed with five different solutions containing initial concentrations of 25, 20, 15, 10 and 5 mg L⁻¹ of the Co(II) ion. The solutions were treated at a constant current density, frequency, and potential of 0.04 A m⁻², 50 Hz and 50 V, respectively and different times of electrolysis. It is evident from Fig. 3, that ACE enables lowering [Co²⁺] to Ca. 0.2 of the initial concentration within a reasonable time scale (in the first 5 min of operation), indicating that ACE with Al electrodes is a promising method for reducing the contamination level of cobalt without adding mediators. These observations are in line with results of previous studies of the Arsenic removal efficiency (Kumar *et al.*, 2004) and Cr(VI) removal (Chaudhary *et al.*, 2003; Bazrafshan *et al.*, 2008) by EC processes. A complete removal is observed at the end of 35 min of process. The higher initial concentrations needed longer operating

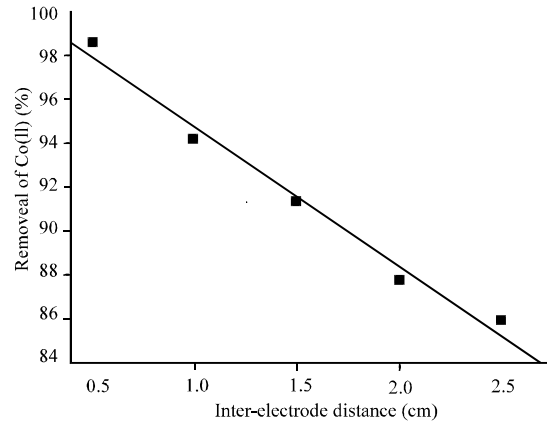


Fig. 4: Effects of inter-electrode distance on Co(II) removal. Current density: 0.04 A m⁻², AC of frequency: 50 Hz and Potential: 50 V, pH: 7.5

time to be quantitatively removed. Certainly, when the initial cobalt concentrations were higher, more aluminum hydroxides were required to decrease the dissolved cobalt concentrations.

To explore the effect of inter-electrode distances on removal efficiency, the distance between electrodes was varied at the same energy input. As can be seen from Fig. 4, When the inter-electrode distances changed from 0.005-0.025 m under 50 Hz and 50 V, the removal (%) of the Co(II) was decreased from 98.60-85.90%. As expected, An increase of local concentration of the Co(II) ions with monomeric and polymeric hydroxo cationic species generated in a smaller space will increase electrostatic interactions, leading to an increase of % removal of dissolved ions (Mansour and Hasieb, 2012).

It appears that conductivity also had some effect on the removal efficiency of Co(II) in the investigated range shown in Fig. 5. It is observed, that the % RE of Co(II) ion increased with increasing conductivity. An increase in conductivity decreases the internal resistance (or the ohmic) drop between electrodes and therefore more aluminum ions could be produced at the same energy input. Also, the formation of (AlCl₂⁺) ions is expected to enhance chemical dissolution of Al electrodes (Szynkarczuk *et al.*, 1994). All the results obtained were consistent with the previous studies (Daida, 2005; Kim *et al.*, 2002). Concentration: 25 mg L⁻¹, Current frequency: 50 Hz and Potential: 50 V.

In the ACE process, the removal rate of Co(II) ions is proportional to the amount of hydroxyl cationic complexes (Al(OH)₃) which can effectively remove Co(II) ions. Further, the applied current density determines the rate of aluminum hydroxide production. In order to process, both pseudo first-order and pseudo second-

Table 1: Pseudo-kinetic rate constants with first-order and second-order models for cobalt ion removal at various initial cobalt concentrations

Parameters [Co(II)] ₀ (mg L ⁻¹)	First-order model		Second-order model	
	k ₁ × 10 ³ (L mg ⁻¹ min ⁻¹)	R ²	k ₂ × 10 ³ (L mg ⁻¹ min ⁻¹)	R ²
5	160.00	0.92066	619	0.288
10	156.79	0.96860	546	0.563
15	159.97	0.96214	2475	0.899
20	146.20	0.98216	2372	0.718
25	125.83	0.99811	8391	0.785

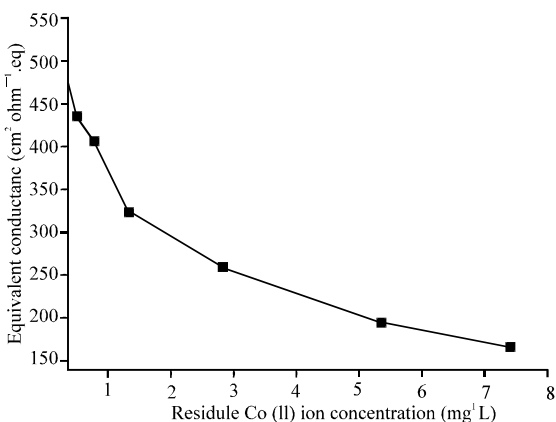


Fig. 5: Equivalent conductance (cm² ohm⁻¹ eq) as a function of residual cobalt ion concentrations (mg L⁻¹). Inter- electrode distance: 0.005 m, initial Co(II) concentration: 25 mg L⁻¹, Conductivity: 13 S m⁻¹ current frequency: 50 Hz and potential: 50 V

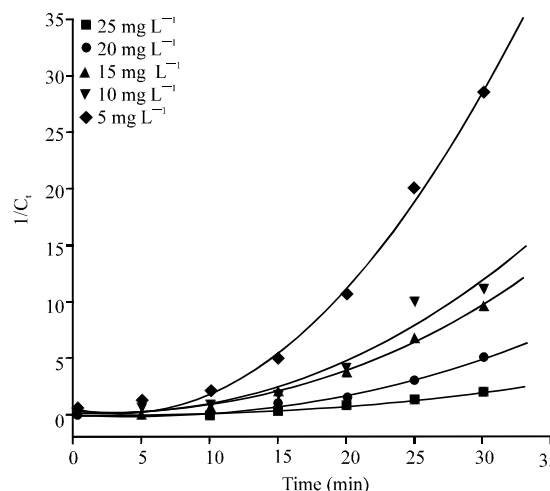


Fig. 7: Pseudo-second-order kinetics plot for the adsorption of various initial cobalt ion concentrations on hydroxyl cationic complexes

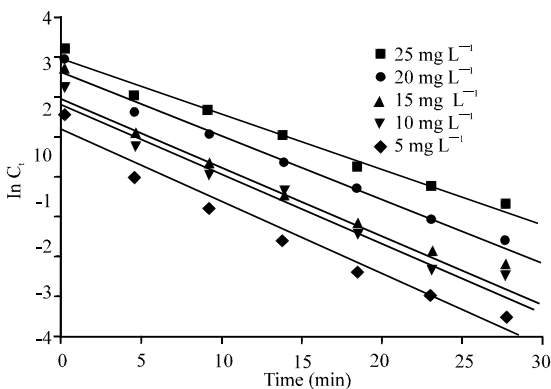


Fig. 6: Pseudo-first-order kinetics plot for the adsorption of various initial cobalt ion concentrations on hydroxyl cationic complexes

order kinetic models were used to fit the experimental data. For a pseudo-first-order kinetic model, the integrated rate law is:

$$\ln C_t = -k_1 t + \ln C_0$$

Here, C₀ (mg L⁻¹) is the initial concentration and C_t (mg L⁻¹) is the concentration at time t. As shown in

Fig. 6, The slopes of the plots of ln C_t versus t give the values of the rate constants k₁ (min⁻¹). For a pseudo-second-order kinetic model, the integrated rate law is:

$$1/C_t = k_2 t + 1/C_0$$

The plots of 1/C_t versus t should give the value of the rate constant k₂ (L mg⁻¹ min). The values of the rate constants for first order and second-order models for Co(II) ion removal at various initial Co(II) ion concentrations are listed in Table 1. The conformity between experimental data and the model values was evaluated using the correlation coefficient values R². As shown in Table 1, regardless of the initial Co(II) ion concentration, R² values for the first-order model were dramatically higher than that for the second-order model. It may also be ascertained from the experimental results that the reaction rate constant k₁ is independent of the initial cobalt concentration and other system parameters.

Therefore, the adsorption of Co(II) ion on hydroxyl cationic complexes is more appropriately followed by the pseudo-first-order kinetic model. Further, the nonlinearity plots at various initial concentrations of second-order model shown in Fig. 7 suggested that the experimental data was best fitted pseudo-first order kinetics. Similar

Table 2: Thermodynamic parameters of the adsorption of Co(II) ions in ACE process

Temperature (K)	ΔG (kJ mol ⁻¹)	ΔH (10 ³) (kJ mol ⁻¹)	ΔS (kJ mol ⁻¹)	T ΔS (10 ⁻³) (J mol ⁻¹)
303	-22.123	-0.363	0.0718	21.76
313	-22.833			22.47
323	-23.550			23.19
333	-24.270			23.91
343	-24.980			24.62

modeling results are also found in the kinetic studies on removal of Mn²⁺ ions from synthetic wastewater by EC process (Shafaei *et al.*, 2010) and the removal of arsenate (Vasudevan *et al.*, 2010). It was also reported (Emamjomeh and Sivakumar, 2006) that the defluoridation rate of the EC follows first order kinetics with respect to fluoride concentration.

The Gibbs free energy change (ΔG) is the fundamental criterion of the spontaneity of a process. The thermodynamic parameters of the adsorption process are summarized in Table 2. The negative values of free energy ΔG indicate the feasibility of the process and its spontaneous nature. The ΔG values at different temperatures approximately remain constant for adsorption of Co(II) ions indicating that there is no effect of temperature on free energy of adsorption. The ΔH and ΔS were calculated from the plot of $\ln K$ versus $1/T$ and their values are shown in Table 2.

The negative values of ΔH for the present system confirmed the exothermic nature of adsorption. The positive value of ΔS observed for the adsorption of Co(II) ions suggested the increased randomness at the solid-solution interface during the adsorption process. The Co(II) ions in the aqueous media are hydrated. When the Co(II) ions get adsorbed on the adsorbent surface, the water molecule bonded to the Co(II) ions by hydrogen bonds get released and dispersed in the solution, this results in an increased in the entropy. The positive values of entropy change also reflect good affinity, either physical or chemical, of the Co(II) ions toward the adsorbent. The entropy changes results in the present study are in excellent agreement with the literature (Vasudevan *et al.*, 2011).

CONCLUSION

The results of this study on cobalt ions removal from aqueous solution using Alternating Current Electrocoagulation (ACE) system can be summarized as follows:

- The gelatinous charged aluminum hydroxides generated in ACE process can efficiently remove cobalt ions by adsorption. Considering the removal efficiency at a specific energy input, a current density: 0.04 A m⁻², an inter-electrode distance:

0.005 m, operating time: 35 min, pH: 7.5, conductivity: 13 S m⁻¹, frequency: 50 Hz and voltage: 50 V were found to be the optimum values for the present electrocoagulation

- It was found that increasing the initial cobalt ion concentration from 5 to 25 mg L⁻¹ decreased the removal efficiency of cobalt ions
- Values of kinetic rate constants for cobalt ion removal at various initial concentrations were calculated. The kinetic results showed that a pseudo-first-order kinetic model matched satisfactorily with the experimental observations
- Values of thermodynamic parameters for cobalt ion removal as a function of temperature were calculated. The temperature studies showed that the adsorption was exothermic and spontaneous in nature

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REFERENCES

- Babu, R.R., N.S. Bhadrinarayana, K.M.M.S. Begum and N. Anantharaman, 2007. Treatment of tannery waste water by electro coagulation. *J. Univ. Chem. Technol. Metall.*, 42: 201-206.
- Barceloux, D.G., 1999. Cobalt chloride administration in athletes: A new perspective in blood doping?. *J. Toxicol. Clin. Toxicol.*, 37: 201-206.
- Bazrafshan, E., A.H. Mahvi, S. Naseri and A.R. Mesdaghinia, 2008. Performance evaluation of electrocoagulation process for removal of chromium (VI) from synthetic chromium solutions using iron and aluminum electrodes. *Turk. J. Eng. Environ. Sci.*, 32: 59-66.
- Bazrafshan, E., A.H. Mahvi, S. Naseri and M. Shaieghi, 2007. Performance evaluation of electrocoagulation process for diazinon removal from aqueous environments by using iron electrodes. *Iran. J. Environ. Health Sci. Eng.*, 4: 127-132.
- Benefield, L.D., J.K. Judkins and B.L. Weand, 1982. *Process Chemistry for Water and Wastewater Treatment*. Prentice-Hall, NJ, USA.
- Chaudhary, A., N. Goswami and S.M. Grimes, 2003. Electrolytic removal of hexavalent chromium from aqueous solution. *J. Chem. Technol. Biotechnol.*, 78: 877-883.
- Daida, P., 2005. Removal of arsenic from water by electro coagulation using Al-Al Fe-Fe electrode pair systems and characterization of by product. *UMI Microform*, pp: 1-68.

- Daneshvar, N., A. Oladegaragoze and N. Djafarzadeh, 2006. Decolorization of basic Dye solutions by electrocoagulation: An investigation of the effect of operational parameters. *J. Hazard Mater.*, 129: 116-122.
- Duffey, J.G., 1983. Electrochemical Removal of Heavy Metals from Wastewater. Product Finishing Inc., Hertfordshire, UK., pp: 72.
- Emamjomeh, M.M. and M. Sivakumar, 2006. An empirical model for defluoridation by batch monopolar Electrocoagulation/Flotation (ECF) process. *J. Hazard. Mater.*, 131: 118-125.
- Ghermaout, D., A. Badis, A. Kellil and B. Ghermaout, 2008. Application of electrocoagulation in *Escherichia Coli* culture and two surface waters. *Desalination*, 219: 188-205.
- Holt, P.H., G.W. Barton, M. Wark and C.A. Mitchell, 2002. A quantitative comparison between chemical dosing and electrocoagulation. *Colloids Surf. A: Physicochem. Eng. Aspects*, 211: 233-248.
- Karim, Z., 2011. Risk assessment of dissolved trace metals in drinking water of Karachi, Pakistan. *Bull. Environ. Contam. Toxicol.*, 86: 676-678.
- Khosla, N.K., S. Venkatachalam and P. Somasundaran, 1991. Pulsed electrogeneration of bubbles for electroflotation. *J. Appl. Electrochem.*, 21: 986-990.
- Kim, T.H., C. Park, E.B. Shin and S. Kim, 2002. Dechlorination of disperse and reactive dyes by continuous electro coagulation process. *Desalination*, 150: 165-175.
- Kobyas, M., E. Demirbas, O.T. Can and M. Bayramoglu, 2006. Treatment of levafix orange textile dye solution by electrocoagulation. *J. Haz. Mater.*, 132: 183-188.
- Kumar, P.R., S. Chaudhari, K.C. Khilar and S.P. Mahajan, 2004. Removal of arsenic from water by electro coagulation. *Chemosphere*, 55: 1245-1252.
- Lauwerys, R. and D. Lison, 1994. Health risks associated with cobalt exposure-an overview. *Sci. Total Environ.*, 150: 1-6.
- Mansour, S.E. and I. H. Hasieb, 2012. Removal of nickel from drinking water by electrocoagulation technique using alternating current. *Curr. Res. Chem.*, (In Press).
- Mollah, M.Y.A., P. Morkovsky, J.A.G. Gomes, M. Kesmez, J. Parga and D.L. Cocke, 2004. Fundamentals, present and future perspectives of electrocoagulation. *J. Hazard. Mater.*, 114: 199-210.
- Mollah, M.Y.A., R. Schennach, J.R. Parga and D.L. Cocke, 2001. Electrocoagulation (EC)-science and applications. *J. Hazard. Mater.*, 84: 29-41.
- Moreno, C.H.A., D.L. Cocke, J.A.G. Gomes, P. Morkovsky, J.R. Parga, E. Peterson and C. Garcia, 2009. Electrochemical reactions for electrocoagulation using iron electrodes. *Ind. Eng. Chem. Res.*, 48: 2275-2282.
- Parga, J.R., J.L. Valenzuela and C.T. Francisco, 2007. Pressure cyanide leaching for precious metals recovery. *JOM J. Miner. Metals Mater. Soc.*, 59: 43-47.
- Shafaei, A., M. Rezayee, M. Arami and M. Nikazar, 2010. Removal of Mn²⁺ ions from synthetic wastewater by electrocoagulation process. *Desalination*, 260: 23-28.
- Szynkarczuk, J., J. Kan, T.A.T. Hassan and J.C. Donini, 1994. Electrochemical coagulation of clay suspensions. *Clay Clay Miner.*, 42: 667-673.
- Vasudevan, S., J. Lakshmi and G. Sozhan, 2010. Studies on the removal of arsenate by electrochemical coagulation using aluminum alloy anode. *CLEAN-Soil Air Water*, 38: 506-515.
- Vasudevan, S., J. Lakshmi and S. Ganapathy, 2011. Effects of alternating and direct current in electrocoagulation process on the removal of cadmium from water. *J. Hazard. Mater.*, 192: 26-34.