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Effect of *Opuntia ficus indica* mucilage on copper removal from water by electrocoagulation-electroflotation technique

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Abstract

Electrocoagulation-electroflotation (EC-EF) process assisted with the mucilage of *Opuntia ficus indica* (OFI) plant was investigated in order to enhance copper removal efficiency. EC-EF tests with aluminum electrodes were conducted for the treatment of a synthetic copper solution of 100 mg/L, to estimate the influence of the mucilage on removal of copper metal ions, aluminum and hydrogen Faradaic yields, settling process and specific electrical energy consumption. It was mainly found that: (i) copper removal efficiency reached 100% in less than 5 min with 30 mg/L OFI mucilage at pH 7.8; (ii) OFI mucilage affected aluminum and hydrogen Faradaic yields at high removal efficiencies; (iii) copper sludge settling rate rises with increasing mucilage concentrations, and was enhanced by 15%; (iv) OFI mucilage reduced specific energy consumption at a fixed current density along with removal efficiency increase. Furthermore, the formed flocs, in the presence or not of mucilage, were identified by scanning electron microscope analysis (SEM). This work promotes the use of OFI mucilage as an active natural coagulant aid for the removal of copper species from water, by suggesting the substitution of chemical coagulants that are often added to the EC-EF technique.

Keywords. *Opuntia ficus indica*, mucilage, copper, electrocoagulation-electroflotation.
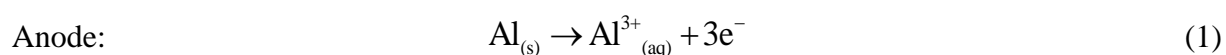
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1. Introduction

Wastewaters contain various types of organic (acid cyanide, alkaline cleaning agent, degreasing solvents, oil, fat) and mineral toxic compounds such as heavy metals [1-3]. Nowadays, heavy metals constitute one of the major concern for the environment and ecologist, since they are non-biodegradable, toxic and for most of them carcinogenic [3]. The stable oxidation states are the most toxic forms of these metals e.g. Cd^{2+}, Pb^{2+}, Hg^{2+}, Ag^+ and As^{3+}, and can react with the body's bio-molecules to form extremely stable biotoxic compounds [4]. Copper is an essential element for living organisms as a micro nutrient, but high levels cause serious health problems [5]. Excessive amount of Cu^{2+} in fresh water causes human mutagenesis [6], and damage the aquatic ecosystem osmo-regulatory mechanism of the fresh water animals [7]. The regulatory agency of Pennsylvania State imposed copper discharge limits of 50 and 40 µg/L for a publicly owned treatment work and on a military station industrial effluent, respectively [8]. Furthermore, a Cu^{2+} effluent limit of 11.1 µg/L was proposed by the Great Lakes Water Quality Initiative, and the Palo Alto (CA) publicly owned treatment work admitted 4.9 µg/L as maximum Cu^{2+} limit for shallow-water [8]. More recent regulation agencies reported a Cu^{2+} permissible limit for industrial effluents of 1.3 mg/L, sets by the United States Environmental Protection Agency (EPA) [6], and 1.5 mg/L for drinking water determined by the World Health Organization (WHO) [9]. Several recent studies achieved copper removal through different methods, Bilal et al. [10] (Bilal et al., 2013) summarized most available Cu^{2+} treatment technologies. Among these techniques, Electrocoagulation process had been often used for the removal of copper [3, 11-13]. The advantages of EC-EF techniques include simple equipment and easy operations [14], high efficiency [13, 15], low operating costs [16], short reaction time and low sludge volumes [17]. The flocs formed by EC are relatively large and more stable containing less bound water [13]. Compared to conventional coagulation and flocculation it removes small colloidal particles and reduces excessive amount of chemical coagulants [14].

On the other hand, biological methods are the actual promising alternatives due to the abundance, low cost, biodegradability and non-toxicity of the biomaterials [18-20]. Different plants proved their efficiency in heavy metal removal. A large number and variety of plant extracted natural substances have been used for their coagulation abilities [21], these biocoagulants are comparable to their chemical equivalents in terms of efficacy when used for treatment of waters of 50-500 NTU turbidity [20]. *Opuntia ficus indica* being a source of natural polyelectrolytes [21, 22], is well known for mucilage production. Mucilage appears directly as a slimy fluid when cactus pad is cut, it has the ability to precipitate ions and particles from aqueous solutions through surface-active mucilage properties [23]. It is a pectic polysaccharide
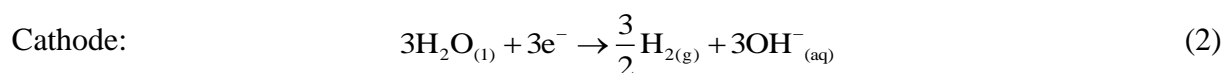
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of high molecular weight that contains neutral sugars, mostly L-arabinose, D-galactose, L-rhamnose, D-xylose, and polygalacturonic acid with varying proportions [22, 23]. In a consideration of new ecofriendly techniques that consume less solvents, time and energy, mucilage had been extracted using microwaves technology to enhance its extraction yield and obtain a better product [24, 25], nevertheless, mucilage had not been extracted yet by microwave procedure to be used in wastewaters treatment until now.

Mucilage had been used for metal reduction (Cu(II), As(V), Cd(II), Fe(III) and Pb^{2+}) [26, 27] in water treatments by several researchers using standard jar tests due to its availability and efficiency, and the pure mucilage extracted by organic solvents also showed its efficiency for arsenate (As(V)) removal by metal sorption batch tests [26]. Recently, *Opuntia ficus indica* pad juice showed its efficiency in the enhancement of EC-EF turbidity removal performance by 15%, after optimization by response surface methodology [28]. Regarding the impact of wastewaters pollution on environmental damage, and besides the ever-rising supply for water mainly in developing countries, there is a serious need to the progress and application of technologies that are cost-effective and eco-friendly through the substitution of potentially added chemicals to EC-EF process. Copper removal using conventional aluminum electrocoagulation-electroflotation processes has been widely studied. However, copper ions removal involving a combination of EC-EF water treatment process with OFI mucilage as a bio-coagulant adjuvant has not previously been reported in the literature. Consequently, the objectives of this work were to: (i) evaluate the effect of OFI mucilage on the overall operational performance of EC-EF technique, (ii) enhance the copper removal EC-EF efficiency to reduce copper ion levels to permissible limits, (iii) analyze its effect on Al and H$_2$ Faradaic yields, sludge settling process and specific electrical energy consumption.

1.1. Electrocoagulation-electroflotation background

EC-EF process produces coagulants in situ by electrical dissolution of aluminum ions used here as electrode material. It is well known that oxidation reaction arises at the anode where metal ions generation occurs, at an appropriate pH they can form wide ranges of coagulated species and metal hydroxides that destabilize and aggregate the suspended particles or precipitate and adsorb dissolved contaminants. Hydrogen gas, released from the cathode through reduction reaction, would help to float the flocculated particles [15, 16, 29]. Thus, main reactions are as follows:

Anode: $$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^-$$ (1)

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Cathode:
$$3H_2O_{(l)} + 3e^- \rightarrow \frac{3}{2}H_{2(g)} + 3OH^-_{(aq)} \qquad (2)$$

In addition to the water electrolysis occurring at the cathode, the same reaction could occur at the anode [11]:

$$2H_2O \rightarrow 4H^+ + O_{2(g)} + 4e^- \qquad (3)$$

Al^{3+} and OH^- ions generated by electrode reactions (1) and (2), react to form various monomeric species such as $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_4^-$, and polymeric species such as $Al_2(OH)_2^{4+}$, $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, $Al_{13}(OH)_{34}^{5+}$, which transform finally into $Al(OH)_{3(s)}$ according to complex precipitation kinetics (reaction 4) [30-32]:

$$Al_{(aq)}^{3+} + 3H_2O_{(l)} \rightarrow Al(OH)_{3(s)} + 3H^+_{(aq)} \qquad (4)$$
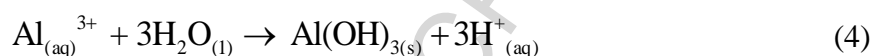
In the presence of metal cations (Me^{n+}), direct reduction, leading to the destabilization and breaking of such particulates, may occur at the cathode (reaction 5) [11]:

$$Me^{n+} + ne^- \rightarrow nMe^0 \qquad (5)$$

In addition, the wastewater pH rise due to cathodic hydroxide ions (reaction 2) induces precipitation of metal ions and their co-precipitation with aluminum hydroxides [11]:

$$Me^{n+} + n\,OH^- \rightarrow Me(OH)_{n(s)} \qquad (6)$$

2. Materials and methods

2.1. Mucilage Extraction

Opuntia spp. pads were collected in May 2014 from the region of Ziama Mansouriah in Jijel in the North east of Algeria. Then, they were cleaned by removing thorns and brown spots, washed with tap water followed by distilled water, peeled (cuticle only) and weighed. The pads were cut into small pieces and mixed with distilled water solution (1:1 mass to volume ratio) for microwave assisted-extraction performed in a domestic microwave (2,45 GHz, Samsung Model NN-S674MF, Kuala Lumpur, Malaysia). After cooling, the mixture was liquidized for 45-50 s at the highest speed in a commercial blender (IKA model-A11, Staufen, Germany). The mixture was then filtered through a kitchen sieve and the pellet was further vacuum filtered through a cloth. The supernatant was separated and precipitated with ethanol (96%) (1:3 volume ratio). The recovered mucilage was spread on Petri dishes, dried in ventilated oven (1 h) for ethanol evaporation, then it was lyophilized using a Lyophilizer (ALPHA 1-2 LD plus, Germany). The yield was about 18,8% $\pm$ 0.2 of dry mucilage powder for 100 grams of dry matter. The final

product is a relatively white to off-white powder, of pH 6.1, and pHpzc 8 (pH of the point of zero charge), the pHpzc was determined following the procedure of Khormaei et al. [33]. The extraction procedure was done following a modified version of Cárdenas et al. [34], and Felkai-Haddache et al. [25]. Prior to each EC-EF treatment, mucilage powder was dissolved in NaOH (1 M).

2.2. Electrocoagulation-electroflotation Set-up

The electrochemical runs were carried out in a discontinuous treatment reactor (Fig. 1) by recirculation of 2 L water volume through a flow system composed of a reservoir tank, a peristaltic pump, and an electrochemical cell. The peristaltic pump (Masterflex *L/S*, USA) allows fluid recirculation and provide a flow of up to 2000 mL/min. The electrocoagulation cell, provided with aluminum electrodes, consisted of two identical polymethyl methacrylate halves (20 cm x 10 cm x 5 cm) in which aluminum electrode plates (15 cm x 7 cm x 1.2 cm) are imbedded. The distance between both electrodes is constant and equal to 1 cm for all experiments. After each run, sulfuric acid solution of 2% (v/v) is poured on the surface of the electrodes. Their surfaces are manually polished with abrasive paper and rinsed with distilled water before each run. The effective area for electrolysis of each electrode is 105 cm^2. The electrodes were related to a laboratory DC power supply (EA-PS 3065-10 B, UK) that provides current range between 0-10 A, the used current was held constant all along the experimental runs. The reservoir tank was connected to a water-filled cylinder used to quantify released hydrogen principally from the cathode during the runs. This cylinder was filled with tap water using a vacuum pump (Vacuubrand MZ2NT, Germany) prior to each run. A gentle mechanical agitation (150 rpm) was set inside the reservoir tank with an agitator control (EUROSTAR 60 control, IKA, France). All experiments were carried out at ambient temperature (≈20 °C), and at current density $j = 11.55$ mA/cm^2, peristaltic flow $Q = 300$ mL/min, agitation rate $r = 150$ rpm, interelectrode distance $d = 1$ cm, and conductivity $\kappa = 2.4$ mS/cm.

2.3. Synthetic Wastewater

Copper removal was investigated by EC-EF in the presence of sulfates. Synthetic solution of CuSO$_4$.5H$_2$O was prepared by dissolving the appropriate amount into distilled water, and was diluted to the desired concentration of 100 mg/L. This choice corresponds to a test concentration. In a study about different metal ion removals by EC-EF, the removal rate of copper was independent of its initial concentrations of 50, 100 and 250 mg/L [11]. To conduct

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the experiments pH was adjusted to the desired values using 0.1 M NaOH or HCl, and conductivity was adjusted with NaCl (1 M).

2.4. Scanning Electronic Microscopy (SEM) analysis

SEM (JSM 6490LV, JEOL society, Japon) was used for the observation of formed flocs from sample solutions obtained after EC-EF mucilage-free copper treatment and EC-EF assisted with 30 mg/L of mucilage. Sample particles were fixed on a specific carbon film (cellulosic) support. Then, all samples were coated with gold/palladium (Au/Pd) layer at 5 Volt during 5 min in a metallizer (Fine Coat - Ion Sputter JFC 1100, JEOl society, Japon). General shape characters were observed using secondary electron detector (SED) with a low vacuum mode.

2.5. Settling Tests

After each EC-EF run, the remaining treated solution was filled into a cylinder ($H \, x \, \phi$; 38.5 cm x 7.8 cm) of 1 L volume for settling tests. Settling was followed for 3 to 4 h during which the height of the sludge-supernatant interface was recorded after visual observation. To examine the effect of time on settling behavior, prolonged settlement tests were carried out (up to 24 h) until equilibrium. The obtained settling test data were used to measure settling velocities.

2.6. Analytical and calculation methods

Liquid fractions of 30 mL were taken from the EC-EF tank at regular intervals during the experimental runs. Ten milliliters samples were allowed to settle for 24 h in order to determine copper concentrations in the upper clear fractions. Then small volumes of each sample were filtered through 0.45 μm membrane filter (HACH, UK) prior to analysis by atomic absorption spectrophotometer (AAS; Thermo scientific iCE 3300, Germany). For aluminum species, the rest of the liquid volume samples (20 mL) of EC-EF treatments assisted with OFI mucilage were submitted to microwave digestion START-D instrument (Milestone, USA) prior to injection to the AAS. pH and conductivity of the samples were also monitored. The change in water volume after each sampling was considered to make calculations. The analyses were done in triplicate and the mean value was calculated.

Faraday's law was used to determine the amount of produced and consumed Al theoretically (m_{th}) (mg/L); it depends on treatment time t (s) and current intensity I (A) (Eq. (7)):

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$$m_{th} = \frac{I.t.M}{V_e.F} \qquad (7)$$

Where M is the molar mass of Al ion species (g/mol), V_e is the number of electrons, and F is the Faraday's constant (96 485 C/mol).

The Faradaic yield (ϕ_{Al}) of Al dissolution was estimated as the ratio of the weight loss of the aluminum electrodes during the experiments (Δm_{exp}) (mg/L) and the amount of aluminum consumed theoretically at the anode (Δm_{th}), as shown in (Eq. (8)):

$$\phi_{Al} = \frac{\Delta m_{exp}}{\Delta m_{th}} \qquad (8)$$

The theoretical hydrogen produced volume (V_{th}) (cm^3), was determined using (Eq. (9)):

$$V_{th} = \frac{I.t.R}{V_e.F} \qquad (9)$$

Where I is the current (A), t the time (s), R the gas constant (0.0224 m^3), V_e the number of electrons, and F is the Faraday's constant (96 485 C/mol).

Hydrogen Faradaic yield (ϕ_{H2}) was then measured according to the following equation (Eq. (10)), using the ratio of the released hydrogen volume during the experiments (ΔV_{exp}) (cm^3) and the amount of hydrogen released theoretically at the cathode (ΔV_{th}):

$$\phi_{H_2} = \frac{\Delta V_{exp}}{\Delta V_{th}} \qquad (10)$$

The specific electrical energy consumption per kg copper removed (E_{Cu}) under steady-state conditions was calculated as follows (Eq. (11)):

$$E_{Cu} = \left(\frac{kWh}{kg\ Cu} \right) = \frac{U.I.t}{1000.V.(C_i.RE)} \qquad (11)$$

Where C_i is the initial copper concentration (kg/m^3), I is the current intensity (A), U is the cell voltage (V), t is the treatment time (h), and V is the volume of treated solution (L).

The effect of the EC-EF treatment, assisted or not by OFI mucilage, was evaluated by calculation of copper removal efficiency (RE%) at the end of the run time using (Eq. (12)):

$$RE(\%) = \frac{C_0 - C}{C_0}.100 \qquad (12)$$

C_0 and C are concentrations (mg/L) of copper before and after electrochemical treatment, respectively.

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A one–way analysis of variance (ANOVA) followed by Tukey's test using JMP (Trial Version 7, SAS, USA) software, were used to show if there is significant differences between mucilage concentrations in term of specific energy consumption and copper removal efficiency. Evaluations were based on the $p < 0.05$ significance level.

3. Results and Discussion

3.1. Effect of initial pH

pH is an important parameter influencing EC-EF process [31, 35, 36]. Prior to EC-EF copper solution treatments assisted by OFI mucilage, varied pH values were tested (pH 4, 7.8 and 9.4) on copper removal efficiency by conventional EC-EF run called control (EC-EF OFI mucilage-free treatment) (data not shown). The aim is to enhance first the removal efficiency of the EC-EF technique and to scrutinize subsequently the role that could have OFI mucilage on residues of such a model. The maximum removal efficiencies were obtained at pH 7.8 and 9.4 at 20 min. With initial pH of 7.8, 15 min are enough to reach 96.35% of copper removal efficiency, while it takes 20 min to reach almost the same removal value at pH 9.4. Identical observations were reported [37] in which high pH values (pH 7 and 9) were appropriate for enhancing copper removal by EC treatment using aluminum electrodes. Several studies obtained high efficiency using alkaline pH. The high removal efficiency is typically attributed to the reduction of copper at the cathode (Eq. (5)), and its precipitation and co-precipitation with aluminum hydroxides due to pH increase (Eq. (6)), besides the probable effect of pH before the start of EC-EF which anticipates the mentioned reactions.

Thus, to maximize the efficiency of copper elimination in this study, pH 7.8 was retained for further EC-EF treatment tests on copper removal, assisted or not with OFI mucilage. Merzouk et al [12], worked on copper (100 mg/L) removal by EC-EF and attained more than 60% of removal efficiency at pH 7.8 at the start of EC treatment. From another side, natural OFI coagulation ability increases at alkaline pH [21, 38], pH around 8 in the presence of electrolytes [21].

3.2. Effect of initial concentration of mucilage

To investigate the effect of OFI mucilage on copper removal efficiency (RE) various OFI mucilage concentrations ranging from 5 to 50 mg/L were tested. The results are shown in Figs. 2 and 3. Copper removal efficiencies increase steadily from 20 mg/L cactus concentrations over time and do not change after 5 min run time (Fig. 2). Enhancement in removal efficiency with mucilage is possibly related to an increase in polymer binding sites and surface areas of the

biocoagulant [39]. The EC-EF performance attained its maximum levels using 30 mg/L mucilage concentration, compared to the other tested volumes (Figs. 2 and 3). At 20 min of electrolysis treatment, when OFI mucilage concentration increased from 5 to 30 mg/L, copper removal efficiency increased until it reached up to 100% with 30 mg/L mucilage concentration (Fig. 3). Further increase of mucilage concentrations beyond 30 mg/L was unfavorable to copper removal, probably due to accumulation of the mucilage polymers preventing efficient interaction with copper. According to these results, optimum mucilage concentration and run time for copper solution treatment was considered to be 30 mg/L and 5 min, respectively. Similarly, Adhoum, et al. [40] indicated that 5 min were sufficient to eliminate Cu^{2+} to permissible limits. However, the kinetic of electrocoagulation required 15 min to reach more than 90% for Cu^{2+} removal in comparison to 5 min for other metals [12].

Small amount (30 mg/L) of OFI mucilage concentration is required to enhance EC-EF copper removal efficiency of 2 L metallic solution. Fox, et al. [26], found that As^{2+} removal enhancement was independent of the mucilage concentration, ranging from 5-100 mg/L in batch biosorption tests. On a large scale, small dosages of natural coagulants are ideal to avoid a rise in organic materials, and to lower wastewater treatment total cost [26, 41]. Similarly, OFI polyelectrolytes of 10% (v/v) was more efficient than higher dosage of 20% (v/v) to remove Cu^{2+} in biosorption medium [27]. However, it was reported that 500 to 4000 mg/L and 500 to 10000 mg/L of *Opuntia* spp. pad powder, were required to treat 100 mg/L of Cd^{2+} and Pb^{2+} respectively, at initial pH of 5.8 for Cd^{2+} and 3.5 for Pb^{2+} in biosorption tests [19].

The evolution of pH during EC-EF runs assisted or not by OFI mucilage is shown in Fig. 4. During all the runs, pH of the medium was observed to decrease suddenly at 1 min of run time, to pH values around 6.3-7.5, then it increases quickly to pH values around 9 to 10 when copper was almost removed.

The same tendency for Cu^{2+}, Zn^{2+} and Ni^{2+} were described [11], at initial pH for copper of ≈ 6.5. The authors related it to the removal mechanisms of these metals, where in addition to the reduction of the metal cations at the cathode surface (Eq. (5)), OH^- ions produced at the cathode precipitate metal ions as hydroxides (Eq. (6)). This reaction buffers the pH as long as all the metal ions are precipitated, then the pH increases. In the absence of the metal cations, the pH rises directly due to OH^- ions not bound to Al^{3+}. Thus, the origin of the pH rise is due to OH^- ions that enhances metal hydroxide precipitation, as also reported [2, 42]. Moreover, several works attributed it to hydrogen growth at the cathode [13, 29, 40]. Also, anions as Cl^- that are

present in the electrolyte solution, could interact with $Al(OH)_3$ to free OH^- and also cause pH increase [36]. This observation does not exclude the presence of soluble cationic forms of copper (Cu^{2+}) in our case even at initial pH of 7.8. Precipitation of a solution of $CuSO_45(H_2O)$ to $Cu(OH)_2$ does not occur before the start of EC in a solution of tap water at initial pH of 7.75, due to the slowness of the reaction under high ionic strength conditions [1]. The addition of salts, as NaCl (1M) for conductivity adjustment in this study, maintains mostly a clear blue/green color of the solution to be treated.

However, removal efficiency of 90% or more seen in Fig. 2 at time 0 could be explained by the probable and expected copper precipitation at the initial pH of 7.8. In addition, as in coagulation flocculation classical processes possible interaction of mucilage with Cu^{2+} mainly (rarely with $Cu(OH)_2$ at time 0) could occur and be synergetic to the precipitation effect of pH when EC-EF is assisted with 20, 30, 40 and 50 mg/L OFI mucilage. From Fig. 4, in general these possible interactions cause a greater pH drop owing to the highest pH values (50 mg/L). It seems that the pH drop at initial time of 1 min is related to the concentration of OFI mucilage (Fig. 4), therefore OFI particles, either free or linked to copper species (at time 0) could bound OH^- ions released from the cathode when they are not linked to Al^{3+} to form Mucilage–OH complex. This causes a temporary pH drop and thus a positive effect on removal at a certain limit (30 mg/L).

Polysaccharides contain a large number of hydroxyl groups, which is why these polymers can be used in flotation systems to interact with different mineral. The observed functions were broadly attributed to hydrogen bonding of the hydroxyl groups to mineral surfaces. It was reported too that the interaction of dextrin with several metal salts in aqueous solutions occurred by co-precipitation of the dextrin with metal-hydroxides. The maximum co-precipitation was found to be related to the isoelectric point of the metal-hydroxides [43].

For turbidity removal in standard jar test, Miller et al. [21] suggested that OFI coagulation capacity functions mostly through adsorption and bridging between molecules of identical electrical charges and not by charge neutralization. In the present work, at pH 7.8 Cu^{2+} ions, when present, are positively charged, and mucilage electrolytes at this pH are in majority positively charged too according to mucilage pHpzc measurement. This is in agreement with the above suggestions, effective coagulation by OFI mucilage is not hindered by electrostatic repulsion, quite the contrary maximum efficiency is attained.

As mentioned above, heavy metal ions are precipitated by interaction with cathodic OH^- as hydroxides ($Cu(OH)_2$) and co-precipitated with aluminum hydroxides ($Al(OH)_3$) to form microflocs ($Cu(OH)_2$–$Al(OH)_3$) in the absence of mucilage [11].

But, these small flocs generated following these interactions, could be consequently trapped and collected by the dispersed free, linked to copper species, or preformed mucilage-OH in water enhancing thereby flocculation and thus flotation or sedimentation. Thus, the advanced hypothesis, is that soluble copper (Cu^{2+}) is removed by double precipitation with OH^- or with mucilage during the first 5 min of treatment, then the precipitated copper form $Cu(OH)_2$ is removed by double co-precipitation with $Al(OH)_3$ or with Mucilage–OH, and that what enhances the EC-EF removal efficiency (Fig. 5).

The addition of mucilage, which is a complex of not less than 55 polysaccharides, renders the treated solution more complex and the explanation more intrigued at this step. As expected mucilage as a mixture of different carbohydrates [24] could easily interact with released OH^- to give rise to additional multi-complexes that enhanced copper removal (Fig. 5). It was suggested by Barka, et al. [18] that carboxylic acid groups are certainly responsible for cationic metal (Cd, Pb) binding by dried cactus biosorbent, as well as C-OH and C-O-C, after FTIR analysis. It should be supposed that the coagulation ability of OFI mucilage is critical to understand in a complex multi-components system as EC-EF, mainly that mucilage is a composite natural material. In addition, according to Mollah, et al. [44], several authors stated that EC-EF is not technically yet well understood, it is still an empirically optimized method that needs more fundamental understanding for better engineering design.

In the present work, 100% copper removal is achieved, using a combination of aluminum electrodes and a natural coagulant under specific operating conditions. Generally, Al is the most used material for electrodes; nevertheless, its effectiveness has not always been highlighted. In a study made by Hanay and Hasar [45], aluminum electrodes were efficient for Cu^{2+} and Zn^{2+} removal, but best removals were obtained in the presence of chemicals; salts: sulphate (302.4 mg/L) and chloride (224 mg/L), where copper removal reached 100% after 5 min of treatment at pH values higher than 7.

Additionally, the highest metal removal efficiencies were accomplished using electrodes made of other types of steel. In Al Aji, et al. [2] work, more than 96% of metal ions (Cu^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}) were removed using iron electrodes [2]. Gatsios, et al. [42] optimized EC using iron electrodes and removed 100% of industrial wastewater toxic metals (Mn^{2+}, Cu^{2+}, Zn^{2+}). More

than 99% of metal reduction (Cu^{2+}, Cr^{6+}, Ni^{2+}) was attained with final Cu^{2+} concentration of 0.10-0.13 mg/L with titanium and ruthenium cathode and anode, respectively [3]. Escobar, et al. [46], reached nearly 100% of copper removal under EC optimized conditions using laminate steel electrodes.

3.3. SEM observation analysis of formed flocs

During EC-EF mucilage-free process and EC-EF assisted with 30 mg/L mucilage, liquid samples taken at 20 min, were left for settling and were observed by SEM (Fig. 6) after gentle agitation. These images are closely similar to SEM images of different extracts of OFI mucilage, in a thesis work, interacting with kaolin particle for turbidity removal or for heavy metal removal in standard jar test assays. At first sight, a more dense aggregation is not clearly distinguished in the presence of mucilage (Fig. 6b). However, when looking accurately, the presence of mucilage creates more void space between particles in the central spread extract, the aggregates are smaller throughout the edge of the extract and larger flocs are observed (indicated with arrows on the image). Conversely, Fig. 6a of control shows homogenous distribution of aggregates in solution and very few spaces between particles. This result is coherent with the obtained results of sludge dehydration where the presence of mucilage led to a fragmented sludge in comparison with the control sludge forming an entire single block (data not shown).

3.4. Faradaic yields

3.4.1. Effect of OFI mucilage on Aluminum Faradaic yield

Faraday's law (Eq. (7)) relates current intensity I to the mass m of Al generated inside the EC-EF reactor, giving a theoretical estimation of the released metal amount in the solution. This relation supposes that the exchanged electrons served only to the considered reaction. While, a part of the imposed current could be used by secondary reactions, hence the Faradaic yield notion.

Aluminum Faradaic yield during EC-EF runs, calculated according to (Eq. (8)), at different mucilage concentrations is illustrated in Fig. 7. The Al Faradaic yield dropped with increasing OFI mucilage concentrations. However, the Faradaic yield increased rapidly and irregularly in the beginning of the treatment reaching 3.51 and 2.93 at 15 min for the control and EC-EF with 5 mg/L initial OFI mucilage concentration, respectively. For EC-EF assisted with 10 mg/L OFI mucilage, Al Faradaic yield raised suddenly to 1.89 at 25 min. Then, for these three EC-EF treatments, Al yield decreased to values in the range of 1.5 and 2.3 from 25 min. While, the

rapid rise of Al was not observed for EC-EF treatments assisted with 20, 30, 40 and 50 mg/L, where Al yield raised to values between 1.2 and 0.6 until they reached a plateau and becomes almost constant from 10 min of treatment time. Actually, the sharp increase of Al was not surprising since the measured amount of experimental aluminum during electrolysis, corresponding to the above cited mucilage concentrations exceeds theoretical values (data not shown), calculated according to (Eq. (7)).

Many works displayed such an excess with a wide spread in the measured values, Mechelhoff et al. [47] (Mechelhoff et al., 2013) described it as super-Faradaic aluminum yield, these differences could be due to the different experimental conditions [13]. Several authors [13, 29, 30, 36, 42] claim that both anode and cathode undergo chemical attack arising from their respective acidity and alkalinity: at the anode vicinity the following reaction occurs:

$$2Al + 6H^+ \rightarrow 2Al^{3+} + 3H_2 \tag{13}$$

While at the cathode vicinity the subsequent reactions occur:

$$2Al + 6H_2O + 2OH^- \rightarrow 2[Al(OH)_4]^- + 3H_2 \tag{14}$$

$$Al(OH)_3 + OH^- \rightarrow [Al(OH)_4]^- \tag{15}$$
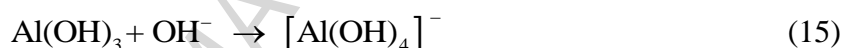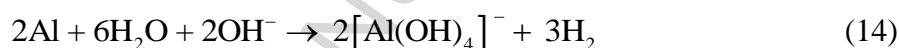
In addition, high value of Faradaic yield can also be due to the presence of Cl⁻ that reduce Al passivation [48]. Electrical release of Al during EC-EF runs, is directly implicated with copper removal according to the main EC-EF reactions, but Al coagulant effect is probably dependent and combined with that of OFI mucilage for copper removal. It appears that, not only the efficiency of aluminum as chemical coagulant in EC-EF process for copper precipitation is enhanced in the presence of OFI mucilage concentration (Fig. 2), but also, the mucilage could hinders the observed excess of released Al (Fig. 7). Aluminum is reduced by mucilage to values close to that of the theoretical anode mass loss (values close to 1), by potential interference with the chemical attack cited above. El-Etre [49], found that *Opuntia* spp. pad juice extract acts as a good corrosion inhibitor of aluminum corrosion in 2.0 M HCl solution, and the inhibition efficiency increased with increasing extract concentration. This is a possible mechanism to prevent the impairing effect of Cl⁻ anions on the passive layer of Al hydroxide, and can explain the decrease of Al Faradaic yield.

3.4.2. Effect of OFI mucilage on Hydrogen Faradaic yield

Hydrogen production is usually considered as an alternative energy to compensate for the treatment cost of industrial effluents. Phalakornkule et al. [50] showed that a significant amount

of hydrogen can be recovered during electrocoagulation treatment of dye-containing wastewater. As hydrogen is principally produced at the cathode by water electrolysis, it is consequently possible to determine hydrogen Faradaic yield by calculation of produced hydrogen volume using Faradaic law (Eq. (10)).

OFI mucilage exhibited almost the same trend on hydrogen Faradaic yield as that of Al Faradaic yield during EC-EF processes with different mucilage concentrations (Fig. 8). However, it was apparent that mucilage concentrations higher than 5 mg/L resulted in a sharp diminution of hydrogen yield. For the control and with 5 mg/L OFI mucilage, hydrogen release attained 1 to 1.2 after 10 min of treatment. However, hydrogen yield dropped to values lower than 1 to reach 0.99, 0.97, 0.86 with 10, 20 and 30 mg/L OFI mucilage respectively, and 0.85 for 40 and 50 mg/L OFI mucilage, after 60 min of treatment. These mucilage concentrations resulted in a weaker drop on Al yield. In addition, hydrogen yield for mucilage concentrations from 0 to 30 mg/L are around the theoretical value of 1. The higher the mucilage concentration, the lower the H Faradaic yield. It seems that mucilage affects hydrogen more than Al release while copper cations are being removed.

Hydrogen yield is mostly produced at the cathode, but hydrogen Faradaic higher than 1 could mean that it is also produced at the anode. It seems that, mucilage concentrations higher than 5 mg/L could reduce anodic hydrogen production by interacting with it, or could reduce both electrode hydrogen production. In addition, H_2 bubble perturbation which also cause a pH increase could be due to the transfer of CO_2 present in over saturated state mainly in acidic electrolyte solution [36].

On the other hand, reduction in Al and H_2 Faradaic yields with increasing mucilage concentration could be due to the formation of an oxide layer on the cathode surface, which widely appear with a DC (direct current) power supply [1-3]. Electrodes passivation generally reduces EC-EF process efficiency, this was not observed in the present work since at mucilage concentration of 30 mg/L the efficiency reached its maximum value. Moreover, the increase of the potential generally caused by the effect of passivation was not observed during the runs. These observations lead to conclude that the poor effect of passivation could be circumvented during the positive effect of OFI mucilage on copper removal.

The gas collected in the water-filled cylinder could be a mixture of H_2 and O_2, but it is well known that few O_2 gas bubbles evolve at the anode (Eq. (3)) in comparison to an abundant H_2 bubbles evolution generally observed at the cathode at each EC-EF run. This minor oxygen formation competes with the aluminum dissolution and could lower the dissolved amount [11].

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3.5. Effect of OFI mucilage on settling

There are four stages for sludge sedimentation. The first phase is the coalescence phase in which flocs of different sizes descended separately due to a transient zone between sediments and supernatant. This is a little period of principally Brownian motion [51]. Consequently, for the second phase the height of the solid-liquid interface decreases regularly with time, characterized by a constant sedimentation velocity. In the third phase, a transition-settling period occurs where the settling velocity decreases. The final phase, is the compression settling in which the solid-liquid interface height is relatively constant [51].

Settling processes were achieved for the control and for EC-EF treatments assisted with various OFI mucilage concentrations (5, 10, 20, 30, 40 and 50 mg/L). Fig. 9 shows the variation of the heights of the sludge-supernatant interface depending on OFI mucilage concentrations and treatment time. A stage of linear settling followed by a relatively stable phase, due to compression of particles, were observed. The height of the interface fell with increasing OFI mucilage concentrations. However, it dropped drastically for effluents treated with OFI mucilage concentrations from 20 to 50 mg/L. The settling was more rapid with 20 mg/L mucilage concentration. Fig. 10 shows the sludge velocity growth in function of increasing OFI mucilage concentrations, sludge velocities were calculated according to the observed interface height of initial time and 120 min. The velocity remains constant; an equilibrium had been reached beyond 30 mg/L mucilage concentration, which was the optimal mucilage concentration for copper removal efficiency. The determined initial interface velocities obtained with 5, 10, 20, 30, 40 and 50 mg/L of mucilage corresponded to 0.11, 0.13, ~~0.20, 0.22, 0.23 and 0.23~~ 0.22, 0.22, 0.23 and 0.22 cm/min, respectively. These values are gradually larger than the velocity value of the EC-EF mucilage-free treated effluent, which is equal to 0.08 cm/min. Thus, the settling rate in the presence of the mucilage was enhanced by 15%, and it remains almost stable from 20 mg/L OFI mucilage concentration. OFI mucilage concentration and sedimentation time highly influenced settling process, the sedimentation process increases with time and with the concentration of the mucilage.

Mucilage at high concentration could interacts with flocs formed after EC-EF process, which gave evidence that final larger flocs descend more rapidly depending on their size, enhancing thereby the effectiveness of the settling, due to high density difference [52]. These settling profiles are similar to those observed by Pichler et al. [53], different *Opuntia* spp. mucilage extracts were used to clarify kaolin turbid water by jar tests in comparison to the commercial

flocculant; aluminum sulfate ($Al_2(SO_4)_3$). They found that all the extracts were better than aluminum for augmenting the settling rates even at high concentrations. Similarly Buttice et al. [54], showed that kaolin settling rate rises with increasing concentrations of gelling and non-gelling mucilage extracts, that exhibited settling rate of 11 and 13.2 cm/min, respectively, versus control settling rate of 0.5 cm/min.

On the other hand, for the treatment of industrial wastewater by EC and optimization of EC and settling processes, Zodi et al. [52], found that the interface velocity increased with increasing current density due to cationic metal dissolution extent increase. OFI mucilage have the same effect on settling as that generated by current density. Consequently, this could be advantageous since the biocoagulant will not rise energy consumption, as the known effect of current density.

3.6. Effect of OFI mucilage on specific energy consumption

In all electrochemical processes, the electrical energy consumption is a significant parameter to the application of the process, mostly because it is related to the operating cost [35, 55].

The specific electrical energy consumption per kg Cu removed (E_{Cu}), determined during EC-EF runs with different OFI mucilage concentration, was calculated according to (Eq. (11)). Fig. 11 shows that energy consumption increases with time but decreases generally when mucilage is added. The augmentation of OFI mucilage concentration from 5 to 30 mg/L led to a maximum slight decrease of E_{Cu} from 0.33 (control) to 0.31 kWh/kg Cu with 30 mg/L after 60 min of treatment, since E_{Cu} depends on time and on removal efficiency (RE%).

The decrease of the specific energy consumption is related to the efficiency of the mucilage on copper removal efficiency; the greater the copper removal efficiency, the lower the specific electrical energy consumption per kg Cu removed (Fig. 12). This figure illustrates the data observed at 20 min operational time. The RE rises from 97% (control) to 99.9% (30 mg/L), and is inversely proportional to the evolution of E_{Cu}. Since aluminum and hydrogen release are related to energy consumption, their low Faradaic yields could also be explained by the effect of mucilage on E_{Cu}.

It seems that at a fixed current density of 11.55 mA/cm^2, OFI mucilage has the advantage to increase copper removal efficiency and decrease the specific energy consumption from approximately 5 min of treatment time (Fig. 12). In general, energy consumption is associated to current density, at high current density large amount of sludge is produced and energy consumption rises, since Al^{3+} cations released from the anode materials and then $Al(OH)_3$ rise too [56]. In the work of Gatsios et al. [42] for (Cu^{2+}), (Zn^{2+}), and (Mn^{2+}) removal by EC process,

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increasing the current density led to a better removal efficiency but caused an increase in power consumption.

From an industrial point of view, energy consumption and hence EC operating costs should be reduced to allow feasibility of efficient processes. The economical side of the EC performance has been neglected for a while, but it is becoming one of the major issue for actual industrial application. Bayramuglu et al. [35] found that energy consumption per kg dye removal constituted more than 80% of the total operating costs for aluminum electrodes. Additionally, operating cost decreases with increasing conductivity. It is well known that electrolyte addition employed to increase the conductivity not only enhances EC performance, but also reduces the ohmic resistance of the wastewater to be treated and hence the cell voltage and consumption of electrical energy [29, 35, 36]. Mucilage polyelectrolytes could rise the ionic strength which lead to the reduction of the repulsion between particles and hence resistance [21].

If some authors [45, 57] endorse the use of cost not environmentally chemicals to enhance EC-EF efficiency and energetic performances, OFI mucilage, besides its effectiveness in enhancing copper removal, is a natural, and biodegradable coagulant, easily obtained from an available plant, without any environmental impact, that allows reduction of energy consumption and hence EC-EF operational cost.

4. Conclusions

Facing a need for eco-friendly and cost-effective solutions, the relative old and known method of EC-EF was assisted with OFI mucilage for treating a copper containing solution. EC, being a simple and inexpensive process, is a method of future that need to be enhanced for more compatibility with environmental respect. Our findings support the application of innovative technologies by valorization and proposing the implementation of a natural resource that eliminates EC-EF copper residues in order to be as much as possible consistent with increasingly rigorous wastewater discharge limits. The OFI mucilage polysaccharides provides enough evidence of being not only ecological, cost-effective, accessible but also well suited for copper species removal. This bio-coagulant allowed the improvement of EC-EF performances. Under the predetermined operating conditions (initial pH 7.8, conductivity $\kappa = 2.4$ mS/cm, current density 11.55 mA/cm^2, agitation rate $r = 150$ rpm, peristaltic flow $Q = 300$ mL/min), EC-EF copper removal was shown to be OFI mucilage dependent, it reached 100% within less than 5 min in the presence of 30 mg/L mucilage concentration. The settling rate was accelerated even beyond this concentration. By reducing specific energy consumption, the mucilage improved the economic feasibility of the EC-EF. This is very profitable since a technically

effective process must be practical economically. Aluminum and hydrogen Faradaic yields were affected. The reduction in Aluminum yield avoids thereby a secondary pollution. Numerous laboratory and scale studies are showing that the use of eco-friendly plant coagulants is technically feasible. In this respect, further studies concerning the exploration of mucilage functional groups, and the mechanism of mucilage action could be required before recommending a large-scale application.

Conflict of Interest

None

Acknowledgments

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Fig. 1. Schematic set up of a batch electrocoagulation-electroflotation system assisted by *Opuntia ficus-indica* mucilage (1: DC power supply; 2: EC-EF cell; 3: mechanical agitator control; 4: reservoir tank; 5: treated effluent outlet; 6: peristaltic pump; 7: water-filled cylinder; 8: vacuum pump; 9: OFI mucilage).

Fig. 2. Effect of OFI mucilage concentration (mg/L) and run time on copper removal efficiency: initial copper concentration $C0 = 100$ mg/L, initial pH 7.8, conductivity $\kappa = 2.4$ mS/cm, current density $j = 11.55$ mA/cm^2, agitation rate $r = 150$ rpm, peristaltic flow $Q = 300$ mL/min.

Fig. 3. Effect of initial concentrations of OFI mucilage on copper removal efficiency: initial copper concentration $C0 = 100$ mg/L, initial pH 7.8, conductivity $\kappa = 2.4$ mS/cm, run time $t = 20$ min, current density $j = 11.55$ mA/cm^2, agitation rate $r = 150$ rpm, peristaltic flow $Q = 300$ mL/min.

Fig. 4. Evolution of pH values during EC-EF with different concentrations of OFI mucilage (mg/L). Initial copper concentration $C0 = 100$ mg/L, initial pH 7.8, conductivity $\kappa = 2.4$ mS/cm, current density $j = 11.55$ mA/cm^2, agitation rate $r = 150$ rpm, peristaltic flow $Q = 300$ mL/min.

Fig. 5. Schematic representation of the possible additional reactions occurring during EC-EF copper removal assisted by OFI mucilage.

Fig. 6. SEM images of formed flocs of liquid samples during EC-EF mucilage-free treatment (a), and EC-EF assisted with 30 mg/L OFI mucilage (b), taken from sample of 20 min treatment time.

Fig. 7. Effect of OFI mucilage concentration (mg/L) on the evolution of Al Faradaic yield during EC-EF treatment: initial copper concentration $C0 = 100$ mg/L, initial pH 7.8, conductivity $\kappa = 2.4$ mS/cm, current density $j = 11.55$ mA/cm^2, agitation rate $r = 150$ rpm, peristaltic flow $Q = 300$ mL/min.

Fig. 8. Effect of OFI mucilage concentration (mg/L) on the evolution of hydrogen yield during EC-EF treatment: initial copper concentration $C0 = 100$ mg/L, initial pH 7.8, conductivity $\kappa = 2.4$ mS/cm, current density $j = 11.55$ mA/cm², agitation rate $r = 150$ rpm, peristaltic flow $Q = 300$ mL/min.

Fig. 9. Settling curves of EC-EF effluents for different initial OFI mucilage concentrations (mg/L): initial copper concentration $C0 = 100$ mg/L, initial pH 7.8, conductivity $\kappa = 2.4$ mS/cm current density $j = 11.55$ mA/cm^2, agitation rate $r = 150$ rpm, peristaltic flow $Q = 300$ mL/min.

Fig. 10. Evolution of sludge settling velocity depending on the OFI mucilage concentration: after EC-EF treatments at initial copper concentration $C0 = 100$ mg/L, initial pH 7.8, conductivity $\kappa = 2.4$ mS/cm, current density $j = 11.55$ mA/cm^2, agitation rate $r = 150$ rpm, peristaltic flow $Q = 300$ mL/min.

Fig. 11. Evolution of the specific energy consumption as a function of mucilage concentration (mg/L) and time: initial copper concentration $C0 = 100$ mg/L, initial pH 7.8, conductivity $\kappa = 2.4$ mS/cm, current density $j = 11.55$ mA/cm², agitation rate $r = 150$ rpm, peristaltic flow $Q = 300$ mL/min.

Fig. 12. Effect of OFI mucilage concentration on copper removal efficiency and on specific energy consumption: initial copper concentration C_0 = 100 mg/L, initial pH 7.8, conductivity κ = 2.4 mS/cm, run time t = 20 min, current density j = 11.55 mA/cm², agitation rate r = 150 rpm, peristaltic flow Q = 300 mL/min. Results are reported as mean ± S.D. Different letters indicate that samples are significantly different ($p < 0.05$). The results are ranked in decreasing order (a > b > c > d > e > f > g).

Highlights

- Electrochemical treatment assisted with mucilage removes residual copper at 100%.

- Faradaic yields are lowered during electrochemical tests assisted with mucilage.

- Growing mucilage concentrations accelerates sludge settling rate.

- Specific energy consumption is reduced with the augmentation of mucilage.
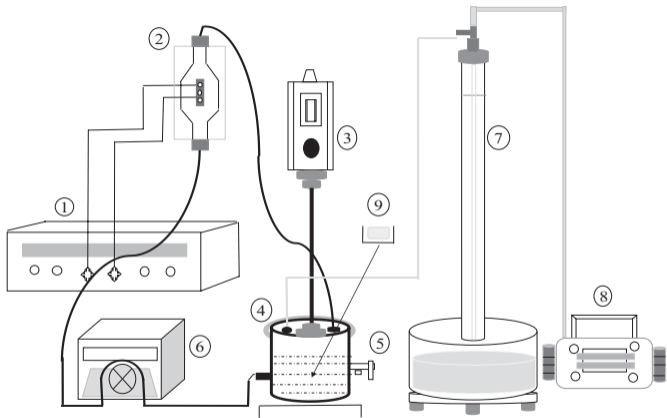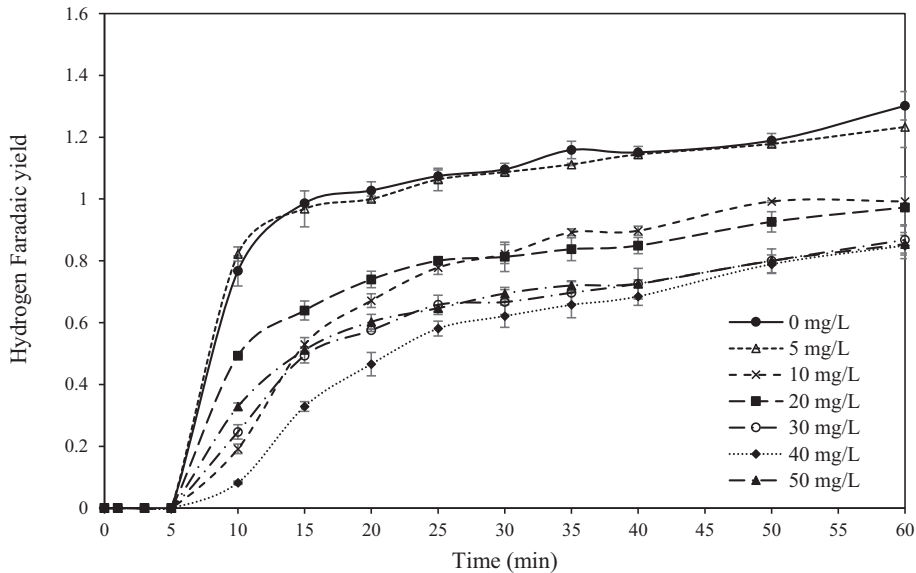
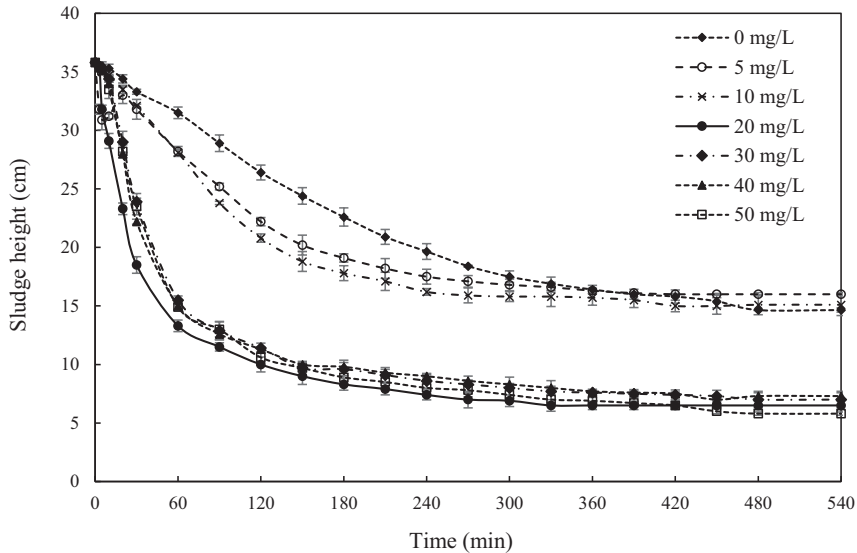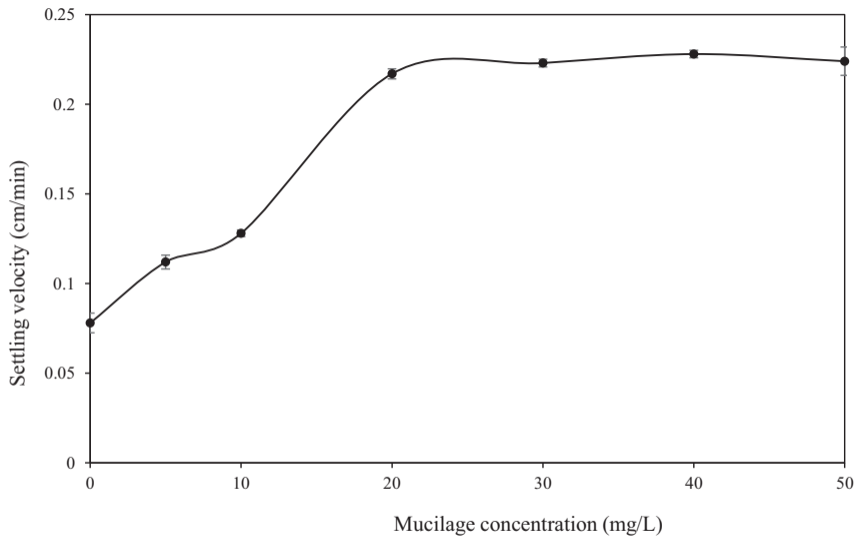Figure 1
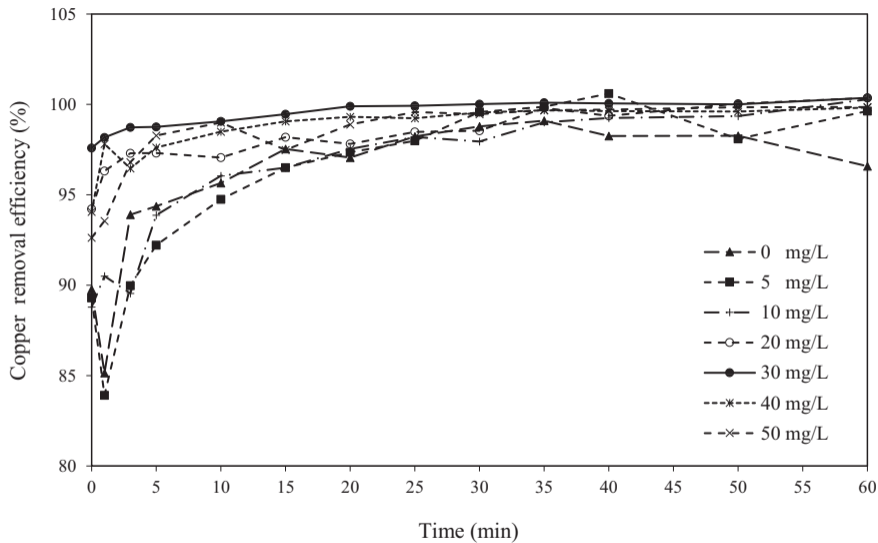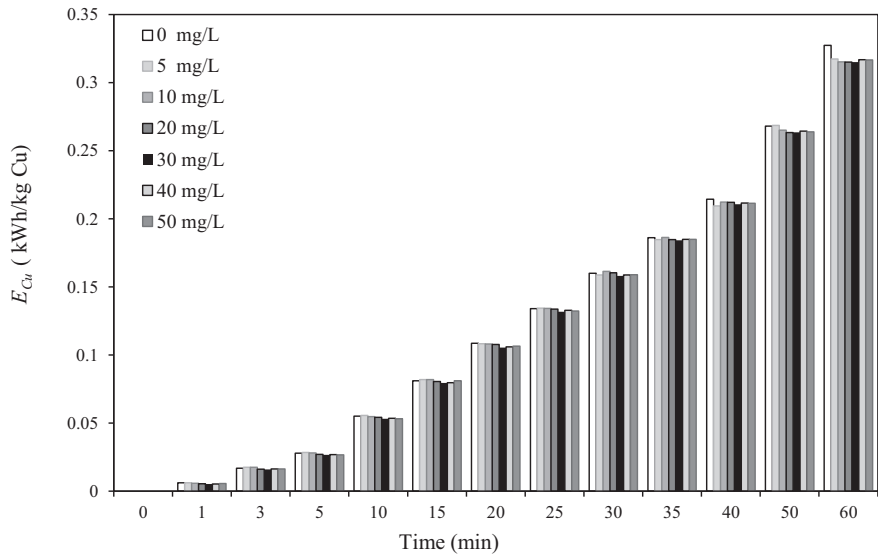
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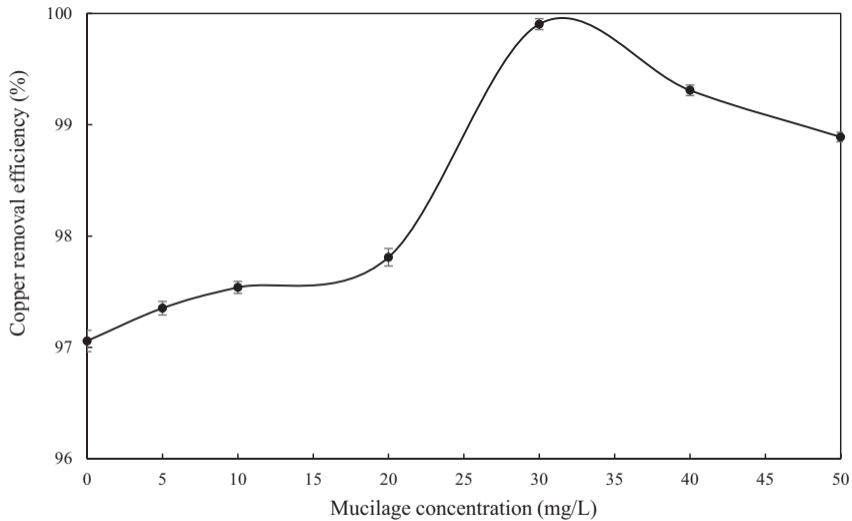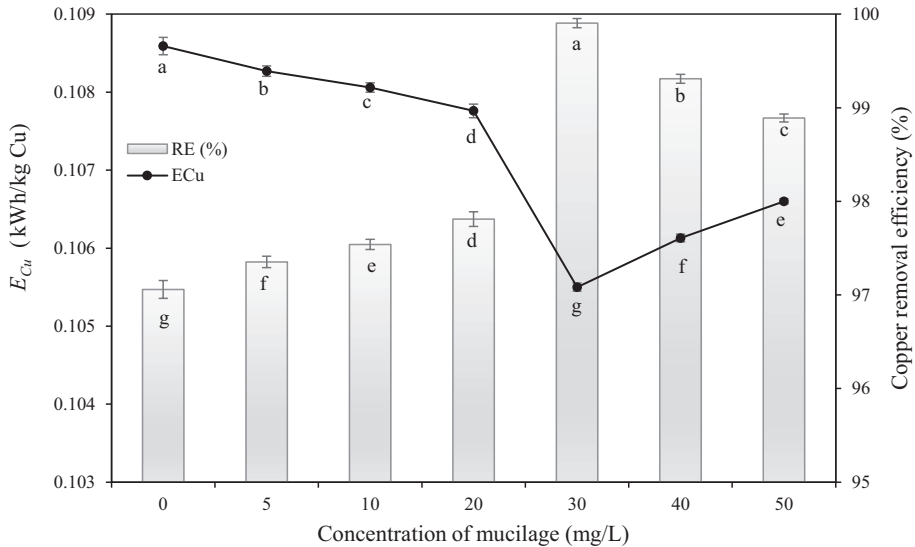
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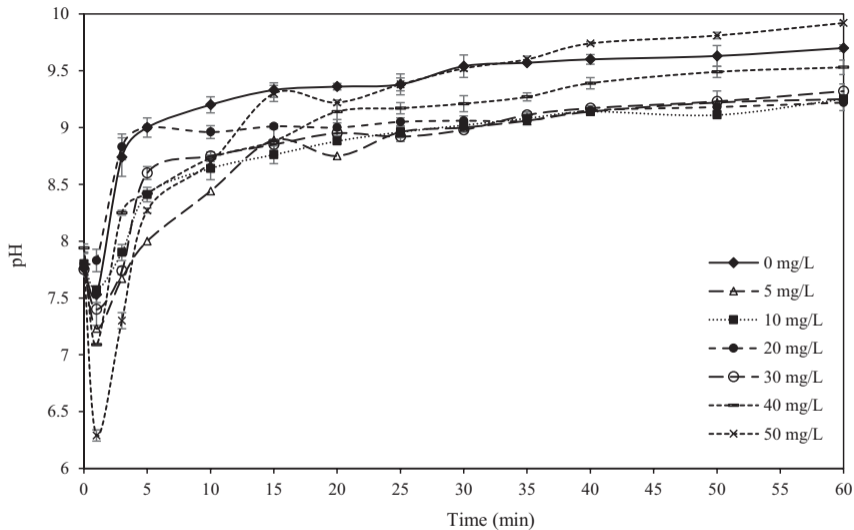
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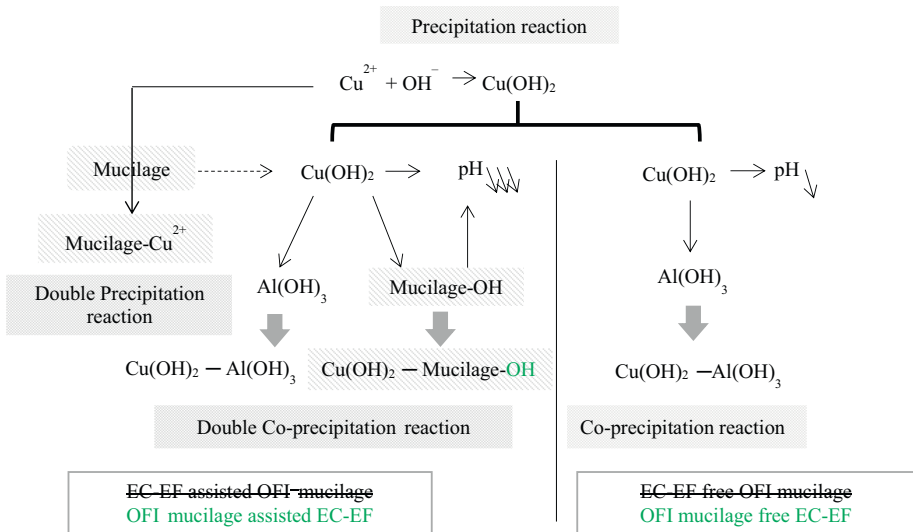
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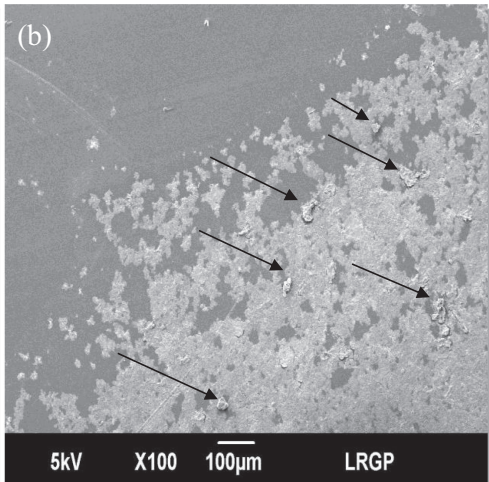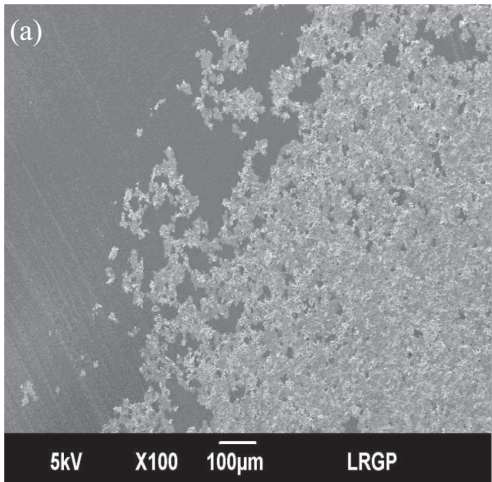
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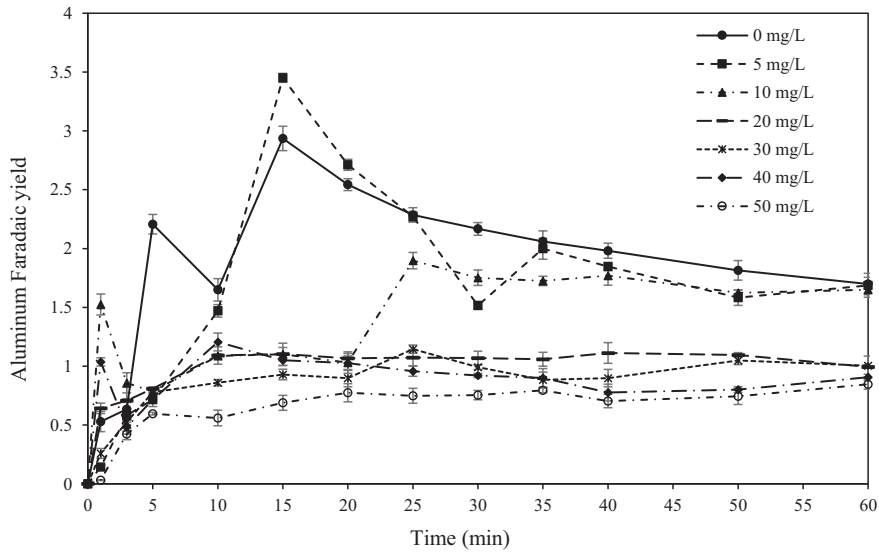
Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12