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Combining adsorption on activated carbon with electrocoagulation process for copper removal from used water

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ABSTRACT

In this work, electrocoagulation (EC) combined to adsorption onto granular activated carbon (GAC) was studied for the removal of copper ions. EC process was firstly optimized. The effect of the main parameters such as: pH (4–8), electrolysis time t_{EC} (5–60 min), current density j (0.277–1.388 mAcm^{-2}), conductivity, inter-electrode distanced_{ie}(0.5–2 cm), area volume ratio S/V (3.6–14.4 m^{-1}), initial concentration (10–70 mgL^{-1}), stirring speed (0.0–600 rpm) and the mode of connection (bipolaire-monopolaire) on copper removal were explored. Under optimum conditions (pH = 5.0, J = 1.388 mA cm^{-2}, t_{EC} = 30 min, d_{ie} = 1 cm, S/V = 7.2 m^{-1}, stirring speed = 300 rpm and monopolaire connection) 97% copper removal was achieved with an energy consumption of W = 0.065 KW hm^{-3}. Combining adsorption on GAC with EC notably reduces the electrolysis required time inducing a strong decrease of energy consumption. The removal of copper from industrial waste water showed the advantage of combining adsorption on GAC with EC in order to reduce the processing time and thus the process energy cost.

Keywords: Electrochemistry; Electrocoagulation; Copper removal; Adsorption onto granular activated carbon

1. Introduction

Heavy metals are the most toxic mineral pollutants which are mutagenic, carcinogenic … [1,2]. Copper is one of vital element for human. However, if it consumed in surplus amounts, copper can be toxic, and even deadly to organisms [3,4]. For the United States Environmental Protection Agency (USEPA) the highest contaminant concentration for Cu (II) in industrial effluent was fixed at 1.3 mg L^{-1} [5]. For these purposes, the removal of excess copper from water and wastewater is imperative for saving public health and the environment. Various methods have been used to remove copper ions from water and wastewater including chemical coagulation, biological treatment, adsorption, ultrafiltration, ion exchange and electrocoagulation … [6].

Recent researches reported that EC and adsorption are the most favorable methods for metals ions removal due to convenience, easy operation, compact treatment,simplicity of design and environmental compatibility [7]. Furthermore, the search for cheap treatment methods has led to the development of combined processes.

EC is an electrochemical process consisting of forming metallic hydroxide flocks within the wastewater by electrodissolution of sacrificial anodes. The generation of metallic cations takes place at the anode (usually made of iron or aluminum) due to the electrochemical oxidation, whereas at the cathode the production of H_2 typically occurs [8]. When metal ions are neutralized with ions of opposite electric charge provided by an EC system, they become unstable and precipitate in a settled form [9]. These insoluble metal hydroxides react with the suspended and/or colloid solidsand precipitate.

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Appropriately, the current study was undertaken to copper removal using aluminum electrodes because of their superior performance to iron in a similarly designed reactor. The most common mechanism of action using aluminum electrode as shown in Fig. 1 is:

At Anode: $Al \rightarrow Al^{+3}_{(aq.)} + 3e$

At cathode: $3H_2O + 3e \rightarrow 3/2H_2 + 3OH^-_{(aq.)}$

Aluminum hydroxides are produced:
$Al^{3+} + 3OH^- \rightarrow Al(OH)_3$

The essential quality of EC is simple equipment, uncomplicated operation, brief reactive time, decreased amount of sludge… [10]. EC has been successfully used for the treatment of wastewaters such as pulp and paper mill industry wastewater [11], chemical mechanical polishing wastewater [12], textile wastewater [13], tannery wastewater [14], slaughterhouse wastewater [15] mine water [16] and effluents containing algae, phosphates, sulfides, sulfates, sulfites, fluoride, and heavy metal ions such as $Fe^{2+,}$ Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}.... [17].

The aim of this study is to investigate the feasibility of removing copper ions from an aqueous solution by EC. The effect of several chemical parameters such as pH_i, NaCl concentration, current density (j), initial concentration (C), operating time (t).. and the reactor geometry (electrode surface area (S), interelectrode distance (d), connection mode…) on the removal efficiency is explored to determine the optimum operational conditions. As the adsorption process is characterized by a fast kinetics, flexibility in design and mild regeneration condition [18], adsorption on activated carbon combined with electrocoagulation process for copper removal was studied. Ultimately, the optimal parameters of the combined process were applied to the treatment of waste water containing copper with the goal of improving the efficiency of the process and significantly reducing its cost.

2. Materials and methods

2.1. Experimental set-up

The EC tests are conducted using an electrolytic cell (1 L glass beaker) and two parallel metallic plates. Aluminum plates (anode and cathode) were cut from a commercial grade aluminum sheet of 2 mm thickness. Only one side of each electrode was taken as working surface: the effective area of each electrode used was 72 cm^2 (9 cm × 8 cm); the other section of the electrodes was wrapped and inactivated with durable water-resistant sellotape. The anode–cathode distance (die) was varied from 0.5 to 2 cm. To ensure surface reproducibility and avoid passivation film, the electrodes were first mechanically rubbed with abrasive paper, rinsed with distilled water, degreased with NaOH and HCl and dried prior to any EC test.

2.2. Electrocoagulation procedure

Synthetic stock solution of 1000 mgL^{-1} Cu (II) was prepared by dissolving the required amount of $CuSO_4{\cdot}5H_2O$. Solutions of lower concentrations: 10–70 mg L^{-1} were prepared by proper dilutions. If required, the pH of the electrolyte was adjusted with HCl (0.1 M) and NaOH (0.1 M) solutions before each EC test. NaCl was used as supporting electrolyte to adjust solution conductivity. Solution pH and conductivity were measured using a pH meter Cyber Scan 510 (WDW, Germany) and a conductivity meter Jenway 4510 (Ω Metrohm) respectively. The current intensity and voltage were controlled by means of a precision regulated Direct Current power supply (Dual TRACKING, WITH 5 V FIXED. MODEL GPC 3030D) providing current and voltage in the range of 0–3A and 0–30 V, respectively. If required, the adsorbent was admitted at varying dosage to each electrolyte solution. A magnetic stirring was applied to the electrolyte in all tests.

To follow the progress of the treatment, samples were periodically taken from the EC cell then filtered to eliminate sludge formed during electrolysis and adsorption.

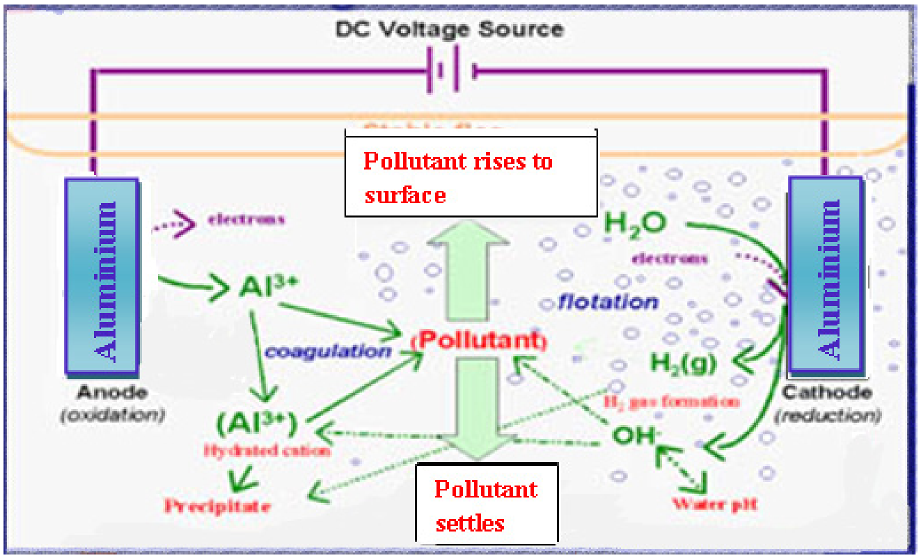

Fig .1. Electrocoagulation reactor.

Residual copper concentration was determined using Atomic Absorption Spectroscopy with Flame (Analytic Jena Nova 400).

3. Results and discussions

3.1. Electrocoagulation process

3.1.1. Optimization of initial pH

The wastewater pH (pHi) has a considerable influence on the performance of EC process [20]. Hence, in order to optimize the pH, the efficiency removal and the final pH evolution as a function of the initial pH were studied for a copper solution of 70 mg L^{-1}. The initial pH effect was determine dover a pH range of 4–8, a current density (J) of 1.388 $mAcm^{-2}$, an electrolysis time (t_{EC}) of 60 min and a sodium chloride concentration of 1 g L^{-1}.

Fig. 2 shows that an increase in pH from 4.0 to7.0 yields a considerable increase in copper removal efficiency from 39 to 97% corresponding to decrease of the residual concentration from 42.7 to 2.1 mg L^{-1} respectively, after 5 min of treatment and copper is completely removed after 30 min of electrolysis. Fig. 3 depicts the time dependence of electrolyte pH. As it can be seen, the pH increased during EC process. The electrolyte pH evolution depended on its initial pH which influenced the production and the consumption of OH^- [19]. From (Fig. 3), for an initial pH of 4, 5 and 6 the final pH underwent slight increase, it is due to the rapid consumption of ions to form Al $(OH)_3$ as well as the anodic dissolution to Al^{3+} ion is maximal in this pH range. Therefore, the pH increase as the operating time progressed depended on the buffer capacity due to the production and consumption of OH^- ions during the EC and thus avoided a sudden change in pH.

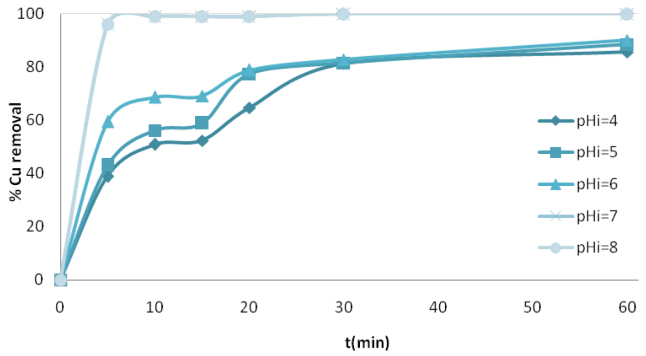

Fig. 2. Effect of pH on Cu removal from wastewater (Cu]: 70 mg L^{-1}, current density: 1.338 mA cm^{-2}, [NaCl]: 1 gL^{-1}, , d_{ie}: 1 cm, Stirring speed = 300 rpm).

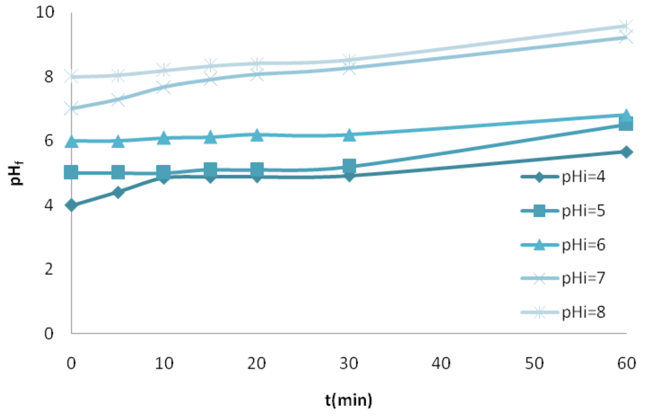

Fig. 3. Evolution of final pH for different initial pH([Cu^{2+}]: 70 mg L^{-1}, current density: 1.338 mA cm^{-2}, [NaCl]: 1g L^{-1}).

On the other hand, pH affects also bubble size [20], much smaller than those observed in the flotation assisted by conventional air, which allows for the same time a sufficient surface for gas-liquid-solid interfaces and mixing efficiency for favors aggregation little particles destabilized .

For the aluminum anode, at highly acidic pH cationic monomeric species Al^{3+} and $Al(OH)^{+}_{2}$ predominate so the copper removal efficiency decreased . When pH is between 4 and 8, the electrodes generated the Al^{3+} and OH^-, and these ions react to form various monomeric and polymeric species such as $Al(OH)^{+}_{2}$, $Al(OH)_2^{2+}$, $Al_6(OH)_{15}^{3+}$, $Al_7(OH)17^{4+}$, and $Al_{13}(OH)_{34}^{5+}$. Finally an insoluble aluminum hydroxide $Al(OH)_3(s)$ was formed through complex polymerization/precipitation kinetics [21].

Besides, for pH superiors to 5, OH^- ions can also partially combine with Cu^{2+} to form insoluble copper hydroxide precipitation $Cu(OH)_2$ [22]. This could explain the total elimination of copper for initial solution pH of 7 and 8.

In order to reach a compromise between best coagulation and copper solubility, pH should be adjusted in the optimum range. In the following sections, initial pH will be fixed at about 5 to maximize copper removal efficiency by EC process.

3.1.2. Optimization of electrolysis time tEC

Electrolysis time is one of the most important parameters in EC process, it has a really effect for the pollutant removal and the treatment cost (the energy and electrode consummation) [Eqs. (1)–(3)].

The electrical energy consumption W (kWh m^3) is given by:

$$W = \frac{U \cdot I \cdot t}{V} \quad (1)$$

where U is the cell voltage (V), I the current (A), t the electrolysis time (h) and V the volume of treated solution (m^3).

Faraday Act:

$$R_{Faradique} = \frac{m_{\exp}}{m_{th\varnothing}} \times 100 \quad (2)$$

with:

$$m_{th\varnothing} = \frac{M \cdot I \cdot t}{n \cdot F} \quad (3)$$

To examine the effect of the electrolysis time on copper removal, The evolution of the percentage of copper removal was studied for initial pH of 5, initial conductivity (σ) of 1.175 mS cm^{-1} and a current density (J) of 1 .388 Acm^{-2}.

Fig. 4, shows that an increase in the electrolysis time results an increase in the efficiency of Cu removal. But it is readily noticeable that increasing electrolysis time from

30 min to 60 min results in a negligible increase in Cu removal from 81.57 with an increase of energy consumptions from 0.17 to 0.45 kWh m^{-3}.

Thus, an electrolysis time of 30 min would be sufficient to obtain a maximum copper removal by EC.

3.1.3. Effect of supporting electrolyte (NaCl)

The increase of wastewater conductivity or the addition of electrolyte affected the electrical transport. On the other hand, it is ensuring better chemical dissolution of the sacrificial electrodes. Previous studies [22–24], provided evidence that increasing the electrolyte conductivity resulted in a decrease of cell voltage U at constant current density due to the drop of the ohmic resistance of wastewater. Soa proportional decrease of energy consumption would be noticed.

In order to optimize the supporting electrolyte dose, five EC tests were performed by varying the NaCl concentration from 0.3 to 1.5 g L^{-1} at pH 5.0, current density of 1.338 mA cm^{-2}, initial concentration of copper of 70 mg L^{-1} and electrolysis time of 30 min. The results are summarized in Table 1 and Fig. 5.

The experimental results show that increasing the sodium chloride dose from 0.3 to 1.5 g L^{-1} resulted in an increase in the removal efficiency of Cu from 71.32 to 92.51% and a decrease of the energy consumption from 0.17 to 0.065 kWh m^{-3}. The availability of metal coagulants increases with increasing conductivity [23] and the electrical energy consumption decreased with increasing wastewater conductivity [10,24].

It is clear that the addition of salt has a good effect in terms of the removal efficiency of metal and energy consumption, but, on the other hand, we perceive that there is a consumption of electrodes due to corrosion if the NaCl concentration exceeded 1 g L^{-1}. Therefore, NaCl concentration of 1 g L^{-1} would be sufficient to obtain a reasonable copper removal by EC of 89.93% with minor energy consumption of 0.07 kWh m^{-3}.

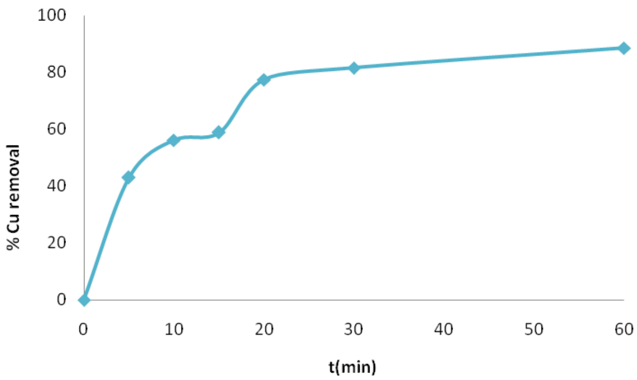

Fig. 4. Effect of electrolysis time on Cu removal from wastewater ([Cu^{2+}]: 70 mg L^{-1}, current density: 1.338 mA cm^{-2}, [NaCl]: 1g L^{-1}, pH$_i$: 5).

Table 1
Variation of energy consumption as a function of NaCl concentration

[NaCl] gL^{-1}	0.3	0.5	0.7	1.0	1.5
I (A)	0.1	0.1	0.1	0.1	0.1
U (V)	3.4	2.3	1.8	1.4	1.3
W (kWh m^{-3})	0.170	0.115	0.090	0.070	0.065
%Cu removal	71.32	81.45	83.70	89.93	92.51

3.1.4. Effect of current density on copper removal

3.1.4.1. Evolution of copper removal percentage

Previous studies [21,23] have proved that current density has been known to be an important factor that influenced the performance of the EC process, especially on the kinetics of metal removal. The effect of current density was investigated in the range 0.277–1.388 mA cm^{-2} at pH of 5.0 and a conductivity of 1.77 mS cm^{-1} an electrolysis time of 30 min. Fig. 6 shows that copper removal increased significantly from 33.67 to 89.93% when the current density was increased from 0.277 to1.388 mA cm^{-2}. Similar results have been reported for copper removal by EC [24].

This is ascribed to the fact that the extent of anodic dissolution of aluminum increases at high current density so the quantity of aluminum oxidized and the kinetics of coagulant formation was increased. In the other hands, electrical current determines the bubble production (rate and size), and the flocs growth. These effects would be beneficial for high pollutant removal by H$_2$ flotation [25]. Nevertheless, the increase of the anodic dissolution increased the electrode consumption [Eqs. (2) and (3)].

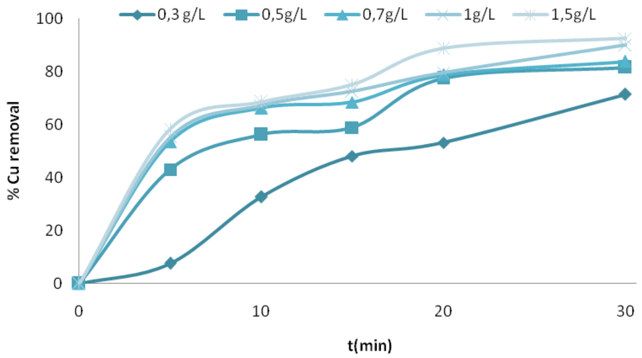

Fig. 5. Effect of NaCl concentration on Cu removal from wastewater ([Cu^{2+}]: 70 mg L^{-1}, current density: 1.338 mA cm^{-2}, pH$_i$: 5).

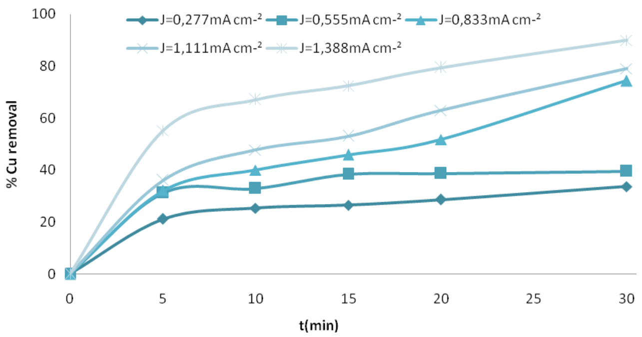

Fig. 6. Effect of current density on Cu removal from wastewater ([Cu^{2+}] = 70 mg L^{-1}, [NaCl] = 1 g L^{-1}, pH$_i$ = 5).

3.1.4.2. Economic evaluation

Energy and electrodes consumption was directly related with the current density. The energy and electrode consumption changed lineary when the current density increased. The EC electric power consumption W (kW hm^{-3}) and Faraday Act were calculated by Eq. (1) and Eq. (2). Figs. 8 and 9 show that the increase in the current density from 0.555 to 1.66 mA cm^{-2} resulted in a increase in energy consummation from 0.01 kWh m^{-3} to 0.07 kWh m^{-3} and electrode consumption from 0.0119 to 0.063 kg m^{-3}. Table 2 depicts that the experimental mass varies proportionally with J, but remains slightly higher than the theoretical mass for values of J at or below 0.833 Am cm^{-2}.

From Fig. 8 the faradic efficiency is still higher than 100%, the consumption of aluminum electrodes can be explained by the chemical hydrolysis of the cathode according to Eq. (4). It can also be explained by the phenomenon of corrosion and oxidation of the electrode surface. The electrodes corrosion mechanism suggested involved chloride ions [Eqs. (5) and (6)].

$$2Al + 6H_2O + 2OH^- \rightleftharpoons 2Al(OH)_4^- + 3H_2 \tag{4}$$

$$2Al + 6HCl \rightleftharpoons 2AlCl_3 + 3H_2 \tag{5}$$

$$AlCl_3 + 6H_2O \rightleftharpoons Al(OH)_3 + 3HCl \tag{6}$$

For this reason, the optimal current density is considered to be 1.388 mA cm^{-2}.

3.1.5. Effect of inter-electrode distance (die) on metal removal

Inter-electrode distance (d_{ie}) is a vital parameter in EC process. Increasing the inter-electrode distance will reduce the treatment efficiency. Hence, an optimization of this parameter is critical [26]. Removal of copper at d_{ie} of 0.5, 1, 1.5, 2 and 3 cm was studied for 30 min. Variation of copper removal as a function of interelectrode distance is presented in Fig. 9.

Fig. 9 shows that maximum removal efficiency was observed at an interelectrode distance of 0.5 cm. The removal efficiency of EC process for copper decreased as the inter-electrode gap increased. And increasing the electrode gap increase the power consumption because the volume treated between electrodes decreased as the electrode gap decreased [27].

On the other hand the increase of the inter-electrode distance causes a decrease in the electrostatic attraction,

Table 2
Effect of current density on electrode and electrical energy consumption

J (m A cm^{-2})	0.277	0.555	0.833	1.111	1.388
%Cu removal	33.67	39.51	74.35	78.99	89.93
U (V)	1.1	1.1	1.2	1.3	1.4
W (kWh m^{-3})	0.010	0.022	0.036	0.052	0.070
$m_{theoretical}$	0.01185	0.02370	0.03556	0.04742	0.05927
$m_{expérimental}$	0.01190	0.02500	0.04100	0.05600	0.07100
Faradic yield (%)	100.421	105.485	115.298	118.09	119.79

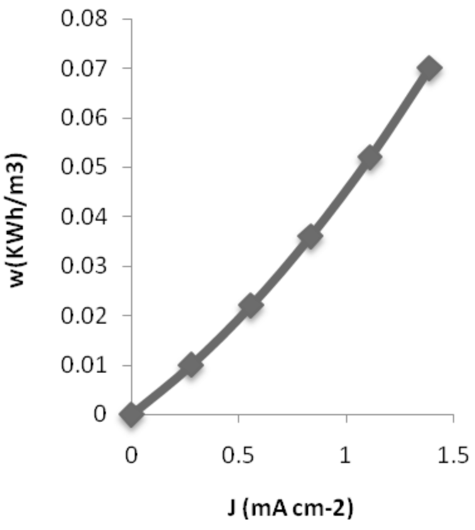

Fig. 7. Evolution of energy consummation.

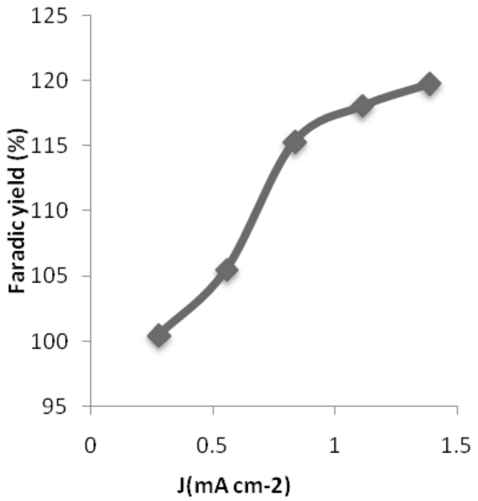

Fig. 8. Evolution of Faradicyield.

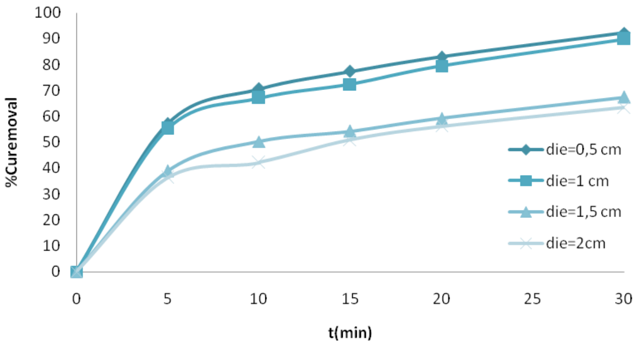

Fig. 9. Effect of Inter-electrode distance (d_{ie}) on Cu removal from wastewater (Cu: 70 mgL^{-1}, current density: 1.338 mA cm^{-2}, pHi: 5.0).

therefore the decrease in the formation off locs necessary to coagulate the pollutant [28]. Consequently, for the studied operational conditions, an interelectrode distance of 1 cm could be feasible for the removal of copper using EC process.

3.1.6. Effect of area volume ratio S/V on metal removal

The area volume ratio (S/V) is one of the most important that exerts a significant influence on reaction kinetics and energy consumption of EC process. To determine the effect of S/V, three areas volume ratio were tested (3.6, 7.2, 14.4 m^{-1}).

As shown in Figs. 10 and 11, when the area volume ratio was increased from 3.6 to 14.4 m^{-1}, it was observed that the percentage of Cu removal increased from 37.04 to 95.55% and the energy consumption increased from 0.035 to 0.22 kWh m^{-3}. The increase of Cu removal efficiency is due to the fact that increasing S/V ratio activate the formation of aluminum hydroxide Al(OH)$_3$ because it facilitates the electrical movement and promoted better chemical dissolution of aluminum. But the increase of the S/V ratio is accompanied by an increase in the electrical energy consumed which limits the use of large active surface of the electrode. Plus the increase of S/V from 7.2 to 14.4 m^{-1} causes a small increase in the Cu removal percentage. For that reason, the optimal current density is chosen to be 7.2 m^{-1}.

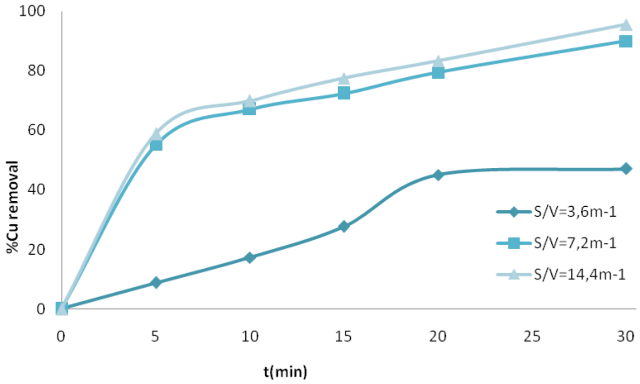

Fig. 10. Effect of area volume ratio S/V on Cu removal from wastewater (Cu: 70 mg L^{-1}, current density: 1.338 mA cm^{-2}, d$_{ie}$: 1 cm, pHi: 5.0).

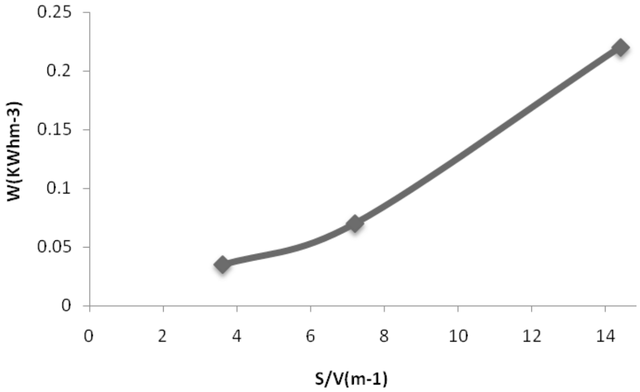

Fig. 11. Effect of area volume ratio S/V on energy consumption (Cu: 70 mg L^{-1}, current density: 1.338 mA cm^{-2}, d$_{ie}$: 1 cm, pHi: 5.0).

3.1.7. Effect of initial concentration on copper removal

The initial concentration of the metal is an important parameter that controls the limits of the EC process. Therefore in order to evaluate the influence of the initial concentration of copper on the course of treatment by the EC process, five initial concentration [Cu$_i$] were tested (10, 20, 30, 50 and 70 mg L^{-1}).

Fig. 12 shows that the percentage of Cu removal increases with the decrease of the initial concentration of the metal. The copper removal efficiency reached 100% of removal for low concentration of 10 mg L^{-1} and decreases when the initial concentration increased, only 89.93% was removed for an initial concentration of 70 mg L^{-1}. In other hand, for initial concentration of 70 mg L^{-1} the copper removal efficiency reached 72.4% for only 15 min, after this first 15 min the kinetic of elimination was slower. These results could be explained by an insufficient training of coagulants to remove copper ions and by the increase in the probability of contact between flocculants and Cu(II) ions at high concentration. Therefore, we can conclude that when the concentration is higher the EC process is more effective at the first step of the reaction.

3.1.8. Effect of stirring speed on copper removal

The agitation helps maintain homogeneous conditions and avoids the formation of concentration gradient in the electrolysis cell. The effect of the Stirring speed on Cu removal was explored in the range of 0.0–600 rev/min at initial pH of 5, a current density of 1.388 mA cm^{-2} and a conductivity of σ_i = 1.175 mS cm^{-1}. Fig. 13 shows the effect of the agitation on copper removal by EC.

There is an increase in the copper removal efficiency from 75.14 to 95.07% with an increase in agitation speed from 0 to 300 rev/min. This could be attributed to the fact that the flocs are formed in a short time when the mobility of the generated ions increased. But with a further increase in the agitation speed beyond 300 rev/min, there is a decrease in copper removal efficiency from, because the flocs get degraded by collision with each other due to high stirring speed [29].

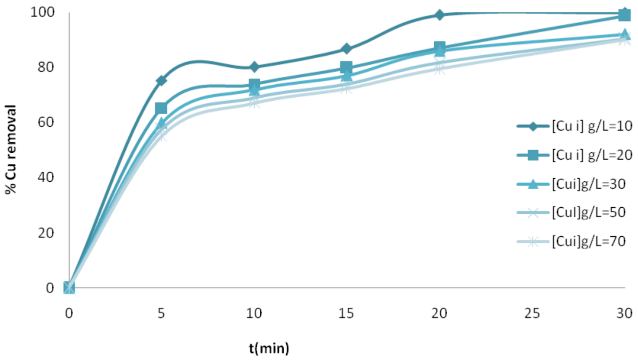

Fig. 12. Effect of initial concentration on Cu removal from wastewater (S/V: 7.2 m^{-1}, current density: 1.338 mA cm^{-2}, d$_{ie}$: 1 cm, pHi: 5.0).

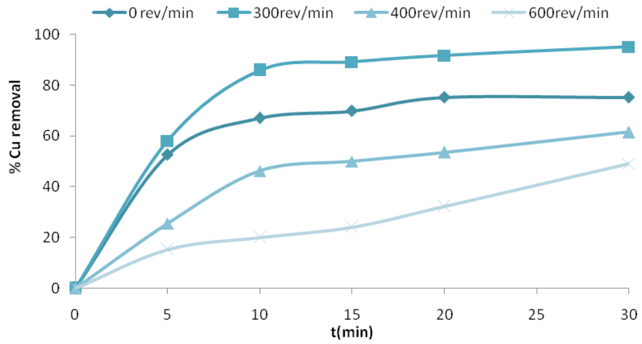

Fig. 13. Effect of Stirring speed on Cu removal from wastewater (S/V: 7.2 m^{-1}, current density: 1.338 mA cm^{-2}, d_{ie}: 1 cm, pHi: 5.0).

Table 5
Variation of energy consumption as a function of electrode configuration

t (min)	Bipolar configuration			Monopolar configuration		
	U(V)	W $(KWhm^{-3})$	%Cu removal	U(V)	W $(KWhm^{-3})$	%Cu removal
0	6.2	0.000	0.00	2.0	0.000	0.00
5	6.0	0.0499	93.67	1.9	0.0158	89.76
10	5.9	0.098	94.87	1.8	0.0130	91.61
15	5.8	0.1450	96.65	1.6	0.0400	93.34
20	5.7	0.1899	98 .09	1.4	0.0466	95.84
30	5.5	0.2750	100	1.3	0.065	98.05

3.1.9. Arrangement of electrodes

The connection mode of the electrodes plays a significant role in EC process. When the number of electrodes increases, the active surface increases resulting in a better removal percentage of the pollutant in a short time. However, it is important to note that the number of electrodes must be chosen so that we allow a maximum elimination without causing excessive power consumption. This compromise depends not only on the number of electrodes, but also the type of the electrode configuration.

To compare the performances of various electrode connection modes two different modes of electrode connection was studied shown are as follows:

- Monopolar electrodes (MP): The anodes and cathodes are connected and the current is divided between all the electrodes to the resistance of individual cells.
- Bipolar electrode (BP): In this connection mode, the outer electrodes are connected to the power supply and there is the no electrical connection between the inner electrodes [29].

Fig. 12 and Table 5 show that for bipolar electrode connections, total copper removal was obtained for an energy consummation of W= 0.275 kWh m^{3-}. Monopolar electrodes in parallel connections results in a removal of 98% with an energy consummation of W= 0.065 kWh m^{-3}. It is clear that a bipolar electrode connection is more efficient but this mode consumed higher energy. In view of that, the choice of monopolar configuration would more reasonable.

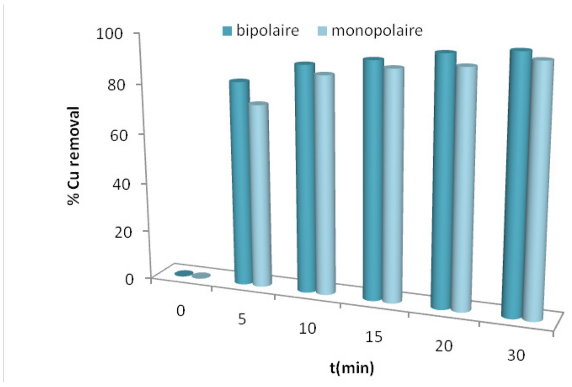

Fig. 14. Effect of the connection mode on Cu removal from wastewater ([NaCl] = 1 g L^{-1}, [Cu] = 70 mg L^{-1}, Stirring speed= 300 rpm, d_{ie}: 1 cm, pH: 5.0).

3.2. Adsorption process

Adsorption experiment was carried out by agitating activated carbon with test water at the room temperature in a stirrer operating at 300 rpm. To optimize the mass of activated carbon for removal of Cu, the study was performed with different initial doses ranging from 0.1 g L^{-1} to 0.7 g L^{-1} in the conditions already fixed for the EC process; pH 5, during 30 min and up to a volume of 1 L.

The curves representing the variation of the elimination percentage of copper in the solution as a function of dosage of activated carbon are shown in Fig. 15.

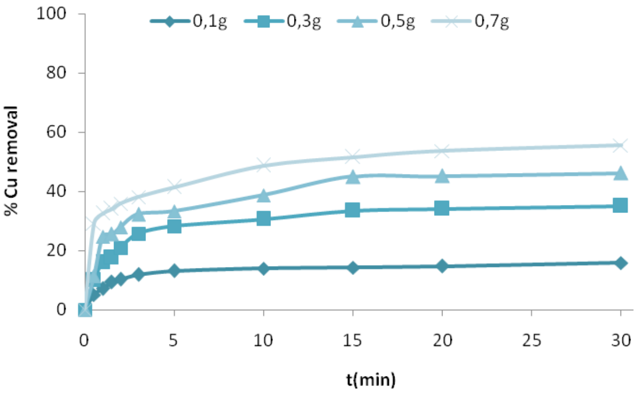

Fig. 15. Effect of activated carbon doses on the removal of Cu by adsorption.

Fig. 15 shows that adsorption performance was improved by increasing adsorbent dose. Activated carbon dosage up to 0.7 g L^{-1} results in a considerable increase of copper removal (from 15.9 to 55.58 %). This result could be attributed to the increase in surface area available for adsorption. The percentage of copper removal was not linearly proportional to the dosage of activated carbon. After 15 min of mixing, the copper removal was 52, 45, 34 and 14% for activated carbon doses of 0.7, 0.5, 0.3 and 0.1 respectively. For the subsequent every five minutes, the percentage of increment in copper removal was less than 2%. Thus, adsorption equilibrium was reached after 15 min. This laps of time was sufficient for the adsorption process to take place and approaches saturation.

The distribution of copper between the liquid phase and activated carbon is a measure of the position of equilibrium in the adsorption process and can be expressed by the widely used Freundlich [31], Langmuir [32] and Dubinin-Redushkevich [33] isotherms. The values of the studied models parameters are summarized in Table 6.

Results reported in Table 6 show that copper adsorption is favorable since the value of 1/n is less than unity [34] and is of L shape [35]. Moreover, the K value reveals a high adsorption capacity. Both Freundlich and Langmuir isotherms fitted with a correlation coefficient greater than 0.99. According to the model of Langmuir the adsorption of copper on activated carbon is favorable since $r = 0.3$ ($r < 1$).

The obtained value of E is 28.209 kJ mol^{-1}, which is greater than the energy range of the adsorption reactions (16 kJ mol^{-1}), wherein the values energy ranging from 1–7 kJ mol $^{-1}$ indicates physisorption and energy values ranging from 8–15 kJ mol^{-1} indicates the exchange of ion [36].

3.3. Combining adsorption on AGC with EC

In order to investigate the effectiveness of combined EC and adsorption processes for copper removal, different activated carbon doses (0, 0.1 ,0.3, 0.5 and 0.7 g) were used together with 2 aluminum electrodes at the optimum parameters of (EC) process: t_{EC}= 30 min, [NaCl] = 1g L^{-1}, [Cu] = 70 mg L^{-1}, Stirring speed = 300 rpm, d_{ie}: 1 cm, pH: 5.0.

Fig. 16 depicts the copper removal dependence of time for various GAC doses. As it can be seen, increasing the adsorbent dose increases the removal efficiency for the first stage of the combined process (0–4 min). During the second stage (5–15 min), for all studied doses of adsorbent, copper removal reached an unvarying value. The process efficiency was enhanced only for GAC dose up to 0.5 g. During the third stage (15–30 min), copper removal shows a slight increase owing to the aluminum hydroxide precipitation. At this stage, adsorption equilibrium was reached and removal efficiency is attributed to EC process.

The percentage of Cu removal increased from 66.09 to 88.86% when the dosage of activated carbon increased from 0.1 to 0.7 g L^{-1}. For electrolysis time of 3 min copper removal with and without activated carbon is 50% and 26.78% respectively. Consequently; combining adsorption on GAC with EC would remarkably reduces the electrolysis required time and could be beneficial in terms of energy consumption.

4. Electrocoagulation of electroplating wastewater.

To examine the faisability of the EC process for the treatment of industrial wastewater contained Cu, we studied the treatment of wastewater of electroplating industry in the EC conditions already optimized, pH of 5, the current density at 1.388 mA cm^{-2}, the inter-electrode distance at 1 cm, the surface-area-to-volume ratio (S/V) at 7.2 m^{-1} and the mode rate agitation speed at 300 RPM with a monopolar connection mode. The wastewater of the electroplating industry contained a Cu concentration of 40 mg L^{-1}, a conductivity of 12.49 mS cm^{-1} and a pH of 8.89. To adjused the pH at 5 we adding HCl (0.1 M). The characteristics of the effluent before and after the treatment are figured in Table 7 and the results are summarized in Table 8.

The experimental results showed that both EC and EC combined to adsorption on GAC are efficient and copper ions were totally removed for an electrolysis time of 30 min. At

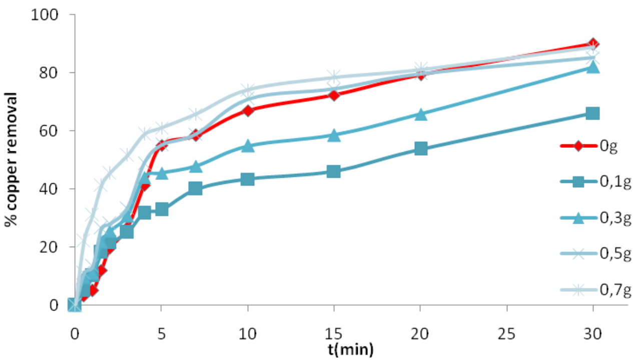

Fig. 16. Effect of the concentration of activated carbon on Cu removal from wastewater by combination of EC and adsorption ([NaCl] = 1 g L^{-1}, [Cu] = 70 mg L^{-1} Stirring speed= 300 rpm, d_{ie}: 1 cm, pH: 5.0).

Table 7
Characteristics of the industrial wastewater before and after the treatment by EC and by combination of EC and adsorption

	Sample characteristics before the treatment	After the treatment by EC for initial pH 5	After the treatment by combination of EC and adsorption for initial pH 5
pH	8.89	6.65	5.53
Conductivité	12.49	12.38	12.31
[Cu] (mg L^{-1})	40	0.00	0.00

Table 6
The constants of adsorption isotherms of copper on activated carbon

Frendlich			Langmuir				Dubinin-Redushkevich			
K	n	R^2	q_m (mg g^{-1})	b10^3 (L mg^{-1})	R^2	r	*qs* (mol g^{-1})	B10^4 (mol^2 kJ^{-2})	E (kJ mol^{-1})	R^2
0.871	1.121	0.992	46.728	32.8	0.9953	0.303	135	2	28.209	0.9285

Table 8
Variation of the percentage of Cu removal, final pH and energy consumption as a function of treatment time

t (min)	Final pH	%Cu removed (EC)	%Cu removed (EC + adsorption)	W (KWh m^{-3}) (EC)
0	5	0.00	0.00	0.000
1	5.11	59.76	81.55	0.002
2	5.18	68.65	84.08	0.004
3	5.20	74.87	87.23	0.006
4	5.29	82.14	89	0.008
5	5.32	90.21	89.67	0.01
10	5.52	95.61	93.54	0.02
15	5.68	98.02	97.43	0.03
20	6.12	100	99.05	0.04
30	6.65	100	100	0.06

the first stage of the processes (0–5 min) copper was observed to be faster removed from the effluent by combining adsorption on GAC with EC. During the last stage (5–30 min) no noticeable difference in the treatment efficiency was found when EC and the combined process were used. The testing of copper removal from industrial wastewater showed that the removal by was effective. Copper removal reached about 82% for an electrolysis time of only 1 min corresponding to negligible energy consumption of 0.002 KWh m^{-3} when using the combined process. This efficiency was reached for EC time of 4 min. Consequently; combining adsorption on GAC with EC notably reduces the electrolysis required time inducing a strong decrease of energy consumption. This application showed the advantage of combining adsorption on GAC with EC in order to reduce the processing time and thus the process energy consumption.

4. Conclusion

The present study attempted to investigate the performance of the EC process and the combination of EC and adsorption process in the treatment of wastewater loaded with copper.

The influence of the main parameters of EC process such as wastewater pH, electrolysis time t_{EC}, current density j, conductivity, inter-electrode distance d_{ie}, area volume ratio S/V, initial concentration, stirring speed and the mode of connection on copper removal was investigated. Cu is removed by precipitation as hydroxides by the hydroxyl ions formed at the cathode via water electrolysis and by co-precipitation with aluminum hydroxides.

The EC parameters are studied one by one in order to determine and choose the optimum value of each parameter then investigate the effect of all these selected parameters on the removal efficiency of copper from the case-study wastewater. The highest rate for Cu removal of 98% was obtained at pH 5.0 with Al–Al electrodes in monopolair connection.

Both EC and EC combined to adsorption on GAC are efficient and copper ions were totally removed for an electrolysis time of 30 min. Increasing the adsorbent dose increases the removal efficiency for the first stage of the combined process (0–4 min), afterward, copper removal reached an unvarying value. The testing of copper removal from industrial wastewater showed that combining adsorption on GAC with EC notably reduces the electrolysis required time inducing a strong decrease of energy consumption.

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