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Removal of Cu and Cr from an industrial effluent using a packed-bed column with algae *Gelidium*-derived material

Vítor J.P. Vilar [a], Ramiro J.E. Martins [b], Cidália M.S. Botelho [a], Rui A.R. Boaventura [a,*]

[a] *LSRE – Laboratory of Separation and Reaction Engineering, Departamento de Engenharia Química, Faculdade de Engenharia da Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal*

[b] *Department of Chemical Technology, Superior School of Technology, Polytechnic Institute of Bragança, Campus de Santa Apolónia, 5301-857 Bragança, Portugal*

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ABSTRACT

The purpose of this work was to evaluate the potential of algal waste from the agar extraction industry, immobilized in a polymer, and the algae *Gelidium* itself, the raw material of agar extraction, to remove Cu(II) and Cr(III) from industrial effluents. The study involved a Cu(II) bearing effluent and the mixture of this effluent with an effluent containing Cr(VI), previously reduced to Cr(III). The two effluents were collected from metal plating plants, and then filtered and diluted before the biosorption studies. Biosorption results were compared with those obtained from pure Cu(II) and Cu(II)/Cr(III) solution adsorption experiments. Three consecutive adsorption (≈50 mg Cu(II)/l)-desorption (0.1 M HNO_3) cycles were carried out with algae *Gelidium* and two with the composite material, for the Cu(II) effluent. The biomass uptake capacity remained almost constant and close to the obtained for adsorption from pure Cu(II) solution, suggesting that the biomass lifetime was long enough to be used in a continuous industrial process. In the biosorption from Cu(II)/Cr(III) mixtures it was observed that Cr leave the column after the residence time, suggesting that the reduction of Cr(VI) to Cr(III) was not completely achieved. Cr(VI) speciation in aqueous solution produces negatively charged species, that do not bind to the negatively charged carboxylic groups on the biosorbent surface and a low breakthrough time is obtained. An “overshoot” was observed for the Cu(II) concentration, suggesting that Cr(III) has a higher affinity to the binding sites than Cu(II).

1. Introduction

Metal plating processes generate large volumes of diluted metal-contaminated wastewaters creating a localized and accumulative safety hazard. There are emission limits for most of the metals and then they must be removed before the liquid waste can be discharged. However, the large volumes and dilute concentrations make traditional treatment methods, such as precipitation, ion-exchange, membrane technology, economically non-viable. Different kinds of natural biomass have been used as low cost biosorbents to remove toxic metals from diluted solutions. Tobin and Roux (1998) showed that *Mucor meihi* biomass can be an effective biosorbent for the removal of chromium from leather tanning effluents. Acid elution of biosorbed chromium increased when decreasing the eluant pH to a minimum value of 0.7. An 80% desorption efficiency was obtained for a loading chromium concentration of 40 mg Cr/g. The possibility of using ground, dried and classified *Pinus sylvestris* bark for trivalent chromium removal in tannery wastewater “polishing” was studied by Alves et al. (1993). Tests were carried out using synthetic solutions with chromium concentrations (5 and 20 mg/l) close to those found in some effluents of Portuguese tannery industries, after physico-chemical treatment, achieving a maximum uptake of 8.7 mg Cr(III)/g^{-1} at pH 4.50. Kratochvil and Volesky (1998) observed an effective copper removal/recovery from ferruginous wastewater using *Sargassum* biosorbent. Vijayaraghavan et al. (2006) used the brown seaweed *Sargassum wigtti* on the treatment of nickel containing electroplating effluents, which exhibited uptakes of 37.2 and 38.6 mg Ni/g for effluent-1 (109 mg Ni/l) and effluent-2 (52 mg Ni/l), respectively, under full column saturation. The data from five regeneration cycles evidenced that reusability of *S. wightii* biomass in the treatment of nickel-bearing electroplating effluents is viable. Zhao et al. (1999) studied the removal and recovery of zinc from aqueous solution and electroplating effluent using *Azolla Filiculoides* and found a maximum zinc uptake of 45.2 mg/g in batch system at an optimum pH of 6.0. Column experiments were performed, showing good efficiency during six adsorption/desorption cycles using HCl or H_2SO_4 0.2 N as eluants. Removal of Pb(II) from real effluents using immobilized *Pinus sylvestris* sawdust was performed in a fixed-bed column at pilot scale (56 cm height and 10 cm diameter) and the results were in accordance with those obtained from synthetic effluents, achieving a service time of 45 h for an inlet lead concentration of 1.40 mg/l and a volumetric flow rate of 25 l/h (Taty-Costodes et al., 2005). Vijayaraghavan et al. (2005) used crab shell biomass for the treatment of nickel-bearing electroplating industrial effluents and

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* Corresponding author. Tel.: +351 225081683; fax: +351 225081674.
E-mail addresses: vilar@fe.up.pt (V.J.P. Vilar), rmartins@ipb.pt (R.J.E. Martins), cbotelho@fe.up.pt (C.M.S. Botelho), bventura@fe.up.pt (R.A.R. Boaventura).

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Table 1
Characterization of the effluents

Parameter	Effluent A	Effluent B
pH	1.6	6.3
Cu^{2+} (mg/l)	720	0.5
Pb^{2+} (mg/l)	0.5	<0.1
Cd^{2+} (mg/l)	0.05	<0.05
Total Cr (mg/l)	3.9	108
Zn^{2+} (mg/l)	2.5	<0.15
Al^{3+} (mg/l)	26.9	<1
Fe^{2+} (mg/l)	49.1	<0.2
Ni^{2+} (mg/l)	25	<0.2
Mn^{2+} (mg/l)	1.0	<0.1
Conductivity (mS/cm)	11.5	1.1
ORP (Mv)	382.0	343.0
TOC (mg/l)	123.7	15.1

obtained uptake capacities of 15.08 and 20.04 mg Ni/g from two different effluents. The reusability of crab shell during seven sorption–desorption cycles is viable.

In this study, the treatment of two effluents (one that mainly contains Cu(II) and the other Cr(VI)) from metal plating industry was performed using as biosorbents algae *Gelidium* and an algal waste from the agar extraction industry immobilized in polyacrylonitrile, in an up-flow packed-bed column.

2. Materials and methods

2.1. Biosorbents preparation

An algal waste from agar extraction industry granulated by Polyacrylonitrile-PAN, and the algae *Gelidium*, the raw material for agar extraction, were used in this study. The characteristics and preparation of both materials for the experimental work were presented in previous works (Vilar et al., 2006, 2005).

2.2. Preparations of standard copper and chromium solutions and pre-treatment of the industrial effluents

Cu(II) and Cr(III) solutions were prepared by dissolving a weighed amount of copper(II) chloride dehydrate (Riedel-de Haën, 99%) and chromium(III) nitrate nonahydrate (Carlo Erba, 98%) in distilled water. The solutions pH was adjusted by adding dilute 0.01 M HCl and 0.01 M NaOH solutions.

Cu(II) and Cr(VI) effluents were collected from metal plating industries. Both effluents were first filtered (0.45 µm membranes from Whatman) and then diluted and mixed to have a new solution with 50 mg/l of each metal.

The acid effluent A is characterized by high Cu(II) and organic carbon concentrations (Table 1). The effluent B is essentially a Cr(VI) ($HCrO_4^-$,CrO_4^{2-} and $Cr_2O_7^{2-}$) solution at alkaline pH (Table 1).

Usually, the treatment of effluents containing Cr(VI) is performed by reduction to the trivalent oxidation state and precipitation as $Cr(OH)_3$ in alkaline conditions. In this work Cr(III) biosorption has been studied after Cr(VI) reduction by sodium bisulphite, at pH<2.5:

$$4H_2CrO_4 + 6NaHSO_3 + 3H_2SO_4 \rightarrow 2Cr_2(SO_4)_3 + 3Na_2SO_4 + 10H_2O \tag{1}$$

or

$$H_2Cr_2O_7 + 3NaHSO_3 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3NaSO_4 + 4H_2O \tag{2}$$

2.3. Analytical procedure

The residual metal concentration was determined by atomic absorption spectrometry (GBC 932 Plus Atomic Absorption Spectrometer). The total organic carbon was measured in filtered solutions (0.45 µm membranes from Whatman), using a TOC-5000 A SHIMADZU analyzer. The conductivity was measured by a WTW model LF 538 conductivity meter.

3. Results and discussion

3.1. Copper industrial effluent

The operating conditions for each experiment are presented in Table 2. Cu(II) biosorption from diluted effluent A was performed using the algae *Gelidium*, in three consecutive adsorption/desorption cycles (Fig. 1 (a)), and the composite material in two consecutive adsorption cycles (Fig. 1 (b)). The difference between the three cycles breakthrough times (t_b (2nd cycle)>t_b (1st cycle)>t_b (3rd cycle) is due to the final pH: (2nd cycle)>(1st cycle)>(3rd cycle). The same trend is obtained for the copper removal: 9.4 mg/g, 8.8 mg/g and 6.2 mg/g, respectively for the 2nd, 1st and 3rd cycles. The breakthrough time for the 3rd cycle is 35% lower than for the 2nd cycle. Fig. 1 (a) also shows the breakthrough curve for the synthetic copper solution, which has the same shape as the breakthrough curve for the real effluent, but is 13% displaced in terms of breakthrough time relatively to the 1st cycle,

Table 2
Operation parameters for the breakthrough and elution curves of industrial effluents

Material	Exp.	Metal	Type	Q (cm^3/min)	pH_{SE}	pH_{CI}	pH_{CE}	C_{Ei}/C_{CI} (mg/l)	$C_{final}(i)$ (mg/l)	W (g)	ε	τ (min)
Gelidium	1	Cu (1° cycle)	S	4.0	5.3	5.6	4.0	21.6/0	21.2	10.5	0.894	16.4
	2		E	8.0	0.8	3.9	0.8	0/21.8	0.43	10.5	0.894	8.2
	3	Cu (2° cycle)	S	4.0	5.3	4.8	4.1	22.9/0	22.0	10.5	0.894	16.4
	4		E	8.0	0.8	4.1	0.8	0/21.5	0.07	10.5	0.894	8.2
	5	Cu (3° cycle)	S	4.1	5.3	3.6	3.7	22.1/0	18.5	10.5	0.894	16.4
	6		E	8.0	0.8	3.7	0.8	0/18.3	0.25	10.5	0.894	8.2
	7	Cu/Cr	S	4.0	5.0	5.8	4.1	Cu – 43.0/0 Cr – 45.8/0	Cu – 52.0 Cr – 15.0	11.8	0.880	16.2
	8		E	8.0	1.0	4.1	0.8	Cu – 0/80.0 Cr – 0/2.0	Cu – 1.4 Cr – 10.0	11.8	0.880	8.1
Composite material	9	Cu (1° cycle)	S	4.0	5.5	5.2	3.7	21.3/0	20.0	8.6	0.533	9.8
	10		E	8.0	0.6	3.7	0.6	0/14.0	0.45	8.6	0.533	4.9
	11	Cu (2° cycle)	S	4.0	5.3	5.2	3.7	22.2/0	19.0	8.6	0.533	9.8
	12		E	8.0	0.6	3.6	0.6	0/12.0	0.6	8.6	0.533	4.9
	13	Cu/Cr	S	4.0	5.0	5.8	4.0	Cu – 44.8/0 Cr – 32.3/0	Cu – 32.6 Cr – 19.0	10.0	0.457	8.4
	14		E	8.0	1.0	4.0	1.0	Cu – 0/32.0 Cr – 0/18.0	Cu – 0.6 Cr – 2.4	10.0	0.457	4.2

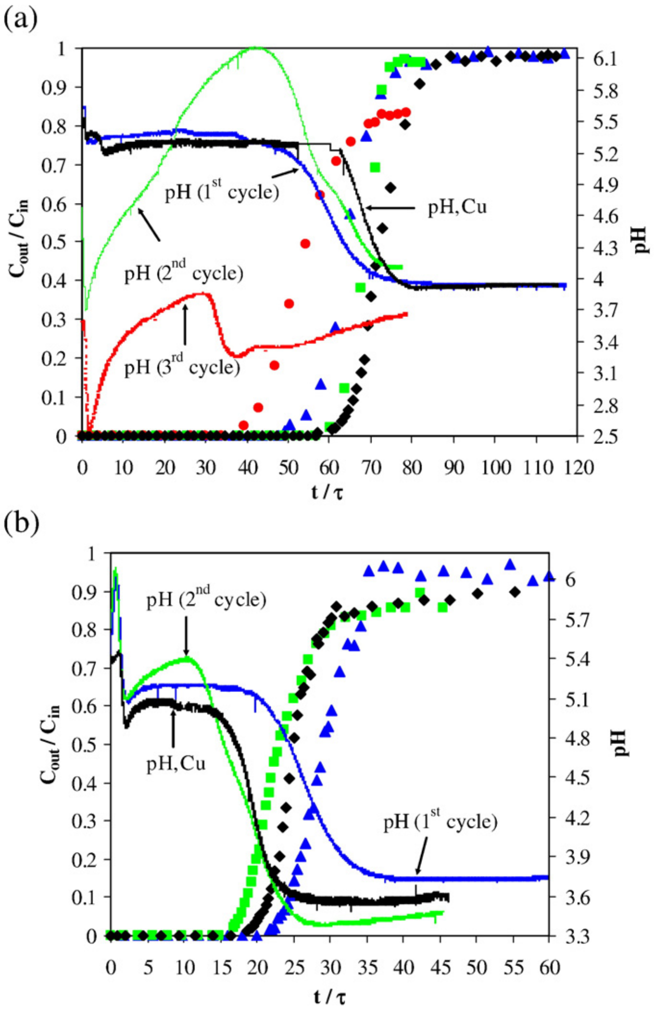

Fig. 1. Comparison of experimental synthetic Cu solution and real effluent A (practical solution) adsorption curves: (a) – algae *Gelidium* and (b) – composite material. ▲ – real effluent (1st cycle), 🟩 – real effluent (2nd cycle), ● – real effluent (3rd cycle), ◆ – synthetic Cu solution, —— pH real effluent (1st cycle), —— pH real effluent (2nd cycle), —— pH real effluent (3rd cycle), ——,pH synthetic Cu solution. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

although with the same final pH. This difference may be explained by the competition of Cu(II) with other ions present in the effluent (essentially iron, aluminium and nickel) and organic matter. Mass transfer zones are 7.1, 4 and 8.3 cm long, corresponding to non-used bed fractions of 23.6%, 13% and 27.6%, respectively for 1st, 2nd and 3rd cycles. This indicates that after a pre-treatment with concentrated acid in the elution step, the performance of the biosorbent increased in the 2nd cycle.

Using the composite material as biosorbent (Fig. 1 (b)), the 1st cycle breakthrough time for the real effluent is higher than for the synthetic copper solution and the 2nd cycle, due to the variations in the final pH (1st cycle ≈3.7; synthetic copper solution ≈3.6 and 2nd cycle ≈3.5), which is directly related with the uptake capacity of the adsorbent (2.7 mg/g for the 1st cycle; 2.0 mg/g for the 2nd one and 2.3 mg/g for the synthetic copper solution), the mass transfer zone (7.6 cm for the 1st cycle and 8.2 cm for 2nd one) and the fraction of unused bed (25.3% for the 1st cycle and 27.3% for the 2nd one).

The use of a concentrated strong acid as eluant, allows the biosorbents reutilization in a rapid and efficient way (Fig. 2 (a) and (b)), resulting in high metal concentration in the eluate (1811 mg/l and 578 mg/l) and high concentration factors (CR of 84 and 27), respectively for algae *Gelidium* and composite material. Desorption generates a relatively small volume of highly concentrated metal solutions and makes possible to eventually recover the metal by the conventional electrowinning process or by separation from the ashes, after incineration (Volesky, 2003).

From these results it can be concluded that this kind of effluents can be treated by biosorption in packed bed columns, using algae *Gelidium* and composite material. The regeneration of the biosorbents allows operating in consecutive adsorption–desorption cycles. In order to have a constant uptake capacity during consecutive cycles, after desorption with a strong acid solution, the regenerated biosorbent must be washed with an alkaline solution to remove the excess of acid.

3.2. Copper/chromium industrial effluent

A 0.68 mmol/l Cu/0.88 mmol/l Cr solution has been prepared from effluents A and B. The resulting effluent was treated in the packed bed column using algae *Gelidium* as biosorbent.

Fig. 3 (a) compares the breakthrough curves for Cu and Cr biosorption from the mixed effluent and from a Cu(II)/Cr(III) synthetic solution.

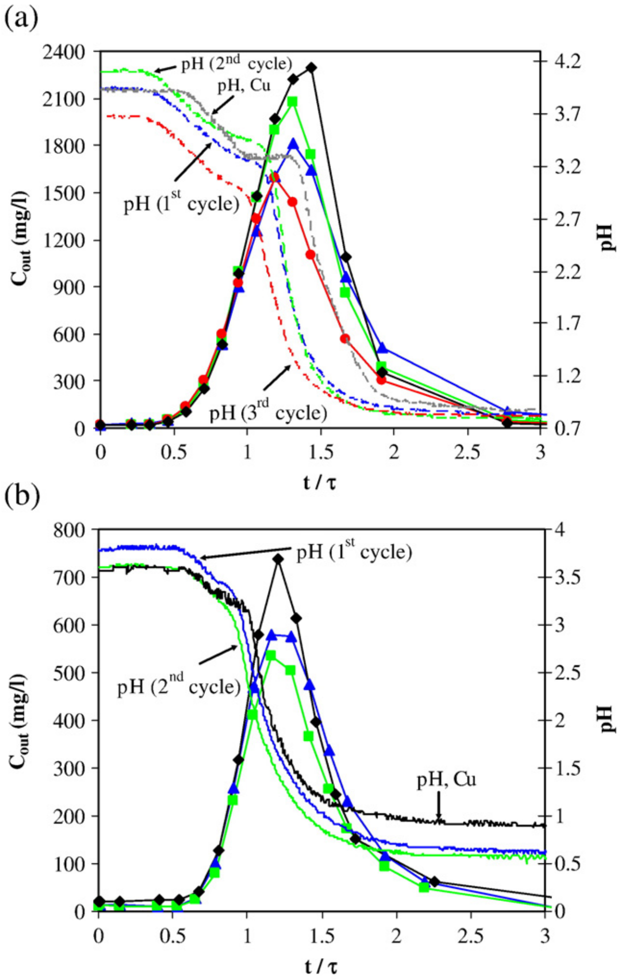

Fig. 2. Comparison of experimental synthetic Cu solution and real effluent A (practical solution) elution curves: (a) – algae *Gelidium* and (b) – composite material. ▲ – real effluent (1st cycle), 🟩 – real effluent (2nd cycle), ● – real effluent (3rd cycle), ◆ – synthetic Cu solution, —— pH real effluent (1st cycle), —— pH real effluent (2nd cycle), —— pH real effluent (3rd cycle), —— pH synthetic Cu solution. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

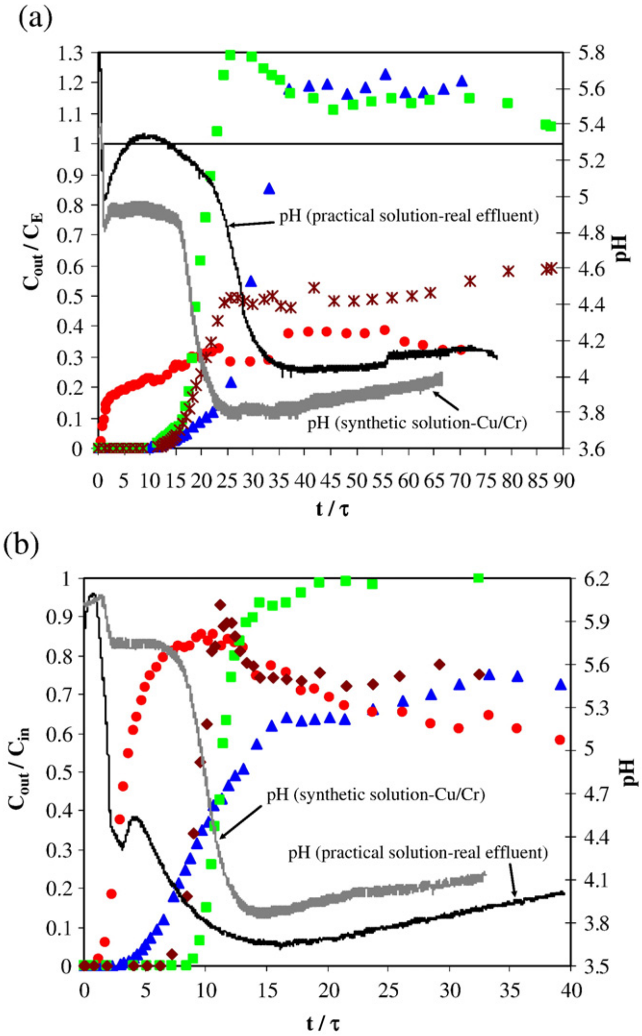

Fig. 3. Comparison of experimental synthetic Cu/Cr solution and real effluent B (practical solution) adsorption curves: (a) – algae *Gelidium* and (b) – composite material. ▲ – real effluent (Cu), 🟩 – synthetic solution (Cu), ● – real effluent (Cr), ◆ – synthetic solution (Cr), —,pH real effluent, —,pH synthetic Cu/Cr solution. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

It can be observed that the Cr ions were not totally adsorbed from the effluent suggesting that the reduction of Cr(VI) to Cr(III) was not complete. Hexavalent chromium in aqueous solution produces negatively charged species ($HCrO_4^-$, CrO_4^{2-} and $Cr_2O_7^{2-}$), which are not adsorbed on the negatively charged biosorbent surfaces.

The concentration front of Cu for both experiments reach the end of the column, approximately, at the same time. However, the Cu breakthrough curve for the synthetic mixture reaches the feed concentration firstly, due to the low final pH value and to the higher copper feed concentration (0.784 mmol/l). An overshoot region is observed in the two curves, reaching a concentration 13% higher than the feed, suggesting that copper ions, initially bound to the algae active sites are replaced by chromium ions, with a higher affinity and in a greater concentration. This is in agreement with equilibrium results obtained for the synthetic Cu/Cr effluent presented in a previous work, where the ratio between the two affinity constants, K_{Cr}/K_{Cu}, is 1.4 (Vilar et al., 2009).

The adsorption experiment was stopped before equilibrium and, desorption step was started 8 h later. The concentrations of copper and chromium in the first sample of the desorption process were 82 mg/l and 2 mg/l, respectively, suggesting that almost all the chromium present in the interstitial fluid was adsorbed, releasing copper ions to the solution, and Cr(VI) had been effectively reduced to Cr(III) and exchanged with copper ions previously bound to the surface active sites.

Kratochvil et al. (1998) concluded that Cr(VI) can be adsorbed after CrO_4^{2-} and $Cr_2O_7^{2-}$ reduction to Cr(III) by biomass oxidation, followed by Cr(III) adsorption to the negatively charged groups on the algae *Sargassum* surface. Adsorption of negative species to the surface positively charged groups can occur too. The biomass oxidation process was very slow and Cr(VI) reduction increased for pH>2.0. Similar results were obtained using the *Bacillus sp*. bacterium and *Ecklonia* brown algae (Chirma and Wang, 1997; Park et al., 2004).

Fig. 4 (a) compares copper and chromium elution curves for a synthetic mixture and the real effluent. As the real effluent experiment was interrupted earlier, a higher amount of copper was desorbed, as it can be seen by the area under the elution curve. If both experiments were extended until complete saturation of column, almost all Cu(II) would be exchanged with Cr(III). So, when decontaminating binary Cu(II)/Cr(III) solution by biosorption on algae *Gelidium*, in a packed column, only chromium ions are retained.

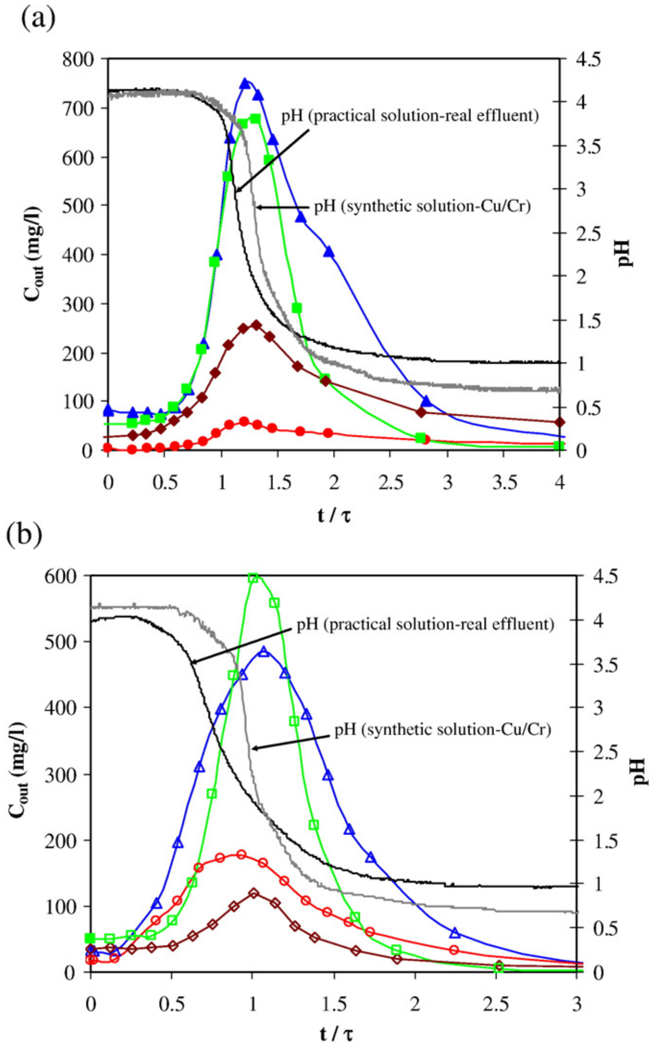

Fig. 4. Comparison of experimental synthetic Cu/Cr solution and real effluent B (practical solution) elution curves: (a) – algae *Gelidium* and (b) – composite material. ▲ – real effluent (Cu), 🟩 – synthetic solution (Cu), ● – real effluent (Cr), ◆ – synthetic solution (Cr), —,pH real effluent, —,pH synthetic Cu/Cr solution. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

For the column experiments using the composite material as biosorbent, a real effluent and an aqueous synthetic solution with higher Cu than Cr concentrations (0.71 mmol/l Cu and 0.62 mmol/l Cr) have been prepared. The breakthrough curves for the adsorption and desorption processes are presented in Figs. 3 (b) and 4 (b), respectively.

As for the algae *Gelidium*, the chromium concentration front reaches the end of the column at the residence time, achieving a maximum concentration of 27 mg/l, followed by a decrease due to ion exchange of the adsorbed Cu(II) with Cr(III) in solution.

The copper effluent breakthrough curve reaches the end of the column earlier than the synthetic copper solution curve, due to the difference in the final pH. For the composite material, as it was observed in the equilibrium experiments (Vilar et al., 2009), the copper affinity is higher than the chromium one ($K_{Cu}/K_{Cr} = 1.4$), which can explain the higher breakthrough time for copper ions in the synthetic Cu/Cr solution.

Low chromium desorption efficiencies (30–40%) were obtained for the synthetic Cr solution (Vilar et al., 2008), suggesting that eluant concentration and elution time must be increased, to remove all the chromium from the loaded biomass. However, approximately 80% and 100% desorption efficiencies were obtained for the synthetic Cu/Cr solution and the real effluent. These results can be explained by the low amount of Cr loaded in the biomass when using Cu/Cr mixtures compared with the synthetic Cu solution. Tobin and Roux (1998) found similar results for chromium desorption from *Mucor* saturated biomass. However, they observed that increasing the acid concentration until 5 M, the desorption efficiency increased to 80% for 40 mg Cr(III)/g loaded biomass, although the use of the more concentrated acid (5 M) caused visible modification on the biomass structure. Kratochvil et al. (1998) showed that 70% of Cr(VI) bound to the seaweed, can be desorbed with 0.2 M H_2SO_4 via reduction to Cr(III) after 24 h, confirming the low rate of the reduction process.

4. Conclusions

This study indicates that algae *Gelidium* and algal waste from agar extraction industry can be used to remove copper and copper/chromium from metal plating industry effluents. The biosorption efficiency from pure copper solutions is similar to that obtained with the copper bearing effluent during three consecutive adsorption–desorption cycles. Total copper desorption was obtained during three adsorption/desorption cycles applied to the industrial effluent. If Cr(VI is present in the effluent, a previous reduction to Cr(III) is required. Reduction using sodium bisulphite at pH 2.5 was not totally achieved. However, the “overshoot” of the initially bound copper ions suggests that they have been exchanged with chromium ions with higher affinity for the binding sites. Moderate desorption efficiencies were obtained for Cr loaded biomass using 0.1 M HNO_3 solution, as eluant.

Nomenclature

S	Saturation;
E	Elution;
Q	flow rate (cm^3/min)
C_{out}	metal concentration at the column outlet (mg metal/l fluid)
C_{in}, C_{Ei}	feed concentration (mg metal/l fluid)
C_{CI}	initial metal concentration inside the column (mg metal/l fluid)
$C_{final(i)}$	metal concentration in the solution at the end of the saturation or elution process (mg metal/l fluid)
pH	solution pH;
pH_{SE}	pH of feed solution
pH_{CI}	initial pH of interstitial fluid inside the column
pH_{CF}	final pH of interstitial fluid inside the column
t	experimental time (s)
TOC	Total Organic Carbon (mg/l)
W	mass of biosorbent (g)
ε	porosity of the bed
τ	space time (s);

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