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Removal and recovery of copper from aqueous solutions by *Streptomyces rimosus* biomass: Enhancement of regeneration by desorption-electrolysis coupling

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ABSTRACT

Biosorption has emerged as an alternative treatment for the removal of heavy metals. Although it is simple, effective and economic, it is nevertheless merely considered as a displacement of pollution. The loaded biomass constitutes a solid waste requiring regeneration, which is often achieved by a spontaneous desorption. In this study, we investigated the effect of an electric field applied through desorbent solution to enhance desorption flow. Moreover, desorbed metal ions may be recovered as metal deposit. The regeneration by the desorption-electrolysis process of *Streptomyces rimosus* biomass loaded with copper was carried out and the effects of the operating parameters, such as desorbent nature, pH and current intensity, were examined. Our results showed that adsorption agreed with the Langmuir isotherm. A maximum capacity of 25.32 $mg.g^{-1}$ was reached. Among tested desorbent solutions, sulphuric acid was kept as more efficient. It allowed appreciable desorption rates, with an optimum pH of 1.5. An applied current intensity of 0.1 A led to an effectiveness of 86% at height of the released mass. We proved that the treatment by coupling desorption-electrolysis improved not only the desorption efficiency up to 99.77% but metal was also recovered as a pure electrochemical deposit.

Keywords: Biosorption; Desorption; Electrolysis; Copper

1. Introduction

Biosorption is an interesting depollution process. Since it is simple, effective and economic, it emerged as an alternative treatment technology for the removal of heavy metals [1–7]. However, this process is a displacement of pollution. Indeed, loaded biomass constitutes solid waste, the size of which will increase with the augmentation of the volume of treated water. Incineration may partially solve the storage problem by transforming the biomass into ashes, but does not eliminate this new form of pollution.

The regeneration of the used biomasses constitutes an interesting stage in order to concentrate and recover the metals. The operation is often achieved by a spontaneous desorption of fixed metal ions in an appropriate electrolyte by an exchange of ions. The desorption depends on the desorbent nature, its concentration and pH [8–11].

In addition, the electrolysis was used for the treatment of industrial wastewater [12]. The metal was recovered as an electrodeposit from concentrated electrolytes. However, this technique suffered in the case of diluted solu-

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tions from some drawbacks: weak transfer coefficient, limited current density, low current yield, etc. [13]. Therefore, the use of the adsorption-desorption stage permits concentration of the amount of metals which can be easily recovered by electrolysis [8,14,15]. Moreover, the specificity of biosorbents with respect to some metals leads to a cathodic deposit with high degree of purity [1, 14].

This paper suggests a scheme of a complete depollution process. An electric field was directly applied through the desorbent solution to enhance desorption flow and to recover metal as electrochemical deposit. The regeneration, by desorption-electrolysis process of *Streptomyces rimosus* biomass loaded with copper was carried out and the effects of the operating parameters such as desorbent nature, pH and current intensity were examined. Thus, the regenerated biomass could follow a new biosorption cycle.

The used biosorbent in this paper, *S. rimosus*, is a gram+ bacteria; its cell wall is formed essentially by peptidoglycan and teichoïc acids, carriers of carboxyl, hydroxyl and phosphate groups [16]. Its efficiency in heavy metal removal has been proven in several studies [15,17–21].

2. Materials and methods

2.1. Biosorbent preparation

The biosorbent used, *S. rimosus*, was provided by the Saidal Antibiotics Unit of Medea (Algeria). The biomass wafers were cleaved, laid out on big trays and dried with air. When the biomass is dry, it is washed several times in distilled water then dried in air for 24 h and finally baked at 50 °C for another 24 h. The clean biomass is mechanically ground and sifted to get a powder of 250 to 560 μm. The chemical pre-treatment was performed on this biomass with a 0.1 N NaOH solution using a biomass/volume of the solution ratio of about 10 $g.L^{-1}$. This solution is maintained under a stirring velocity of 250 rpm during 30 min at room temperature. The biomass is then filtered, washed and dried at 50 °C for 24 h.

2.2. Adsorption isotherm of copper

The adsorption isotherm of copper is performed aiming at a maximum adsorption capacity in order to be able to prepare biosorbent samples loaded with copper. For this reason biosorption experiments were conducted under the following conditions: initial concentration, C_0, of Cu(II) varied between 12.5 $mg.L^{-1}$ and 400 $mg.L^{-1}$, volume of the solution was 250 cm^3, initial $pH_i = 5$, stirring velocity $\omega = 250$ rpm, temperature $T = 25$ °C and the biosorbent content $m = 7$ $g.L^{-1}$.

2.3. Preparation of the biosorbent loaded with copper

Samples were prepared under the following conditions: biosorbent content $m = 10$ $g.L^{-1}$, $C_0 = 250$ $mg.L^{-1}$. A duration of 24 h was necessary to obtain the equilibrium. The samples were then analysed and the equilibrium concentrations were determinated. After filtration the obtained biomass was dried at 50 °C during 24 h. The dry biomass samples loaded with copper were then mixed together. The load of the mixture, expressed in mg of Cu(II).g^{-1} of the biomass, is calculated from the average of the adsorption capacities obtained for mixed samples.

2.4. Desorption

2.4.1. Spontaneous desorption

A quantity of 2.25 g of biomass loaded with copper is put in contact with 500 cm^3 of a desorbent solution, stirred at 500 rpm. Samples were taken at fixed times in order to follow the desorbing kinetics of copper in the solution. The studied parameters are:

- Desorbent nature: H_2SO_4, HCl and NaOH with pH solutions respectively equal to 1, 1 and 12.
- pH of H_2SO_4 desorbent was fixed at 1, 1.5, 2 and 3.

2.4.2. Forced desorption with electrolysis

When the spontaneous desorption equilibrium was reached, electrodes were put in the "biomass-desorbent" solution and the electrolysis started (Fig. 1). Copper was therefore recovered in the form of cathodic deposit. This trial was performed with an iron cathode and a stainless steel anode. The distance between electrodes was of 3 cm; the surface of the electrodes was 25.62 cm^2. The pH of the H_2SO_4 desorbent solution was fixed at 1, 1.5, 2 and 3. The electrolysis was carried out by applying various current intensities: 0.03, 0.1 and 0.4 A.

2.4.3. Electric field effect assessment

The aim of this experiment is to assess the contribution of the electric field in the displacement of the desorption

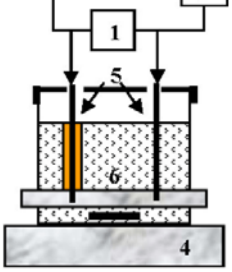

Fig. 1. Set-up for the recovery of desorbed copper. 1 voltmeter, 2 amperemeter, 3 power supplier, 4 magnetic stirrer, 5 electrodes, 6 solution containing a biomass.

equilibrium. For this we proceeded to a mineralization [22] of three biomass samples: 1 g of a biomass sample loaded with copper (capacity X = 17.58 mg.g^{-1}), 1 g of a spontaneous desorbed biomass sample and 1 g of a biomass sample that underwent an electrodeposition. This method gives the real load of the biomass at each stage of treatment.

3. Results and discussion

3.1. Adsorption isotherm of copper

Fig. 2a shows that the variation of the quantity of metal adsorbed per g of the biosorbent (X) as a function of the equilibrium concentration (C_e) for different initial concentrations follows a type I isotherm, which corresponds to a single layer at the saturated active sites of the surface. Among different adsorption models tested—Langmuir, Freundlich, etc.—Fig. 2b shows that the Langmuir isotherm appears to be the most appropriate (R^2 = 0.99). It agrees perfectly with our experimental values. The maximum capacity (X_m) was found to be 25.32 mg.g^{-1} (0.398 mol.g^{-1}), with an equilibrium constant K of 12.26 mg.L^{-1} and an affinity of b = 0.081 5 L.mg^{-1}.

For copper biosorption on different biomasses, it was rationalized that the Langmuir model is the most adequate. Our maximum capacity is located in the average of the capacities found by the majority of authors [7,8,23–33]. Therefore, in order to prepare the samples loaded with copper for desorption trials, a capacity of 25.32 mg.g^{-1} justifies the choice of a copper concentration equal to 250 mg.L^{-1} for a biomass quantity of 10 g.L^{-1}.

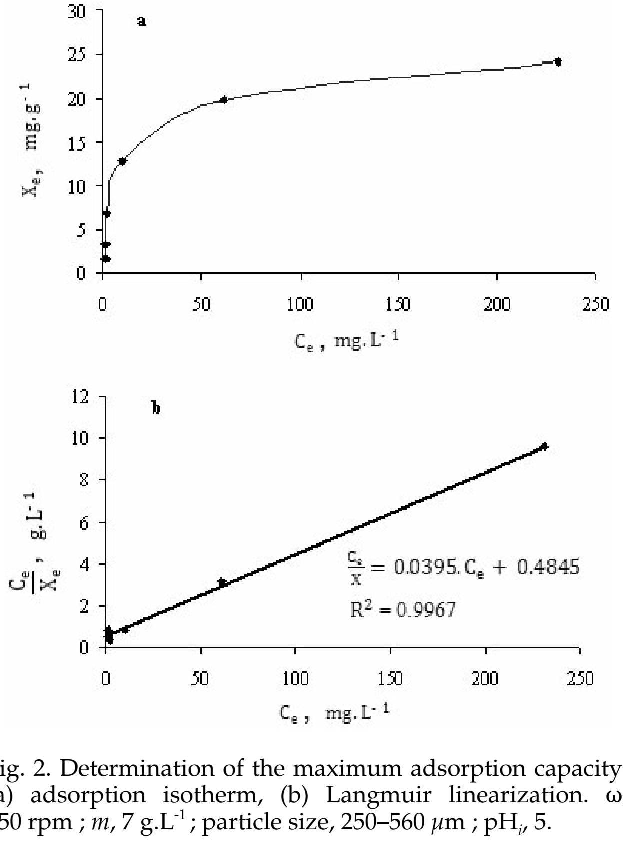

Fig. 2. Determination of the maximum adsorption capacity. (a) adsorption isotherm, (b) Langmuir linearization. ω, 250 rpm ; m, 7 g.L^{-1}; particle size, 250–560 μm ; pH$_i$, 5.

3.2. Desorption process

3.2.1. Spontaneous desorption

Effect of the desorbent nature — Two types of desorbents were tested; an acid desorbent (HCl or H_2SO_4, at pH = 1) and an alkaline desorbent (NaOH, at pH = 12). In Fig. 3, the desorption in acidic solutions proves to be instantaneous; the concentration of the desorbed copper tends to reach a plateau in the first 10 min which is stabilised after 30 min. Hydrochloric acid, at pH 1, can attain a maximum regeneration rate of 96% (16.88 mg of the desorbed Cu(II) per g of the biomass) as well sulphuric acid that gives a regeneration rate of 91% (16 mg.g^{-1}), unlike NaOH, which seems not to be desorptive since the regeneration rate obtained in this case is almost nil (1.40% or 0.24 mg.g^{-1}).

Several studies affirm that hydrochloric acid has an excellent desorptive capacity. Indeed, Wilhelmi et al. [34] managed to desorb more than 90% of the adsorbed copper on *Saccharomyces cerevisiae* by using HCl 0.1 M. Also, 80% of adsorbed cadmium on *Sargassum baccularia* sea alga was desorbed by using HCl at pH 2 [35]. With the same biomass, Adour et al. [18] recovered 90% of adsorbed zinc by using HCl 0.1 M. According to Kratochvil et al. [36], a *Sargassum* type biomass saturated with copper can be regenerated with HCl 0.1M. Zulfadhly et al. [37] regenerated a column full of a *Pycnoporus sanguineus* biomass saturated with copper by using HCl 0.1 M.

Other desorbents were successfully used such as sodium acetate 0.05 M at pH 5 or pH 2 [38], HNO_3 0.05 N [39] and EDTA 0.1 M [40]. However, just a few works exist on the use of sulphuric acid in the available bibliography.

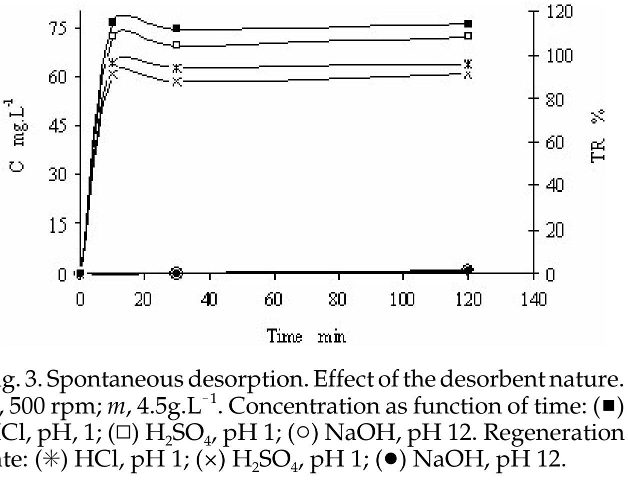

Fig. 3. Spontaneous desorption. Effect of the desorbent nature. ω, 500 rpm; m, 4.5g.L^{-1}. Concentration as function of time: (■) HCl, pH, 1; (□) H_2SO_4, pH 1; (○) NaOH, pH 12. Regeneration rate: (✳) HCl, pH 1; (×) H_2SO_4, pH 1; (●) NaOH, pH 12.

Lister et al. [41], Banat et al. [42], and Al-Qodah [8] found that H_2SO_4 was the most effective acid desorbent; their desorption rates were respectively, 60–70% for copper, 93.88% for zinc and 93% for copper. Concerning the NaOH, our regeneration rate is similar to those of Zhao et al. where only 5.2% Cr^{6+} (2.3 mg) was recovered with 0.1 M NaOH [43]. However, it does not agree with those presented by Kurek [44]. Adsorbed cadmium may be extracted by using NaOH 0.1 M, the highest extraction rate for the bacteria is obtained with *Arthrobacter globiformis* (74.5%), while it reaches only 44.6% with *Penicillium chrysogenum* in the case of mushrooms.

The final choice of desorbent is not only based on the desorption capacity; we must also consider the compatibility of the used acid with the more favourable electrolysis conditions for the forced desorption. The hydrochloric acid presents two disadvantages: anode corrosion and production of Cl_2, a toxic gas resulting from the following anodic reaction:

$$2\,Cl^- \rightarrow 2\,Cl_2 + 2e^- \qquad (1)$$

Thus, sulphuric acid is considered to be the most appropriate desorbent.

Effect of desorbent pH — Sulphuric acid as a desorbent (at pH 1, 1.5, 2, and 3) was studied. Fig. 4 shows that the rise of pH from 1 to 2 improves the regeneration rate: 92% (pH 1), 98% (pH 1.5) and 97.5% (pH 2). The desorbing capacities pass from 15.30 mg.g^{-1} (pH 1) to 16.33 mg.g^{-1} (pH 1.5) and 16.25 mg.g^{-1} (pH 2). For these values of pH, the bonding groups retake their protons, inducing the pH rise. This causes a breaking down of the bond Cu(II)-anionic sites, thereby liberating Cu(II) cations into the solution. From pH 2, the regeneration rate starts to slow down; it reaches 45.23% at pH 3 (pKa = pH of the half dissociation of the -COOH groups), which corresponds to a desorption capacity of 7.53 mg.g^{-1}. This slowdown is due to the reduction (to 50%) of anionic sites.

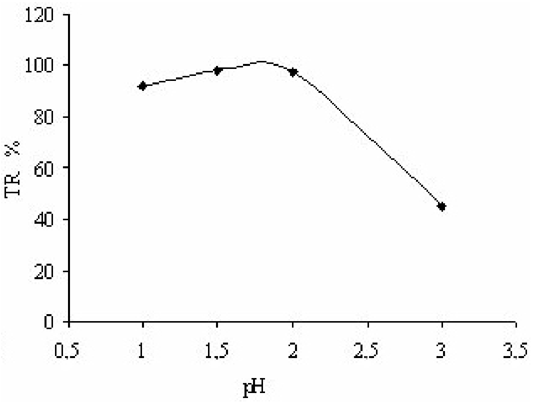

Fig. 4. Spontaneous desorption: Influence of pH on biomass regeneration rate. Desorbent: H_2SO_4; ω, 500 rpm, *m*, 4.5 g.L^{-1}.

Metal ion desorption is then influenced by the desorbent strength. Chen et al. studied the effect of HCl concentration on the copper desorption [45]. They demonstrated that copper elution is dramatically increased with the concentration increase. When the concentration reaches 0.2 M, the elution achieves its maximum of 90%. According to Urrutia et al. [46], nitric acid, at pH 3, regenerates a bacteria biomass loaded with copper to 54%. However, Senthilkumar et al. found that the maximum elution efficiencies were observed in 0.1 M $CaCl_2$ (in HCl, pH 3–3.5) [47]. Therefore, the optimum pH for the spontaneous desorption seems to be located between 1.5 and 2.

3.2.2. Forced desorption by applied electric field

In this case, "forced" desorption, we investigated the effect of the presence of an electric field applied through the desorbent solution to enhance desorption flow of Cu^{2+}. Indeed, the electrodeposition of copper on cathode, reaction (3), induces the impoverishment of the acidified solution, reaction (2), which enhances consequently the flow of desorption (Fig. 5). The main reactions that take place in the process are:

- At the anode:

$$H_2O \rightarrow 1/2\,O_2 + 2H^+ + 2e^- \qquad (2)$$

- At the cathode:

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad (3)$$

Thus, the role of electrolysis is:

1. Impoverishment of the solution which improves the desorption flow by increasing the concentration gradient.
2. Generation of H^+ ions at the anode by water oxidation, which assures a better stabilization of the desorbent acid pH.

Effect of the desorbent pH — The "forced" desorption is carried out at different pH values (1, 1.5, 2 and 3). When the spontaneous desorption equilibrium was reached, electrodes were put in the biomass-desorbent solution and the electrolysis started. Copper was therefore recovered in the form of cathodic deposit. The electrolysis was stopped after 7 h when the electrodeposition rate became very slow, that is, no detected variation of the bulk concentration, and thus the cathode was weighted.

Fig. 6 shows the effect of the applied electric field, 0.1 A, on concentration of copper in the bulk at different pH. We observe that the concentration decreases with time for first three pHs, whereas at pH 3, there is no effect on the concentration. The residual concentrations reached, for pH values 1, 1.5, and 2 are respectively 18.93, 12.51 and 15.01 mg.L^{-1}. The better elimination rate was obtained with pH 1.5 and the estimated recovery yields are

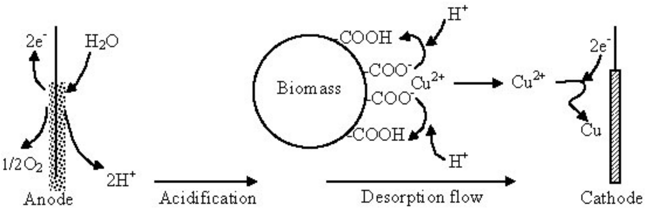

Fig. 5. Schema of the principle of desorption-electrolysis coupling.

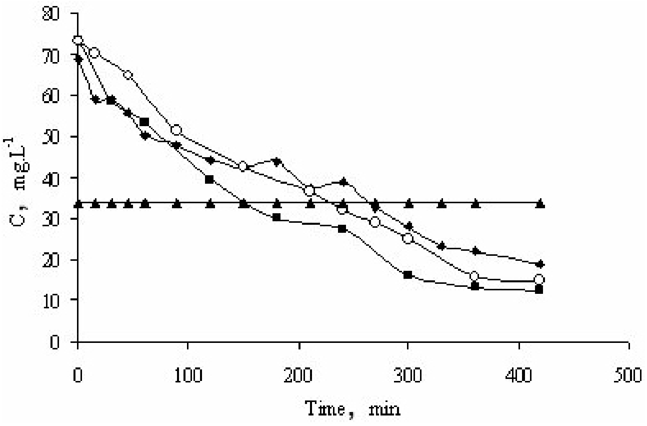

Fig. 6. Forced desorption: Influence of pH on the copper concentration. Desorbent: H_2SO_4; ω, 500 rpm; *m*, 4.5 g.L^{-1} ; *I*, 0.1A: (◆)pH 1; (■) pH 1.5; (O) pH 2; (▲) pH 3.

Table 1
Recovery yields (in %) obtained in sulphuric acid at different pH values

	pH 1	pH 1.5	pH 2	pH 3
$R=\frac{m_{\text{dep}}}{m_d}\times 100$	70.57	78.36	120.86	0
$R' = (C_d - C_f)/C_d \times 100$	72.50	82.00	78.50	0

m_{dep}: electrodeposited copper mass (mg); m_d: desorbed copper mass (mg); C_d: desorbed copper concentration (mg.L^{-1}); C_f: final copper concentration (mg. L^{-1}).

presented in Table 1. The yields obtained from the deposited masses are slightly lower for pH 1 and pH 1.5; this is likely due to experimental errors during the weightings and the mass loss during the samplings. However, for pH 2 the yield (calculated with mass weighted) seems to exceed 100% (120.8%), and the observation of the surface cathode reveals some blackening with the copper deposit. Two reactions may occur in these conditions, the chemical displacement reaction of iron by copper ions and/or the reaction of dissolution of iron in acidic medium. These reactions can significantly affect the assessment of the values of the recovery efficiency. In fact the anode made of stainless steel is not totally inert and its dissolution gets faster with the pH rise. When the conditions are favourable (potential >5 V), the dissolved metals are deposited at the same time with copper. This deposit exercises a competitive effect. For this reason real yield, calculated from residual concentrations, for pH 2 is smaller than that obtained for pH 1.5.

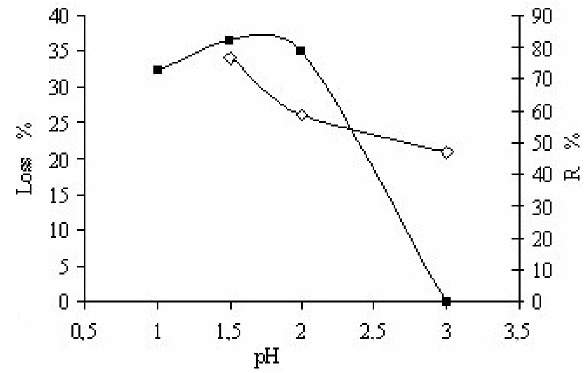

Fig. 7. Forced desorption: Influence of pH on biomass loss and recovery yields. (■) Recovery yields, (◇) Percentage of biomass loss.

Therefore, we can deduce that pH 1.5 is an optimum value which is a compromise between pH 1 and 2. It gives the best yield with a moderate dissolution of anode. The choice of this pH is in agreement with the calculation of the mass loss percentage of biomass (Fig. 7). At pH 1.5, the biomass loss (34%) is intermediate between pH 1 where the biomass is irrecoverable following to the deterioration of used filters, and pH 2 where 26% of the biomass is lost. The loss in biomass is minimum at pH 3; nevertheless, the recovery of copper by electrolysis is practically nil at this latter pH, within our conditions

Effect of the current intensity — Herein sulphuric acid at pH1.5 was used as the desorbent. The current intensity is directly related to the quantity of the deposit [48]. Faraday linked the theoretical deposited mass (m_{dep}) obtained during the electrolysis to the running time and the applied intensity as follows:

$$m_{\text{dep}} = \frac{M_{\text{Cu}} I t}{n.F} \tag{4}$$

where M_{Cu} is the molar mass of copper, *n* the number of exchanged electrons, *I* the current intensity, *t* the electrolysis time and *F* the Faraday number, 96,500 C/mol.

Current intensity has a direct effect on the residual concentrations of Cu(II) and therefore on the real recovery yield (calculated from the residual concentrations) (Fig. 8a and b). With 0.03A the residual concentration is estimated to 15.37 mg.L^{-1} giving a yield of 78%. With 0.1 A the residual concentration is of 10.37 mg.L^{-1}, which corre-

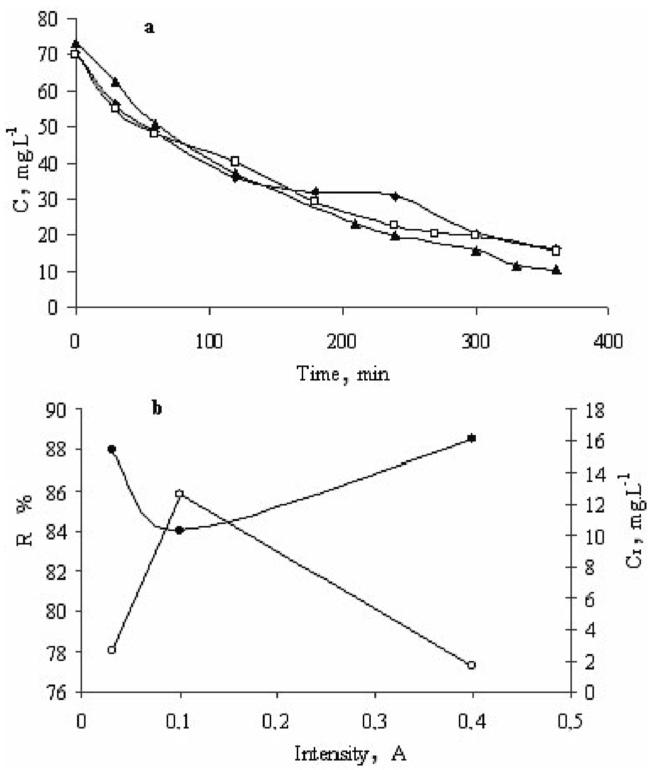

Fig. 8. Effect of the electric current intensity. Desorbent: H_2SO_4; pH 1.5; ω, 500 rpm; *m*, 4.5 g.L^{-1}. (a) Variation of the copper concentration with electrolysis time: (◆) 0.4A, (▲) 0.1A, (◆) 0.03A. (b) Variation of the recovery yield and the residual concentration with the current intensity: (O) recovery yield, (●) residual concentration.

sponds to a larger yield estimated to 85.83%. This yield increase follows the Faraday's law where the deposited mass depends on the current intensity. However, by increasing 0.1 A to 0.4 A, the yield drops to 77.24%, giving a residual concentration of 16.08 mg.L^{-1} and a calculated cathodic deposit $(C_d - C_f)/2 = 27.28$ mg. Nevertheless, the real deposited cathodic mass is estimated to 33.9 mg. So, the calculated yield is over estimated to 95.97%. The corresponding cathode is then analysed and therefore a reasonable explanation of the over estimation is found. The deposit is blackish so there is a co-deposition of another metal coming from the dissolution of the anode (U >5 V). The co-deposited metallic cations constrain the deposition of the Cu(II) ions by giving a real yield (77.24%) inferior to the one obtained with the intensity of 0.1A (85.83%) for which the competitive effect is absent.

An applied intensity of 0.4 A seems to lead to the recovery of impurities, coming from the anode dissolution as a cathodic deposit, which gives a much lower electrodeposition yield. A gradual application of current intensity is recommended in order to improve the operation efficiency.

Table 2
Assessment of the electric field effect — mineralization results

	m_{Cu} (mg/g)	*TR*, %
Loaded biomas	17.67	—
Desorbed biomass	0.72	95.92
Biomass after electrodeposition	0.04	99.77

3.2.3. Electric field effect assessment

This operation can conclude the electrolysis effect on copper displacement. The mineralization gives the real load of the biomass at each stage of treatment and calculates the real regeneration rate (Table 2). We can say that the application of an electric field improves the regeneration rate from 95.92% to 99.77%. Consequently, there is a displacement of the desorption equilibrium; this phenomenon appears when the concentration of copper goes down in the solution. The quantity of biomass loaded with copper used in our experiments is 2.25 g, which may release during the electrodeposition stage a mass of 1.53 mg: this mass is negligible and may not be detectable in electrodeposition process, especially when it is released gradually.

4. Conclusions

The study of the suggested process reveals the following points:

- *S. rimosus* spontaneous desorption is effective only with acid-desorbent solutions. Sulphuric acid is the appropriate desorbent: it allows an appreciating regeneration rate and a better safeguarding of the anode state.
- When sulphuric acid is used, the optimum pH is 1.5. This latter leads to the best regeneration rate (in spontaneous desorption) and a higher recovery yield (in forced desorption); it represents a compromise between pH 1 where the anode dissolution is minimum with a total biomass loss, and pH 2 where the anode dissolution is important with a low biomass loss.
- In forced desorption, it was found that the current intensity of 0.1 A leads to the best copper recovery yield.

Under these conditions, the recovery yield reached was of 85.83%. The electric field in forced desorption displaces the desorption equilibrium to the weak concentrations and improves the regeneration rate of the biomass from 95.92% to 99.77%.

In perspective, we intend to study the optimisation of the biomass quantity per desorbent volume. This quantity could be greater with the application of an electric field. It allows therefore the minimisation of the acid waste and to treat more concentrated solutions, which will limit the volume to be treated by electrolysis and consequently an important gain in electrical energy.

The important objective of the desorption is the reuse of the biomass. Our aims also is the determination of X_m after each cycle of adsorption-regeneration in order to determine the number of cycles allowing reuse of the biomass.

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