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RECAPTURING METALS FROM ELECTROCOAGULATION FLOC

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Abstract

Electrocoagulation (EC) is an emerging technology mainly used for wastewater treatment. In this process, in situ coagulants are produced by passing electric current through a conductive aqueous media in presence of sacrificial electrodes. When iron is used as electrodes, layered double hydroxides (LDH) or green rust are formed as intermediates that turns into iron metallic oxides/hydroxides/oxyhydroxides with time. LDH has a very effective capacity to absorb different kinds of water contaminants, such as arsenic, lead, cadmium, and copper in its structure. In this study, we present our work to treat the EC-floc to recapture the metals, such as copper. Thermal, chemical, and electrochemical methods have been applied for the treatment. The floc and recovered metals have been characterized using XRD, SEM/EDS, and FTIR. A cost analysis is also presented for the recovery processes.

Introduction

Metals are non-renewable resources and the consumption rates of metals in various industrial and domestic purposes have been increasing continually and resources of metals become more and more scarce with time [1]. The growing number of contaminated waste produced by metals causes a serious disposal problem as well as hazardous risk to the environment. Because of this, especially the chemical and other industrial companies are trying to control the release of metals as contaminant with waste and investing for the research to know the better and cost effective disposal processes.

Electrocoagulation (EC) is one of the effective ways to remove the metallic particles from the waste water. The green rust and floc produced during the EC process are responsible for the removal of metals by absorbing them inside its structure. In our previous works, we removed As, Cu, Pb, and Cd from synthetic and real waster waters by EC [2]. After the waste water treatment by EC the floc was separated by filtration, and tehn it was characterized. The present work is to recapture of metals such as copper from the EC floc by different techniques, such as, thermal, chemical and electrochemical.

Currently copper is one of the most used metals for industrial manufacture as well as household materials. The mining and metallurgy industries are main contribution of anthropogenic copper emission to the environment. At high concentration, copper can be toxic to all life forms but at low concentration copper is a micro nutrient and is essential to all plants and animals [3].

Figure 1 shows the release of copper and copper compounds in tons throughout the last few years in United States and it was almost 89,968 tons last year. According to Figure 1 although releasing of copper is decreasing comparing with the year 2000, but still it is a huge amount that is needed either to properly disposed, or better to recover.

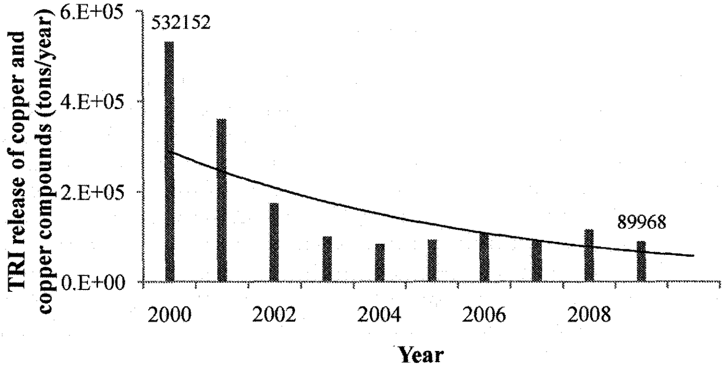


Figure 1: Release of copper and copper compounds in tons vs years [4].

From literature reviews [5-10] it was noticed that metals were recovered by various processes. For example; a number of hydro- and pyro metallugical processes have been proposed for metal recovery from spent catalyst, fly ash and boiler ash. In both cases the metals are recovered as mixed solutions and then separated by conventional separation techniques (solvent extraction, selective precipitation and ion- exchange) [5]. For crushing process to be important for chemical and biological methods it must make the resulting particle approptiate for subsequent contact with the chemical and biological medium [6]. Leaching and selective separation are crucial procedures to enxure effective recovery of metal from industrial sludge [7]. Current methods for copper removal are, among others, cementation, coprecipitaion with calcium carbonate, and adsorption [8-10].

Electrodeposition can play an important role for the recapture of metals from the EC floc after separation of metals. The present work was performed with the synthetic waste water containing copper first to be treated by EC using sacrificial iron electrodes, and then copper to be recovered from the EC floc.

Experimental

Apparatus for electrocoagulation treatment

We used beaker-size EC reactor [2] using scrap iron plates as sacrificial electrodes. The electrodes were connected to a digital DC power supply equipped with potentiostatic or galvanostatic operational options. All runs were conducted at constant temperature of 25 °C. In general, 500 ml of synthetic copper solution was placed into the electrolytic cell. The current density was adjusted to a desired value and then the experimental run was started. The power supply and pump were run in predetermined flow rate and current. One magnetic stirrer was used to homogenize the solution in Beaker. At the end of reaction time the solution was filtered. The electrodes were washed thoroughly with water to remove any solid residues on the surfaces, and dried.

Recapture Processes

The EC-floc that was obtained after filtering the heterogeneous mixture after EC was dried to the air in room temperature. Four types of processes were used to recapture copper from the floc, namely oxidative thermal, reductive thermal, chemical, and electrochemical.

Oxidative Thermal Process: 1 g of EC floc was treated in tube furnace at 600 °C for 4 hours in presence of air. After heating slowly cooled the floc to come at room temperature. The black EC floc was turned to brick red coloured powder after the process. FTIR, XRD, SEM, EDS was done for the characterization of that treated floc.

Reductive Thermal Process: EC floc was heated up to 580°C in Catlab (Hiden Anatytical) micro-reactor with a ramp of 10°C per minute in presence of 5% Hydrogen gas at a flow rate of 80 mL/min. The floc after the process was characterized using FTIR, XRD, SEM, and EDS.

Chemical Process: 2 g of EC Floc was dissolved in 6M HCl. In the solution, a few drops of thioacetamide (CH_3CSNH_2) was added that formed black precipitate of Cu_2S. Cu_2S was separated by filtration. Thus Cu was separated from the Fe of the EC floc. 2.5 ml of concentrated HNO_3 was added to dissolve the copper sulfide solid into free Cu^{2+} and elemental S.

Electrochemical Process: The solution obtained from chemical process was neutralized using 30% ammonia and then diluted with distilled water. The solultion is then put in 3-electrode electrochemical cells and copper ions was electrochemically deposited using Voltalab (Radiometer) electrochemical analyzer on three types of cathodes, such as platinum, copper, and glassy carbon.

Characterization Instruments

Scanning electron microscope (Hitachi S-3400N) with energy dispersive X-ray spectrometer using EDAX detector was used to investigate the morphology and the composition of the EC-floc and the treated floc. XRD analysis weas carried out with a Bruker D8 GADDS Discover diffractometer operating with Cu Kα radiation source filtered with a graphitic monochromator. Fourier Transform Infrared Spectroscopy (FTIR) analyses were carried out by Thermo-electron Nexus 470 FTIR spectrometer using potassium bromide (usually, sample: KBr =1: 50). The spectra were recorded in the range of 400-4000 cm^{-1} with 4 cm^{-1} resolution.

Results and Discussion

Copper Removal from Wastewater

It was found that through electrocoagulation about 100% copper was removed when sacrificial iron was used [2]. The current density was 30 mA/cm^2. The intial copper concentration was used as 1000 ppm. The copper concentration was measured electrochemically using Nanoband iridium electrode system (TraceDetect).

Recapture of Copper from EC-Floc

When iron sacrificial is used in electrocoagulation, the transition byproduct is green rust, which is one kind of layered double hydroxide consisting of Fe(II) and Fe(III) [11]. The strategy we took to recapture copper is of three prongs. In one case, we oxidized all the iron species to ferric state. After that, we can either chemically separate copper by adding acids, thioacetamide, and ammonia, or electrochemically deposit on cathodes as mentioned in the experimental section. In another case, we reduced the copper and iron species into metallic form at high temperature using hydrogen in inert atmosphere. After that, the metallic copper can be separated out using chemical and electrochemical processes. Third, we directly did chemical and electrochemical treatment of the EC-floc without performing any thermal treatment.

Figure 2 shows the XRD patterns for original (black), the oxidized form (green), and the reduced form (blue) of the EC-floc. In the original EC-floc, the presence of goethite α-FeOOH), maghemite (γ-Fe_2O_3), copper hydroxide ($Cu(OH)_2$), tenorite (CuO), copper ferrite ($CuFe_2O_4$), wuestite (FeO), hematite (α-Fe2O3), and lepidocrocite (γ-FeOOH) was confirmed. In the oxidized form, most of the iron species was converted to red powder of hematite. In the reduced form, copper oxide of $Cu_{64}O$ form was confirmed. This indicates that we successfully reduced copper oxides or hydroxides to copper-enriched suboxides.

Figure 3 shows the SEM and EDS results of EC-floc of original, oxidized, and reduced forms. In general, the particle size is in the micrometer range. When the elemental analyses of the flocs are compared, it was found that the reduced floc contains more copper and iron, compared to those elements in the original floc. This also verifies the successful reduction of the floc using hydrogen. When the elemental analysis of the original floc is compared to those of oxidized form, it was found that ratio among Cu, O, and Fe was changed from 2:2:6 to 1:1:8, as shown in Table I. This might happen due to change of concentration of iron on the surface of the floc during heating treatment in air.

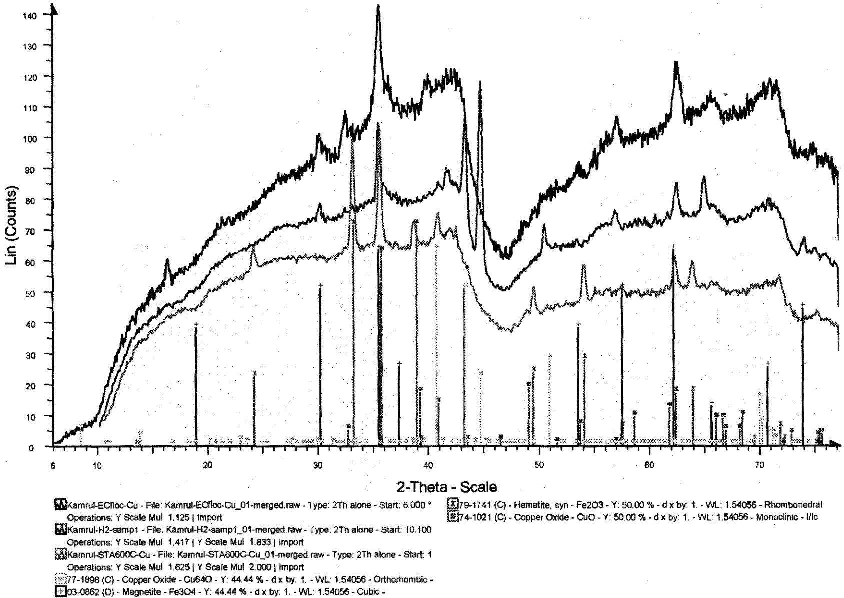


Figure 2: XRD patterns of original (black), oxidized (green), reduced (blue) form of EC-floc.

FTIR Study

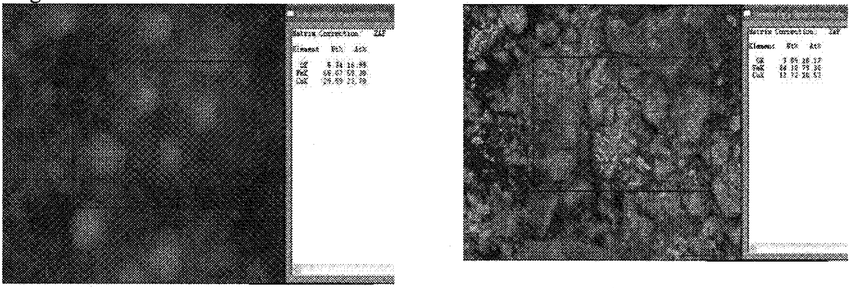
The original and the treated flocs were also characterized using diffuse reflectance FTIR. The spectra shows the vibrational bands for magnetite, hematite, and goethite in all the flocs.

Electrochemical Study

The EC-floc was dissolved, precipitated out, and redissolved, and diluted as mentioned in the experimental section. After that, the clear solution was put in a three-electrode electrochemical analyzer where reference electrode was Ag/AgCl (4 M KCl), and counter electrode was platinum wire. The working electrode was varied among platinum wire, carbon flat plate, and glassy carbon to find out the best option for copper deposition. It was seen that glassy carbon working electrode works better for the copper deposition. Figure 4 shows the voltammogram obtained in the potential range of -0.5 V to 0.5 V at a scan rate of 10 mV/s. The copper reduction was found at -0.225 mV vs Ag/AgCl (4 M KCl) as also mentioned by Figueroa-Ramírez, and Miranda-Hernández [12].

Original EC Floc

Oxidized Floc



Reduced floc #I

Reduced floc #II

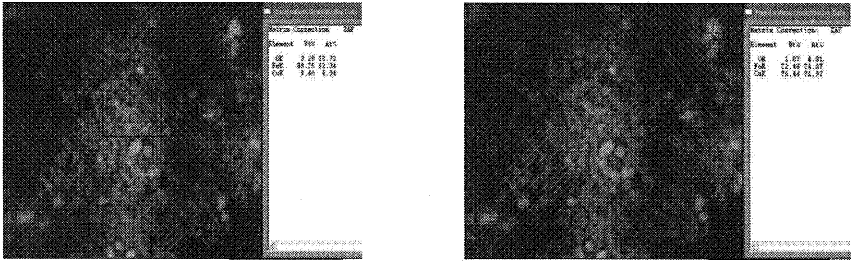


Figure 3: SEM/EDS images original EC-floc and other treated flocs.

Table I. Elemental Analyses of the main constituents of the EC-flocs obtained from EDS analyses

Floc type	O	Fe	Cu
Original floc	17%	59%	24%
Oxidized Floc	11%	79%	11%
Reduced Floc I	11%	82%	11%
Reduced Floc II	4%	24%	72%

Cost Analysis of the Recapture Processes

The cost for treatment of 1 g of base EC-floc was estimated as shown in Table II by considering only the cost for chemicals or gases and electricity required. The cost for infrastructure and instrumentation was not included. Since recapture process involves not only one individual process, but a combination of processes, we calculated the recapture cost estimate in the following three routes: (1) oxidized floc plus chemical plus electrochemical: $ 0.27/g of EC floc. (2) Reduced floc plus chemical plus electrochemical: $ 0.17/g of EC-floc, and (3) original floc plus chemical plus electrochemical: $ 0.11/g of EC-floc. From this estimation, the third route seems to be less expensive. Of course we need to consider the instrument and infrastructure cost.

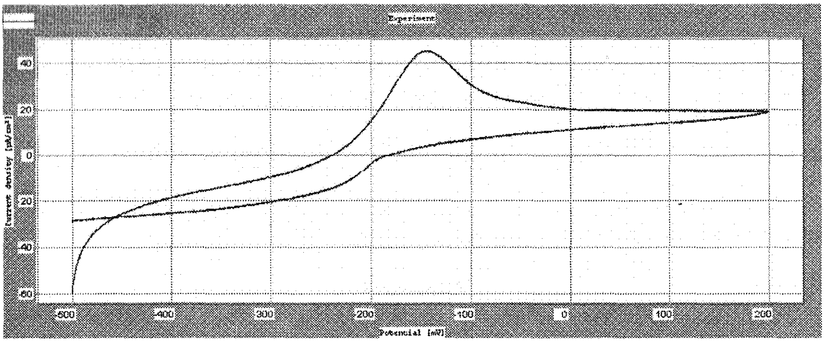


Figure 4. Typical cyclic voltammogram of copper solution obtained by dissolution of EC when performed at 10 mV/s scan rate with glassy carbon as working electrode, platinum as counter electrode, and Ag/AgCl (4 M KCl) as reference electrode.

Table II. Cost analyses of the processes involved in recapture of copper metal from the original EC-floc. Electricity cost was obtained from the following site: http://www.eia.doe.gov/electricity/epm/table5_6_a.html. Chemicals cost was obtained from the following site: http://www.icis.com/staticpages/a-e.htm.

Oxidation Thermal Process			**Reduction Thermal Process**		
Chemicals & Electricity	Chemicals (mL)/ Electricity (KWh)	Current cost ($)	Chemicals & Electricity	Chemicals (mL)/ Electricity (KWh)	Current cost ($)
Electricity	0.025	0.16375	Argon gas	20 mL	0.001
			5% H_2 gas	500 mL	0.025
			Electricity	0.00625	0.04094
Total cost ($)		**0.16375**			**0.06694**
Chemical Process			**Electrochemical Process**		
Chemicals	Chemicals (mL)	Current cost ($)	Chemicals	Chemicals (mL)/ Electricity (KWh)	Current cost ($)
HCl (6 M)	1 mL	0.00005	N_2 gas	20 mL	0.001
Thioacetamide	0.2 mL	0.01268	Electricity	0.01417 KWh	0.09279
Conc. HNO_3	1 mL	0.00017			
NH_4OH	1 mL	0.00026			
Total cost ($)		**0.01316**			**0.09379**

Conclusion

EC is one of the most efficient techniques for almost complete removal of copper from wastewater. The copper in the EC-floc was recaptured by thermal, chemical and electrochemical methods. XRD, SEM/EDS, and FTIR studies showed the effective recapture of copper from the original floc using variation of thermal, oxidation, reduction, chemical, and electrochemical processes. The reduction process generated copper rich suboxides, and the oxidation process generated red colored hematite. The cost estimate without considering the instrument and infrastructure expenses indicates that recapture of copper can be achieved in an inexpensive way through chemical and electrochemical processes compared to other combinations. More research is needed in this area. Implementation of recapture of metals from wastewater streams in industries and other facilities can be not only environment-friendly, but also profitable.

Acknowledgements

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