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Recovery of Cobalt and Copper from Textile, Electroplating and Tannery Effluents Using Electrocoagulation Method

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Abstract

An Electrocoagulation (EC) process has been conducted in an electrolytic cell with iron electrodes to eradicate and, consequently, recover copper and cobalt from synthetic and industrial effluent samples. Purity of recovered metal has been determined by synthesis of crystalline salts and analysis by X-ray diffractometer (XRD). Operating parameters such as metal ion concentration, pH, current density and temperature were investigated for removal efficiency of copper and cobalt. Results indicated that removal efficiency of copper (pH 3.5) and cobalt (pH 4.5) was 98.8% and 97.9% respectively. Adsorption studies were investigated by applying Langmuir and Freundlich adsorption isotherm models. On the basis of regression coefficient R^2 values, Langmuir isotherm models were obeyed. Adsorption kinetic studies demonstrated that the EC process was pre-eminently depicted using a pseudo-second-order kinetic model. The present method is simple and efficient compared to existing water treatment technologies.

Keywords: Asorption; Electrocoagulation; Isotherms; Kinetic model; Copper; Cobalt

Introduction

Rapid industrialization is a major cause for the release of heavy metals into the environment. In recent times, treatment of water to remove heavy metals has become increasingly important due to their fractious and persistent nature in the environment. Contamination of water by heavy metals has led to a number of environmental problems [1]. Heavy metals can gather in environmental elements such as food chains and consequently may pose a substantial risk to human health [2]. Therefore, it is necessary to treat industrial effluents before discharge to aqueous streams to protect public health.

Copper usually occurs in industrial effluents in the bivalent form, either as $Cu(OH)_2$, $CuCO_3$ or as organic complexes. Industries such as dyeing, paper, petroleum, copper plating and those producing copper-ammonium rayon release undesired amounts of Cu(II) ions. Copper cleaning, plating and processing industries discharge effluents with concentrations of copper amounting to 100-120 mg/L. This value is dangerously high with respect to water quality standards, which indicate permissible copper concentrations of wastewaters at a value of 1.0-1.5 mg/L [3]. The permissible limit of copper and cobalt in drinking water is 1.3 and 0.1 mg/L respectively [4]. Cobalt is a bluish-grey, shiny, brittle metal. It is considered to be a very important element for healthy well being. Cobalt is used to generate deep blue glass, ceramics, pottery and tiles, and paint pigments. In addition to these uses cobalt, in combination with other metals, is used to make alloys which are employed to create strong magnets, jet engines and gas turbine engines.

Common treatment processes for metal contaminated water are: chemical precipitation, membrane filtration, reverse osmosis, ion exchange, and adsorption. Although these methods are in use all over the world, they have certain disadvantages [5] and [6]. One of the major drawbacks of these methods is the recovery of metal in pure form and good yield [7]. An alternative technique is electro coagulation which, because of its high capital and running cost, has been neglected until recently. Scientists are turning their attention towards electro coagulation because of its eco-friendly nature, its toxicity free properties and reduced chemical costs which allows for recovery of the metal in pure form possible [7-9]. These advantages reduce the overall cost of the process and enhance the feasibility to treat metal contaminated water.

Electrochemical processes are being used on a large scale for treatment of wastewaters. Refinery [10,11], dye and textile [12,13], municipal [14,15] and industrial wastewaters [16] have been treated and studied in detail. Removal of heavy metals is very important because of the persistent and mobile nature of these toxins. Scientists around the world have studied, and are continuing to investigate the removal of metals by electrochemical procedures. Cadmium [17], chromium [18], selenium [19], nickel [20], arsenic [21] and zinc [22] have been extensively studied and different process parameters evaluated.

In the current study, an electrolytic cell incorporating iron electrodes has been constructed to remove, and subsequently recycle, copper and cobalt from artificial, as well as, actual effluent samples. Various parameters were studied to optimize ideal operating conditions. Moreover, the recovered copper was used to prepare crystalline salts (acetate, sulfate, chloride and nitrate) and the structures of each salt were subjected to x-ray diffraction analysis.

Equilibrium adsorption behavior was analyzed by applying the Langmuir and Freundlich isotherm models. The adsorption kinetics of

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electrocoagulation was analyzed using first and second order kinetic models.

Experiment

Materials and methods

Copper sulfate pentahydrate, cobalt sulfate heptahydrate, concentrated sulfuric acid, concentrated hydrochloric acid, concentrated nitric acid, ammonium hydroxide, sodium hydroxide and acetic acid were used during the course of this work. All these chemicals were of high purity purchased from Merck, Inc and were used without further refinement.

Analytical method

Pyrex glassware was used throughout this work after thorough washing with tap water, chromic acid, soda ash and double distilled water in that order. A glass electrolytic cell was used during this work having dimensions; length 150 mm, width 160 mm and height 125 mm. It was equipped with 1 mm thick iron electrodes. Other devices were pH meter (Jenway, 3505), electronic balance (Sartorius CP 324S), heating magnetic stirrer and power supply (Major Science, MP 300). Atomic Absorption Spectrophotometer (AAS) (Hitachi, Z-5000) was used to estimate the concentration of metals in the sample using their respective hollow cathode lamps. X ray diffractometer (Bruker-axe, D8 Discoverer) was used to study the crystalline characteristics of the salts synthesized from recovered cobalt.

Collection of industrial samples

Samples of effluents were collected from different industrial units situated in and around Lahore, Pakistan. Several random samples were collected from Hafeez Shafi Tanneries (Pvt.) Limited, Batala Textiles, Adarash Textiles Mills and Pakistan Cycle Industrial Cooperative Society, Izhar (Pvt.) Ltd.

Results and Discussion

Industrialization plays a vital role in the development of a country but this can also be the cause of extended environmental inconvenience. Many industrial activities produce a large amount of metal contaminated effluents which are undesirable from an environmental as well as an economical viewpoint. Many metal removal processes are available which are efficient but not proficient. These processes can take out metals with excellent removal efficiency but metal retrieval is neither possible nor feasible. Electrocoagulation is considered a costly technique but when recovery of metal is necessary, it is deemed to be a more suitable technique.

Effect of initial copper and cobalt ion concentrations

In the present work, copper and cobalt has been removed from water using an electrocoagulation process carried out in a glass tank with iron electrodes. Iron electrodes are a good choice as they do not corrode during mechanical or chemical separation of deposited metal from the surface. Metal solution was placed surrounding the electrodes and the desired current was applied so as to direct the metal ions towards the cathode. Figure 1 shows the rate of change in concentration of cobalt solution of different strengths in terms of absorbance of light having wavelength 240.7 nm. Absorbance is a direct measure of concentration when all other parameters are constant. It was found that removal efficiency was uniformly good for all solutions. However, removal efficiency was better in the case of concentrated solution (150 mg/l) in comparison to dilute solution (50 mg/l).

Effect of pH

After preliminary experiments, it was found that in the case of cobalt, the optimum pH was 4.5. Below this pH, hydrogen ions compete with the metal ions to gain electrons from the cathode and become uncharged. There are three parameters, which determine the ability of an ion to discharge at the electrode.

These are:

(i) Position in electrochemical series

(ii) Concentration of ion

(iii) Nature of the electrode

By varying the latter two factors, one can discharge the desired ion at the electrode. For illustration of the case in point, when electrocoagulation is carried out using an aqueous solution of NaCl, OH^- is predicted to discharge at the anode. However, chloride discharges because of the relatively high concentration in solution as compared to hydroxide. Likewise, when graphite electrodes are used, hydrogen will discharge at the cathode because of its relatively lower position as compared to sodium in the electrochemical series. Conversely, when mercury is used as the cathode, sodium will preferentially discharge.

Figure 2 shows removal of cobalt from real industrial effluents. It was found that electrocoagulation can remove nearly every metal cation from effluent. When absorbance was converted into concentration, by comparison adjacent to the calibration graph, it was found that more than 98% of metal ions had been removed.

Figure 3 illustrates removal of copper ions from standard solutions having 500, 1000 and 1500 mg/l. Again, the rate of removal was faster in the case of metal rich solution. In this instance the pH was adjusted to 3.5. It was more beneficial to carry out the process in acidic conditions as compared to basic conditions since this can hinder metal deposition on the cathode by either converting it to species such as $[Metal_x(OH)_y]^{-z}$ (x, y and z are natural numbers) or by precipitating metal as hydroxide. In the former case, ions will move towards the anode where they have an extremely remote possibility to compete with the OH^- to be primarily discharged. Figure 4 shows the results in the case of real industrial samples of copper containing effluent. The removal efficiency was near to 99%.

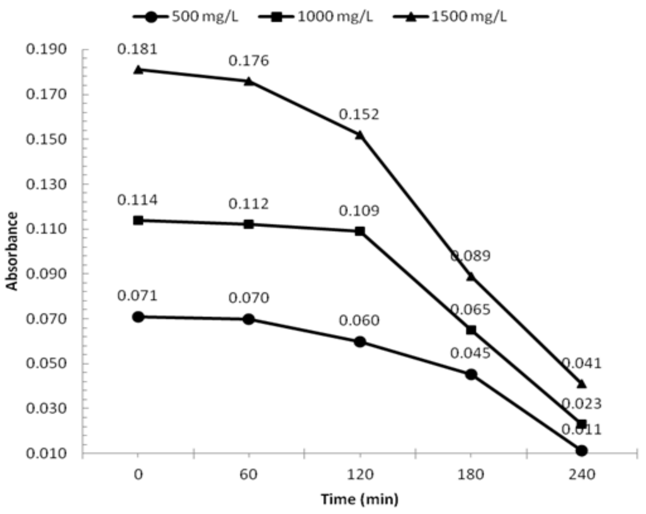

Figure 1: Change in concentration of different solution of Cobalt.

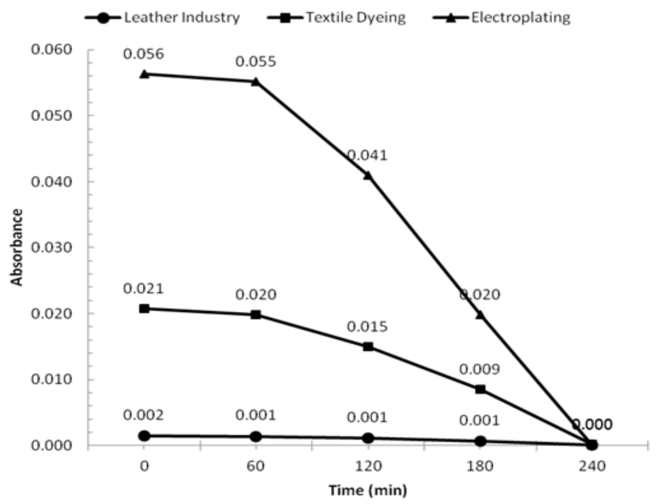

Figure 2: Change in concentration of different Cobalt containing effluents.

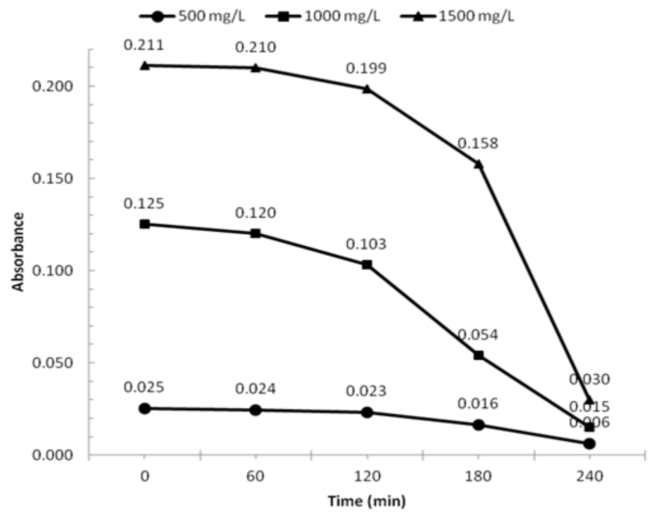

Figure 3: Change in concentration of different Copper solutions.

Recovery of copper

The deposited copper was taken apart from the cathode surface mechanically in conjunction with dilute nitric acid. The reclaimed copper was used to synthesize different salts such as copper acetate, copper nitrate, copper chloride and copper sulfate. The salts were subjected to x-ray diffraction analysis; the results are illustrated in Table 1. In all cases, high purity and yield was obtained, which pointed out the usefulness of the process.

Adsorption isotherms

Isotherm studies provide information about the capacity of the adsorbent material or the amount required to remove a unit mass of pollutants such as Cu (II) and Co (II) from water. The adsorption data have been subjected to Freundlich and Langmuir isotherm models.

The Langmuir model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. Langmuir's isotherm [23] has been used by various workers for the sorption of a variety of compounds and the linear form of this isotherm is given by Eq. 1.

$$1/q_e=1/K_L q_{max}.1/C_e+1/q_{max} \qquad \text{(Eq. 1)}$$

where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/l) and q_{max} and K_L are the Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively. When C_e/q_e was plotted against C_e, straight lines with slopes $1/K_L q_{max}$ were obtained (Figures 5 and 6) indicating that the adsorption of Cu (II) and Co (II) followed the Langmuir isotherm.

The adsorption data of lead and cadmium were also fitted into the Freundlich model. The logarithmic form of the Freundlich model [24] is given by Eq. 2.

$$\ln q_e=\ln K_f+1/n \ln C_e \qquad \text{(Eq. 2)}$$

where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/l) and K_f and n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. When ln q_e was plotted against $\ln C_e$, straight lines with slopes '1/n' were obtained (Figure 7) for Co (II), which indicates that the adsorption of Cu (II) and Co (II) does not follow the Freundlich isotherm.

Electrocoagulation dynamics

The prediction of electrocoagulation/adsorption rate gives important information for designing batch adsorption systems. Information on the kinetics of pollutant uptake is required for selecting

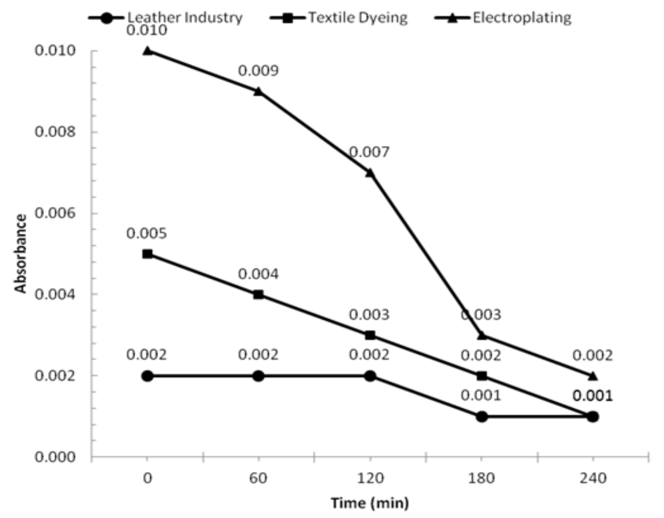

Figure 4: Change in concentration of different Copper containing effluents.

Copper nitrate	d-spacing	6.927	3.463	2.673	2.464	2.354	2.157	2.078	1.712
	2θ	12.28°	25.72°	33.52°	36.46°	38.22°	41.87°	43.55°	53.51°
	Intensity	100	51.82	47.2	36.09	15.83	20.94	35	27.14
Copper chloride	d-spacing	3.13	5.502	4.054	2.726	2.638	2.579	2.548	2.061
	2θ	28.51°	16.11°	21.92°	32.85°	33.97°	34.78°	35.21°	43.91°
	Intensity	100	66.9	60.99	34.04	55.08	30.02	27.9	24.11
Copper sulfate	d-spacing	3.258	5.114	4.865	3.985	3.649	3.422	3.19	2.974
	2θ	27.37°	17.34°	18.23°	22.30°	24.39°	26.03°	27.97°	30.04°
	Intensity	100	79.92	52.47	61.35	87.8	79.55	59.1	39.4
Copper acetate	d-spacing	7.96	7.57	7.05	4.12	3.47	3.05	2.73	2.38
	2θ	11.11°	11.68°	12.56°	21.55°	25.69°	29.27°	32.83°	37.79°
	Intensity	100	61.17	71.09	25.55	32.41	28.18	30.66	33.43

Table 1: XRD analysis of salts synthesized from reclaimed copper.

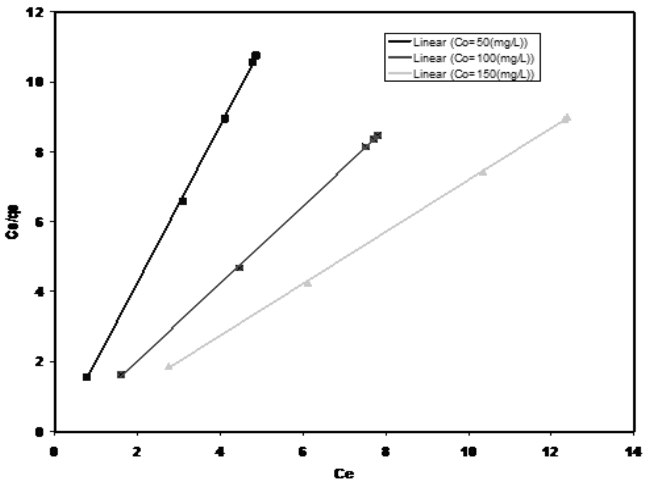

Figure 5: Langmuir adsorption isotherm for Cobalt.

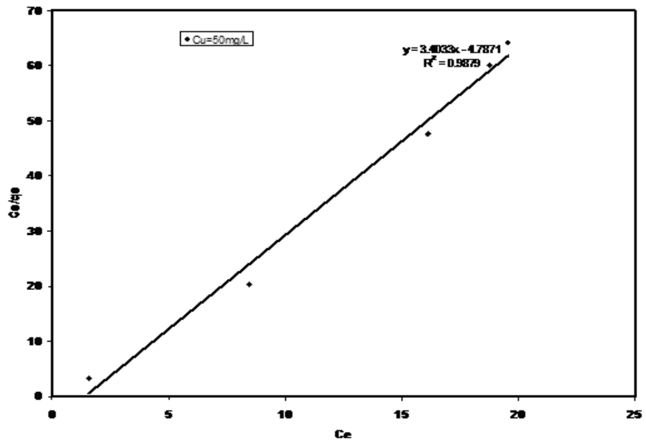

Figure 6: Langmuir adsorption isotherm for Copper.

optimum operating conditions for a full-scale batch process. In order to clarify the adsorption kinetics of Cu (II) and Co (II) ions, two kinetic models were applied to the experimental data.

First order rate equation can be represented as Eq. 3.

$dCt/dt=-kCt$ (Eq. 3)

Its simplest form on integration is

$Ct=Co.e^{-kt}$ (Eq. 4)

where Co and Ct (mg/l) are the amounts of the initial and at time “t” adsorbed metal ion concentrations and t (min) respectively; k_1 is the rate constant of the equation (min^{-1}). The adsorption rate constant (k_1) can be determined experimentally by plotting ln Ct *vs.* t.

The plots of ln Ct versus t for the first order model are shown in Figures 8 and 9. It can be concluded from the R^2 values that the adsorption mechanisms of Cu (II) and Co (II) ions follow the first order kinetic model.

Experimental data were also tested by the pseudo-second order kinetic model [25] which is given in the form of Eq. 5.

$t/q_t = 1/k_2 q_e^2 + (1/q_e)\, t$ (Eq. 5)

Where k_2 (g/mg min) is the rate constant of the second-order equation, q_t (mg/g) is the amount of adsorption time t (min) and q_e is the amount of adsorption equilibrium (mg/g).

This model is more likely to predict kinetic behavior of adsorption with chemical sorption being the rate-controlling step. The linear plots of t/q_t versus t for the pseudo-second order model for the adsorption of Cu (II) and Co (II) ions. R^2 values are very high in the range of 0.996–0.942 for the Cu (II) and Co (II) adsorption respectively. In the view of these results, it can be said that the pseudo-second-order kinetic model provided a good correlation for the adsorption of Cu (II) and Co (II) in contrast to the pseudo-first-order model.

Electrocoagulation–removal and recovery of metals

Two liters of different concentration solutions of copper and cobalt (500, 1000 and 1500 mg/L) were taken in the electrolytic cell one at a time. The electrodes were immersed in the solution and were connected with a source of continuous current. The power was adjusted to apply 3.0 volts of potential on electrodes which allowed 600 mA of direct current to pass between the electrodes. pH was kept constant at 4.5 in the case of cobalt and 3.5 for copper. The current was passed for four hours uninterrupted and after each hour, 1 milliliter of the solution was removed from the cell, diluted to 50 ml with double distilled water and subjected to AAS for metal estimation. A hollow cathode

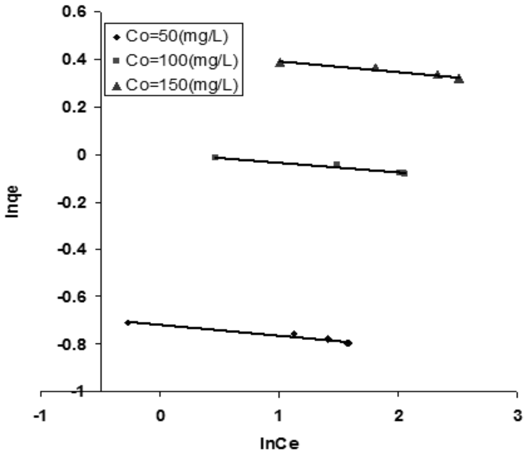

Figure 7: Freundlich adsorption isotherm for Cobalt.

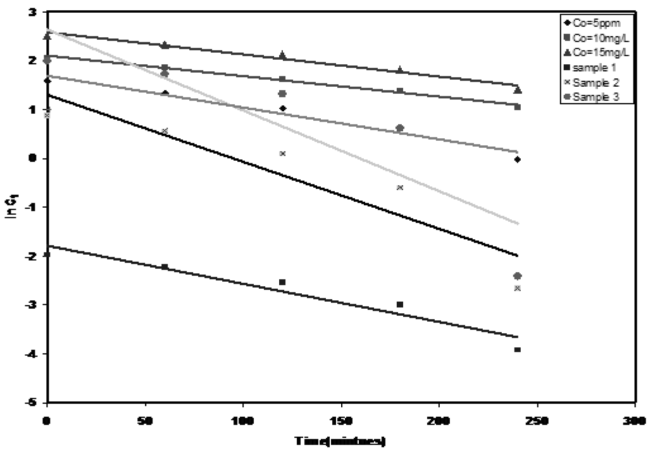

Figure 8: Comparison for first order kinetics for Cobalt.

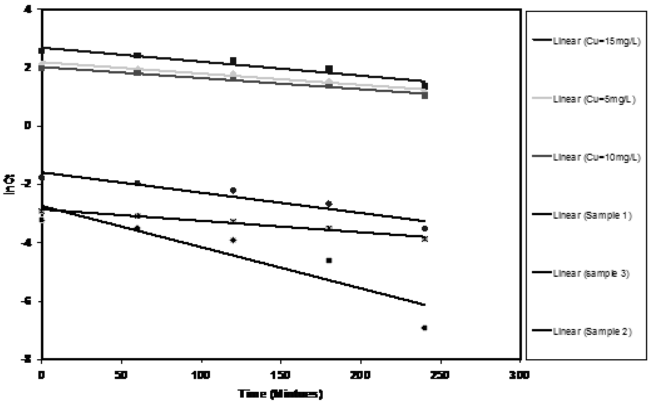

Figure 9: Comparison for first Order kinetics for Copper.

lamp of copper was in operation using 7.5 mA current and producing light of 324.8 nm, while that of cobalt utilized a current of 10.0 mA and produced light of 240.7 nm. The slit width was 1.3 nm for copper and 0.2 nm for cobalt. Air diluted acetylene flame (25%) was used with height 7.5 and 10.0 mm for copper and cobalt, respectively. The same process was repeated for real samples collected by textile, leather and electroplating industries. The metals accrued at the electrode (cathode) were disunited mechanically. The following chemical reactions at the anode (Eq. 6), cathode (Eq. 7) and in solution (Eq. 8) have been proposed to describe the EC mechanism.

$$Fe \rightarrow Fe^{+2} + 2e^{-} \quad \text{(Eq.6)}$$

$$2H_2O+2e^{-}\rightarrow H_{2(g)}+2OH^{-} \quad \text{(Eq.7)}$$

$$Fe^{+2}+2H_2O\rightarrow Fe(OH)_2+2H^{+} \quad \text{(Eq.8)}$$

As a result of this electrochemical process the pH of the medium increased and the $Fe(OH)_2$ formed remained in the aqueous stream as gelatinous suspension, which could be utilized to remove the Co (II) and Cu (II) from waters, either by electrostatic attraction, complexation or a combination of coagulation and flotation.

Reuse of recovered cobalt

The purity of the recovered metals was determined by dissolving a weighed quantity in dilute nitric acid and testing against respective standard solutions using AAS. Afterwards, reclaimed cobalt was treated with suitable reagents (nitric acid, sulfuric acid, hydrochloric acid and acetic acid) to formulate the respective salts, which were analyzed by an X-ray Diffractometer (XRD).

Conclusion

In the present study, an electrolytic cell with iron electrodes has been used to remove and subsequently recover copper and cobalt from synthetic as well as real effluent samples. Various parameters were studied to find the most favorable working conditions. It was found that pH 3.5 is suitable for copper while 4.5 for cobalt. The adsorption kinetic studies showed that the EC process was best described using the pseudo-second-order kinetic model. The Langmuir isotherm model predictions matched satisfactorily with the experimental observations. The process was good for concentrated as well as dilute solutions however, rate of metal removal was high in the case of concentrated solution. Furthermore, the recovered copper was utilized to make crystalline salts, the structure of which were subjected to x-ray diffraction analysis. The salts were obtained in high yield and purity.

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