

A WATER-SOLUBLE POLYCARBOBETAINE FOR SUSTAINABLE COPPER RECOVERY

JULIA MOUTON^{*1,2}, MIREILLE TURMINE¹, HÉLÈNE VAN DEN BERGHE³, & JEAN COUDANE³

¹Sorbonne Universités, UPMC Univ Paris 06, CNRS, UMR 8235, France

²EPF-Graduate School of Engineering, France

³CNRS - UMR 5247 - Université Montpellier, Faculté de Pharmacie, France

ABSTRACT

This study targets betaine-type polymers (polycarbobetaines - PCBets) as complexing agent of metal ions. As PCBets are pH-sensitive, the adsorption isotherms of copper onto PCBet were monitored at various pH (from 3 to 6) by electrochemical measurements. The best fit to the Langmuir model translates the predominantly homogeneous distribution of the chelating groups on the polymer chains because the Langmuir equation assumes that the adsorbent surface is energetically homogeneous. The results obtained for the complexation of copper were greatly enhanced as the pH increase and reached $250 \pm 10 \text{ mg g}^{-1}$ at pH = 6. Such maximal adsorption capacities compete with recent results obtained for molecules of environmental interest such as chitosan, for example. The copper adsorption efficiency was shown stable for soft to hard water. The selectivity of the target PCBets for copper was indicated in the presence of nickel, cobalt, manganese, zinc, calcium or magnesium and partially accounts for the interest in this material and demonstrated the relevance of using PCBet in environmental applications such as copper recovery. The reusability of PCBet was explored by pH adjustment. The results confirm that the efficiency of copper adsorption was maintained over five cycles of PCBet reuse ($99 \pm 3\%$). A full process for copper recovery was then designed at laboratory scale for copper recovery from synthetic wastewaters.

Keywords: copper, polycarbobetaine, recovery, reuse selective.

1 INTRODUCTION

Currently, metals are highly studied in environmental management because of their depletion as resources and because of the increasingly common cases of pollution [1]. Thus, their recovery and valorization are key themes of recent scientific studies concerning the environment. Copper ions are produced as waste in various chemical industries, such as smelting, mining, printed circuit board manufacturing, electroplating, wire drawing, copper polishing, and paint manufacturing [2]. Various techniques, such as chemical precipitation, coagulation, solvent extraction, ultra-filtration, biological systems, electrolytic processes, reverse osmosis, oxidation with ozone/hydrogen peroxide, membrane filtration, ion exchange, photocatalytic degradation and adsorption, have been developed for the removal of metal contaminants from waste [3]. Among these techniques, precipitation appears as the most attractive, primarily because of its economical operation.

This research is devoted to the study of polybetaines as metal ion precipitating agents. Polybetaines are specific polyampholytes that possess anionic and cationic groups on the same monomer unit. Among polybetaines, polysulfobetaines, polycarbobetaines and polyphosphobetaines are prominent [4]. This study investigates polycarbobetaines (PCBets) and their interactions with copper to design chemical processes for copper valorization.



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The interactions of water-soluble polymers with metal ions are treated as surface phenomena as previously reported [5]. The most appropriate method for assessing sorption capacity is the derivation of a whole sorption isotherm [6]. Over the years, a wide variety of equilibrium isotherm models (Langmuir, Freundlich, Brunauer–Emmett–Teller, Redlich–Peterson, Dubinin–Radushkevich, Temkin, Toth, Koble–Corrigan, Sips, Khan, Hill, Flory–Huggins and Radke–Prausnitz isotherm), have been formulated [7].

2 MATERIALS AND METHODS

2.1 Polycarbobetaine synthesis

The monomer was obtained by dropwise addition of ammonium hydroxide 30% aqueous solution (11 mL) to acetoacetic ester (10 mL) under magnetic stirring for 3 hours. The solution was then left overnight to decant (12 hours), and the organic phase containing the key product ethyl-3-aminocrotonate (EAC) was collected. The yield of the monomer was 98%, and its purity was checked by FTIR. The linear water-soluble polycarbobetaine namely polycarboxyethyl-3-aminocrotonate (PCEAC) was synthesized by radical polymerization, as previously reported [8, 9], by mixing EAC, acrylic acid and the initiator 2,2'-azobisisobutyronitrile (5 minutes). The polymer (PCEAC) obtained in bulk was washed with an abundant amount of acetone and oven-dried at 70°C (approximately 55% yield). Its chemical structure is presented in Fig. 1.

FTIR spectra were recorded using a Perkin–Elmer Spectrum 100 FTIR spectrometer using the attenuated-total-reflectance (ATR) method.

The main functional groups were identified by FTIR spectroscopy for PCEAC, including the O-H stretching vibration at 3,192 cm^{-1} ; C-H stretching vibration at 2,939 cm^{-1} ; and C = O stretching vibration at 1,701 cm^{-1} , as previously reported for a similar structure [10, 11]. The results presented in Table 1 compare the characteristic bands between PCEAC and PCEAC/Cu complex obtained in this study and in previous work [12]. No carboxylate asymmetric stretching vibrations were recorded for PCEAC, while a symmetric vibration appeared at 1,407 cm^{-1} . This tendency changes in the case of the PCEAC/Cu complex, with the appearance of a medium asymmetric stretching vibration at 1,608 cm^{-1} , which is characteristic of copper carboxylates [13]. The difference between these two well-known characteristic bands in the PCEAC/Cu complex (201 cm^{-1}) indicated that the coordination of the carboxylate groups occurred in a bridged form [14].

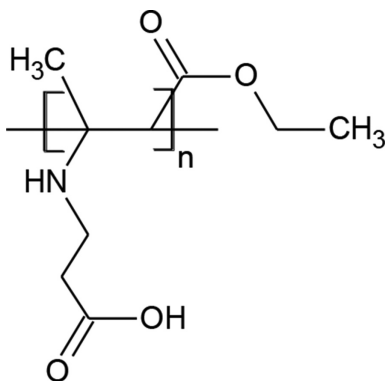


Figure 1: Chemical structure of PCEAC.

$^1\text{H-NMR}$ spectra were recorded using a Bruker spectrometer (AMX300) operating at 300 MHz. Deuterium oxide (D_2O) was used as the solvent. The chemical shifts are expressed in ppm with respect to tetramethylsilane (TMS). CH_2 and CH_3 groups of the ethyl function were clearly identified by the presence of a quadruplet at 3.97 ppm and a triplet at 1.03 ppm, respectively, in $^1\text{H NMR}$ spectra of pure PCEAC. The other hydrogen atoms were observed over the expected range (from 1.43 to 2.54 ppm). No comparison could be performed with the $^1\text{H NMR}$ spectra of PCEAC/Cu complexes due to their insolubility in D_2O .

The UV–vis spectra of the polymer solutions were recorded on a Hitachi U4001 spectrophotometer with a scan range of 220–900 nm. The aqueous solution of PCEAC 0.5 g L^{-1} ($\text{I} = 0.3 \text{ mol L}^{-1}$ at $\text{pH} = 5$) exhibits an absorbance peak approximately 280 nm, which is specific to carboxylic groups (Fig. 2), while the copper solution absorbs at 816 nm. Figure 2 shows that the absorption for the PCEAC/Cu complex shifted from 816 nm to 702 nm and indicated the coordination interactions between the species. This band is characteristic of square-pyramidal copper(II) complexes [13]. In addition, the specific peak of PCEAC at 280 nm was markedly increased in the presence of copper (from 0.72 to 1.15), confirming the interaction between copper and polycarbobetaine carboxylate groups. This band is assigned to the carboxylate-to-copper charge transfer (ligand-to-metal charge transfer) [14].

Table 1: IR spectra of PCEAC and PCEAC/Cu complexes.

Bands	PCEAC		PCEAC/Cu	
	[12]	This study	[12]	This study
$\nu\text{C} = \text{O}$	1,707	1,702	1,701	1,702
$\nu_{\text{as}}\text{COO-}$	-	-	1,619	1,608
dN-H	1,559	1,547	-	1,548
$\nu_{\text{s}}\text{COO-}$	1,401	1,407	1,401	1,407

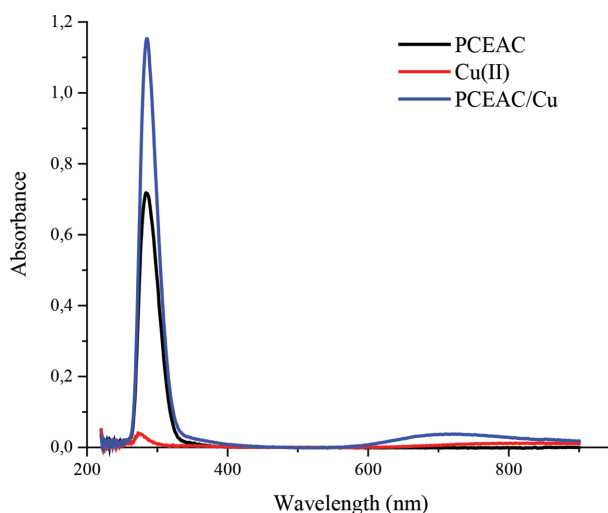


Figure 2: UV–visible spectra of PCEAC (0.5 g L^{-1}), Cu(II) ($0.0005 \text{ mol L}^{-1}$) and/or Co(II) (0.025 mol L^{-1}) in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ at $\text{pH} = 5$.

2.2 Sorption experiments

The sorption experiments were performed by the batch method (10 mL) in a thermostated cell (25°C) with constant stirring, using PCEAC 0.5 g L⁻¹. The adsorption behavior of the copper ions (Cu(II)) was assayed over a range from 5.10⁻⁵ to 5 10⁻³ mol L⁻¹ and over a pH range from 3.5 to 5.5. The ionic strength (I) was fixed at 0.3 mol L⁻¹ with sodium sulfate (Na₂SO₄) 0.1 mol L⁻¹. The pH was adjusted with sulfuric acid (H₂SO₄) or sodium hydroxide (NaOH). Adsorption isotherms were determined by monitoring free copper decay in the solution and were fitted to the Langmuir, Freundlich, Temkin, Dubinin-Radushkevich two parameters models, and to the Redlich-Peterson, Sips and Toth three parameters models. All the equations are given in Table 2.

The amount of copper adsorbed (mg g⁻¹) at equilibrium (Q_e), defined as the soluble and precipitated fractions of PCEAC/Cu complex, was calculated from the mass balance of initial and final copper concentrations as previously reported [15].

Some of the assays were used to test the selectivity of PCEAC toward copper, cobalt (Co²⁺), and nickel (Ni²⁺) using electrochemical measurements and UV-visible spectroscopy. All of the experiments were conducted in triplicate under identical conditions.

Table 2: Equations and parameters used to model the adsorption isotherms of copper on PCEAC.

Name	Equation	Parameters
Langmuir	$Q_e = \frac{Q_m K_L C_e}{1 + K_L \times C_e}$	Q _m = Maximum monolayer adsorption capacity (mg g ⁻¹) K _L = Langmuir isotherm constant (L mg ⁻¹)
Freunlich	$Q_e = K_f C_e^{1/n}$	K _f = Freundlich isotherm constant (mg g ⁻¹ (L mg ⁻¹) ^{1/n}) n = adsorption intensity
Sips	$Q_e = \frac{K_S C_e^{\beta_S}}{1 + a_S C_e^{\beta_S}}$	K _S = Isotherm constant (L g ⁻¹) β _S = Isotherm exponent a _S = Isotherm constant (L mg ⁻¹)
Dubinin-Radushkevich	$Q_e = Q_s \exp[-K_{DR} \varepsilon^2]$ $\varepsilon = RT \times \ln \left(1 + \frac{1}{C_e} \right)$	Q _S = Maximum adsorption capacity (mg g ⁻¹) K _{DR} = Isotherm constant (mol ² kJ ⁻²)
Temkin	$Q_e = \frac{RT}{b_T} \times \ln A_T C_e$	b _T = Isotherm constant A _T = Isotherm equilibrium binding constant (L g ⁻¹)
Redlich-Peterson	$Q_e = \frac{K_R C_e}{1 + a_R C_e^{br}}$	K _R = Isotherm constant (L g ⁻¹) a _R = Isotherm constant (mg ⁻¹) br = Isotherm exponent
Toth	$Q_e = \frac{K_T C_e}{(a_T + C_e)^{1/t}}$	K _T = Isotherm constant (mg g ⁻¹) a _T = Isotherm constant (L mg ⁻¹) t = Isotherm constant

Adsorption isotherms were determined by using non-linear regression analysis. The error function employed to evaluate the fit was the second order corrected Akaike information criterion (AIC_c) defined as follows [16, 17]:

$$AIC = N \times \ln \left(\frac{RSS}{N} \right) + 2P$$

$$AIC_c = AIC + \frac{2P \times (P + 1)}{N - P - 1}$$

where P is the number of parameters in the model (P = 2 or 3), N is the number of data points and RSS the residual squares sum.

AIC_c considers the size of the calibration data set and is therefore preferred over the original AIC [18].

2.3 Sorption/desorption experiments

Sorption/desorption experiments were performed over five cycles by pH adjustments. A solution of copper 0.005 mol L^{-1} and PCEAC 0.5 g L^{-1} was prepared in Na_2SO_4 0.1 mol L^{-1} at pH = 5 (the final pH was 4.5). Desorption experiments were performed by decreasing the pH to 2, and the next adsorption cycle was obtained by pH adjustment back to 4.5. The pH was adjusted with H_2SO_4 or NaOH. This operation was conducted four more times. The free copper in solution was followed by copper selective electrode (CSE) and the concentration was corrected considering the volume increase due to H_2SO_4 or NaOH addition. All of the experiments were conducted in triplicate under identical conditions.

2.4 Copper recovery by electrodeposition

The electrodeposition of copper was operated in a beaker with a glassy carbon electrode of 0.3 cm diameter (homemade) as working electrode, platinum grid (homemade) as counter electrode, and a mercurous sulfate reference electrode (Radiometer REF621). The reduction potential of copper was estimated at -0.75 V by cyclic voltammetry in the following conditions: Na_2SO_4 0.1 mol L^{-1} at pH = 2.

A 100 mL solution of PCEAC 0.5 g L^{-1} was prepared with copper 0.005 mol L^{-1} in Na_2SO_4 0.1 mol L^{-1} at pH = 5. The precipitate was then collected after centrifugation (3 000 rpm 10 minutes), and introduced in 50 mL Na_2SO_4 0.1 mol L^{-1} at pH = 2 for copper desorption. The potential was fixed at -0.8 V and the electrodeposition was followed until the total deposition of copper.

2.5 Analytical method

Free copper in the solutions was followed on a PHM250 ion analyzer equipped with a CSE (Radiometer-ISE25Cu) and a mercurous sulfate reference electrode (Radiometer REF621). The characteristics of the electrochemical method were previously published [15]. The pH was also recorded using a PHM250 ion analyzer equipped with a glass electrode (Radiometer pHG301) and the same mercurous sulfate reference electrode.

3 RESULTS AND DISCUSSION

3.1 Copper adsorption onto PCEAC

The mechanisms of copper uptake by PCEAC at pH 3.5, 4.5 and 5.5, were explored by analyzing the results of the adsorption isotherms (the experimental and predicted isotherms are presented in Fig. 3).

The amounts of copper adsorbed at equilibrium (Q_e) were low at pH 3.5. Thus, it was difficult to consider this pH condition to determine the best model to describe the complexation of copper. With AICc difference ($\Delta AICc$) between the models less than 14, it does not provide any evidence favoring one model to another [19]. As shown in Table 3, $\Delta AICc$ of the Freundlich Dubinin-Radushkevich, Temkin or Toth models and the Langmuir model were greater than 14 (for pH = 4.5 and pH = 5.5), providing strong evidence favoring the Langmuir model as the best to describe the interaction between copper and PCEAC. Considering the Sips, Redlich-Perterson and Langmuir model, $\Delta AICc$ do not provide any evidence favoring one model to another ($\Delta AICc < 11$). This is probably due to the fact that the Sips and the Redlich-Perterson models are hybrid models featuring both Langmuir and Freundlich isotherms. As seen from Table 4 the values of β_s (or β_r) are close to 1 suggesting that the Sips and Redlich-Perterson models are reduced to Langmuir [20]. This explained the very low $\Delta AICc$ between these three models and finally the Langmuir isotherm appeared as the best to describe the adsorption of copper onto PCEAC. The best fit to the Langmuir model translates the predominantly homogeneous distribution of the chelating groups on the polymer chains because the Langmuir equation assumes that the adsorbent surface is energetically homogeneous.

The maximum adsorption capacity (Q_m) was substantially increased (from 51.3 to 226 mg g^{-1}) as the pH increased (from 3.5 to 5.5) and appeared linearly correlated to this parameter ($R^2 = 0.9804$). By comparing our results to the maximum adsorption capacities of various natural and synthetic materials recently studied for copper recovery from waste or wastewater [15], PCEAC clearly appears as a promising agent for these applications.

3.2 PCEAC selectivity to copper

The influence of nickel (Ni(II)), cobalt (Co(II)), manganese, zinc, calcium (Ca(II)) and magnesium (Mg(II)) on copper adsorption was investigated by electrochemical measurements (Fig. 2). Copper solutions at 5.10^{-4} mol L^{-1} ($-215.6 < E_{Cu} < -216.3$ mV) were prepared in 0.1 mol L^{-1} Na_2SO_4 at pH = 5 with several different concentrations of metallic ions. Under these conditions, regardless of the metal and the ratio (R) used, the potential of the electrode remained unchanged (with values between -215.6 and -218.6 mV). The results are presented in Fig. 4 for Co(II), Ni(II), Ca(II), Mg(II).

The potential was kept constant (ranging from -235.2 to -239.1 mV) with the addition of PCEAC (0.5 g L^{-1}) to the same solutions, suggesting that Co(II), Ni(II) or others were not competing for copper adsorption. The selectivity of PCEAC toward copper was confirmed for $R = 50$ with cobalt by UV-visible analyses (Cf. Fig. 2). The spectra of PCEAC/Cu and PCEAC/Cu/Co were equivalent regarding the wavelength absorption maximum and the absorbance. In addition to these results, no desorption of copper occurred in favor of nickel, manganese, zinc, calcium, magnesium ($0 < R < 10$) or cobalt complexation ($0 < R < 50$). This observation agreed with previous results about the selective complexation of copper by other polycarboxylates [15].

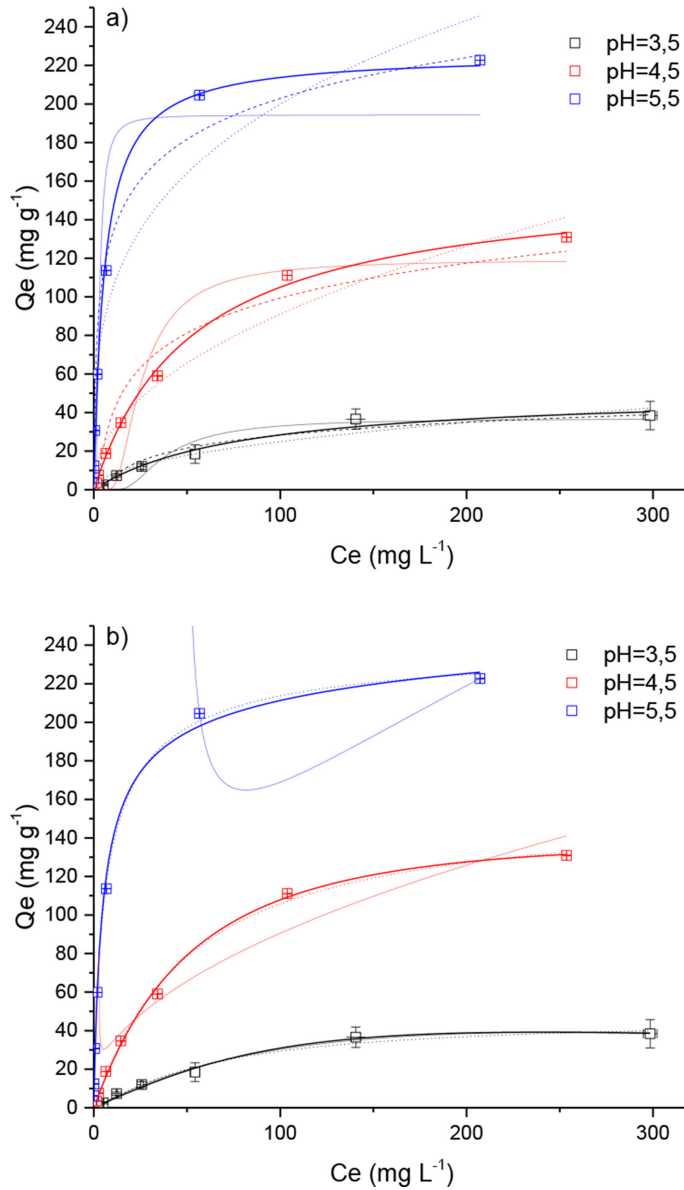


Figure 3: Adsorption isotherms of copper onto PCEAC at various pH values. Experimental data fitted to a) the Langmuir model (dark solid line), the Freundlich model (dot line), the Temkin model (dashed line) and the Dubinin-Raduskevich model (light solid line); b) the Redlich-Peterson model (dark solid line), the Sips model (dot line) and the Toth model (light solid line).

Table 3: Determination of the best fitting model by comparing $\Delta AICc$.

pH	3.5	4.5	5.5
Best model	Langmuir	Langmuir	Sips
Langmuir	0.0	0.0	6.1
Freundlich	7.1	18.8	22.8
DR	10.2	24.3	26.1
Temkin	5.3	20.3	15.9
Sips	9.2	6.6	0.0
Toth	4.6	26.3	41.7
Redlich-Peterson	4.8	4.3	9.9

Table 4: Isotherm model parameters for Cu(II) adsorption on PCEAC at different pH values (Langmuir, Sips and Redlich-Peterson models).

Models	Parameters	pH		
		3.5	4.5	5.5
Langmuir	Qm	51.3±5.0	161±5	226±7
	K_L	0.012±0.003	0.019±0.002	0.18±0.02
Sips	Ks	0.34±0.37	2.65±0.78	51.0±3.0
	β_s	1.19±0.32	1.04±0.10	0.78±0.04
	as	0.007±0.007	0.017±0.004	0.21±0.01
Redlich-Peterson	Kr	0.44±0.06	2.63±0.26	50.9±9.5
	ar	0.0003±0.0005	0.008±0.005	0.31±0.11
	br	1.60±0.33	1.12±0.09	0.94±0.04

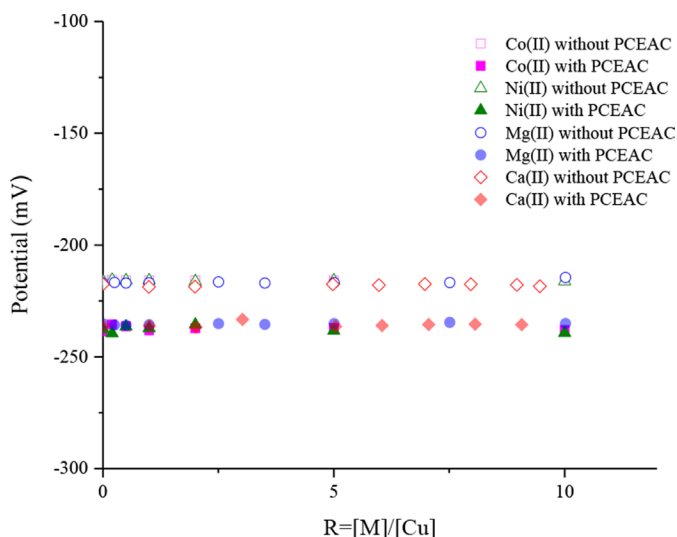


Figure 4: Selectivity of PCEAC toward Cu(II) ($5 \cdot 10^{-4} \text{ mol L}^{-1}$) in the presence of Co(II) or Ni(II) in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ at pH = 5 ($R = [\text{metallic ion}]/[\text{Cu(II)}]$).

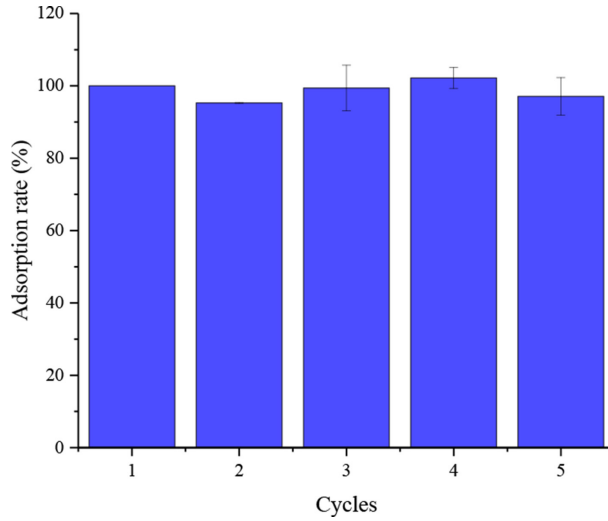


Figure 5: Copper adsorption efficiency over five cycles of sorption-desorption processes.

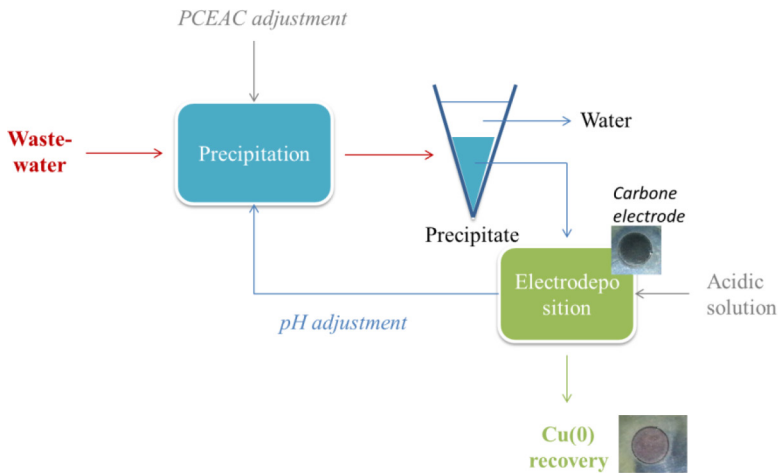


Figure 6: Two steps full process design for copper recovery using a water-soluble polycarbobetaine.

3.3 PCEAC reusability

The reusability of PCEAC was explored by pH adjustment at 2 and 4.5, respectively, for desorption and adsorption. Figure 5 confirms that the efficiency of copper adsorption was maintained over five cycles of PCEAC reuse ($99 \pm 3\%$) as previously reported for other polycarbobetaines [15].

3.4 Full laboratory scale process for copper recovery

The recovery of copper was engaged on PCEAC/Cu precipitate after its dissolution in acidic media (pH = 2). Electrodeposition was operated at -0.8 V on a glassy carbon electrode, and the entire recovery of copper was achieved (see pictures on Fig. 6). From these results, a two steps full laboratory scale process was designed and tested (Fig. 6).

4 CONCLUSION

A full process for copper recovery using a polycarbobetaine as precipitating agent was designed at laboratory for copper recovery from synthetic wastewaters. Two process units were tested: precipitation for selective copper recovery: electrodeposition in acidic media for copper recovery and polycarbobetaine regeneration. Further work will be undertaken to test the overall process with recirculation and polycarbobetaines reuse.

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