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Version of Record: https://www.sciencedirect.com/science/article/pii/S2352492819303885
Manuscript_c82a319f2e84dfa0333950fef86f018e

Performances and behavior of a water-soluble and pH-sensitive polycarboxybetaine used for metal ion recovery

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Zwiterionic functional groups give polycarboxybetaines a great ability to chelate copper and their use for metal ions recovery was suggested in previous studies. The use of a water-soluble and pH-sensitive polymer (polycarboxy-ethyl-3-aminocrotonate - PCEAC) was investigated for the removal of copper from aqueous solution. The equilibrium adsorption level was determined as a function of temperature, pH and initial adsorbate concentration. The good fit to the Langmuir model offered various information about copper uptake mechanisms. The maximal adsorption capacities were found to reach 253±11 mg of copper per g of PCEAC at pH=6. The thermodynamic parameters such as free energy, enthalpy and entropy changes for the adsorption of copper were computed to predict the nature of adsorption process. The removal of copper was varying from 2% to 97% depending on pH and initial copper concentration. A particular behavior of PCEAC at pH=4 is discussed and explained by viscosity measurements as a particular conformation of the polymer. The effect of cadmium on copper adsorption was also tested. Some co-adsorption phenomena were observed at low cadmium concentrations ([Cd]/[Cu]≤1), while copper desorption in favor of cadmium adsorption were quantified at higher cadmium concentrations ([Cd]/[Cu]>1).

Keywords: Polycarbobetaine, Adsorption, Physico-chemical behavior, pH-sensitive

1. Introduction

Even if heavy metals are natural constituents of earths' crust, their geochemical cycles have been radically modified by human activities [1]. It is known that a long exposure to heavy metals such as copper for example can cause adverse effects in humans health [2]. Because they are recalcitrant and persistent in the environment, their treatment is considered of major importance. Various technologies exist for metal ion recovery from wastewater and some are known as the current appropriate methods such as chemical precipitation, ion exchange, adsorption, membrane filtration, flocculation/coagulation, flotation and electrochemical treatment [3].

Water-soluble polymers are often considered for the recovery of metal ions and act as precipitating agents, sorbents, flocculating agents, floating agents. Polymer-assisted ultrafiltration has also tested some water-soluble polymers such as polyethylenimine, polyacrylic acid and poly(dimethylamine-co-epichlorohydrin-co-ethylenediamme) for example in the case of copper removal from wastewaters [4]. Some examples of polymers tested for metal ions recovery are given for various processes in Table 1.

In precipitation processes, water-soluble polymers react with metal ions to form insoluble precipitates separated from water by filtration or decantation processes. This is the most widely used process in industry because it is relatively simple to operate and because of its economical operation [12]. However, one disadvantage remains in the case of wastewater containing many metals because all metals are precipitated together in sludge annihilating the ability to recycle them. Some selective precipitating agents have been tested, but their high costs restrain their use for industrial and/or commercial applications [13]. Dithiocarbamate and their ramifications, 2,4,6-trimercapto-1,3,5-triazine, or dipropyl dithiophosphate are some of them. Recently the use of water-soluble polycarbobetaines for selective precipitation of copper has been demonstrated [14, 15]. As previously explained, interactions between charged mocromolecules such as water-soluble polycarbetaines and metal ions can be considered as adsorption phenomenon [16] but as far as complexed polycarbobetaines form a solid precipitate the distinction between adsorption and precipitation is not easy. Because of the non-systematic precipitation of complexed polycarbobetaines depending on the amount of polymer and metal ions in solution, adsorption phenomenon will be considered. The main point considering such materials for metal ions recovery remains its ability to regenerated after complexation under acidic conditions for further uses as previously demonstrated [14, 15]. Using water-soluble materials for metal ions recovery (leading to precipitation treatment

processes) are preferred to insoluble materials (leading to adsorption treatment processes) because of operating ease and cost. Most of time water-soluble polymers are used to enhance metal ions removal by ultrafiltration [4, 11, 17, 18]. A recent review describes the different uses differentiating water-soluble and insoluble polymers to remove inorganic pollutants from water [19].

This research aims to study the adsorption (precipitation) of copper onto a water-soluble pH-sensitive polycarbobetaine and proposes to test its performance and behavior at various pH and also in presence of cadmium. A special focus on physicochemical mechanisms is discussed.

2. Materials and methods

2.1. Synthesis

The monomer was obtained by dropwise addition of 10 mL ammoniac (NH_4,OH 30% aqueous solution obtained from Carlo-Erba) to 10 mL of acetoacetic ester (AAE ≥99% purchased from Aldrich) under magnetic stirring for 3 hours. The solution was then left overnight for decantation, and the organic phase containing the key product ethyl-3-aminocrotonate (EAC) was collected after 12 hours. The linear water-soluble polycarbobetaine named polycarboxyethyl-3-aminocrotonate (PCEAC) was obtained by radical polymerization, as previously reported [15, 20, 21], by mixing during 5 minutes 1.9 mL of EAC, 1.1 mL of acrylic acid (AA 99.5% obtained from Aldrich) and 3 mg of the initiator 2,2'azobisisobutyronitrile (AIBN obtained from Aldrich). The synthesis is presented in Figure 1. The polymer was then washed with acetone and oven-dried at 70°C (approximately 50% yield).

2.2. Characterization

The characterization of PCEAC and PCEAC/Cu complex was operated by FTIR, ^{1}H-NMR and Uv-Visible spectra as previously reported [15], using respectively a Perkin–Elmer Spectrum 100 FTIR spectrometer using the attenuated-total-reflectance (ATR) method, a Bruker spectrometer (AMX300) operating at 300 MHz, and a Hitachi U4001 spectrophotometer with a scan range of 220–900 nm. PCEAC (0.1 g) was dissolved in 50 mL of hydrochloric acid (HCl) 0.01 M and was titrated by sodium hydroxide (NaOH) 0.05 M. NAOH pellets and HCl 37% aqueous solution were obtained from VWR.

As mentioned in the introduction depending on the amount of water-soluble polymer and metal ion in the solution, some precipitation occurs leading to the production of a PCEAC/Cu precipitate. Copper complexation neutralizes PCEAC charges in solution and may affect

PCEAC behavior in solution. pH changes of water-soluble zwitterrionic polymer solutions may also impact solution properties, that's why PCEAC behavior in solution with and without copper was tested by viscosity and density measurements at 25°C respectively with Lovis 2000 M Viscosimeter and DMA 5000 (Anton Paar). PCEAC solutions at 0.5 g L^{-1} and their mixtures with copper at 63.54 mg L^{-1} were studied at different pH (from 3 to 6) in order to better understand its behavior in solution with copper ions (Cu(II)).

2.3. Copper adsorption equilibrium

The sorption experiments were performed in a thermostated glass cell (Metrohm) with constant stirring, using PCEAC 0.5 g L^{-1} at various pH (3, 3.5, 4, 4.5, 5, 5.5, 6) and temperature (25°C, 35°C, 45°C). The temperature was monitored using a Fisherbrand™ Polystat™ Heating Circulator (±0.03°C). All of the experiments were conducted in triplicate under identical conditions. The instantaneous adsorption (complexation) of Cu(II) onto PCEAC was assayed over a range from 5.10^{-5} to $5\ 10^{-3}$ mol L^{-1}. $CuSO_4{\cdot}5H_2O$ (Obtained from VWR) was used for the preparation of calibration standards and isotherm solutions. The ionic strength (I) was maintained constant at 0.3 mol L^{-1} with Na_2SO_4 (purchased from VWR) and pH was adjusted with H_2SO_4 (diluted 96% aqueous solution obtained from VWR) or NaOH. Adsorption isotherms were determined by monitoring free copper decay in the solution by electrochemical measurements as previously reported [14] and were fitted to the Langmuir model (Eq. 1) already shown as the best to describe such systems [14, 15].

$$Qe = \frac{Q_m * K_L * C_e}{1 + K_L * C_e} \qquad (1)$$

where Qm is the maximum adsorption capacity (mg g^{-1}); K_L is the Langmuir isotherm constant (L mg^{-1}); Ce is the concentration of copper at the equilibrium (mg L^{-1}); Qe is the amount of copper adsorbed at the equilibrium per gram of PCEAC (mg g^{-1}).

Non-linear regression analysis operated with Origin Pro 2015 was used to model the fitting to the Langmuir model already suggested as the best to describe such adsorption phenomena [15, 22]. Orthogonal distance regression was used as iteration algorithm for the nonlinear regression approach and weighted fitting based on experimental errors was applied.

Adsorption free energy ($\Delta G°_{Ads}$) was determined from the equilibrium constant (K_L) by the following equation [23]:

$$K_L = e^{\frac{-\Delta G^0_{Ads}}{R \times T}} \qquad (2)$$

where K_L= Langmuir isotherm constant (L mol^{-1}); T = Temperature (K); R = Gas constant (8.314 J K^{-1} mol^{-1}).

Enthalpy (ΔH^0) and entropy (ΔS^0) changes were estimated using the following equation [24]:

$$Ln\ K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (3)$$

Thus $\Delta H°_{Ads}$ and $\Delta S°_{Ads}$ were obtained by plotting of Ln K_L versus 1/T.

2.4. Effect of cadmium

The selectivity of PCEAC toward copper was tested in presence of cadmium (Cd(II)) $Cd_3(SO_4)_3,8H_2O$ was purchased from Aldrich. Various solutions of copper at 5.10^{-3} mol L^{-1} were prepared in Na_2SO_4 0.1 mol L^{-1} at pH = 5 and T = 25°C with different concentrations of Cd(II). A ratio (R = [Cd] /[Cu]) ranging from 0 to 20 was used. The solutions were filtered at 0.45 µm and the supernatants were analyzed for Cu(II) and Cd(II) by ICP-AES while the precipitate was dried at 105°C for 24h and dry mass determined. The dry precipitate was mineralized by acid digestion according to the Danish Standards DS 259 [25]: the dry filter and 20.0 ml (1:1) HNO_3 were heated at 200 kPa (120°C) for 30 minutes. The liquid was separated from the solid particles by vacuum through a 0.45 µm nucleopore filter and diluted to 100 ml. Cu(II) and Cd(II) were thereafter measured by ICP-AES.

A separation factor ($S_{Cd/Cu}$) for Cd(II) over Cu(II) was calculated from the adsorption data using the equation below [24]:

$$S_{Cd/Cu} = \frac{Cd_{Ads} \times Cu_{eq}}{Cu_{Ads} \times Cd_{eq}} \quad (4)$$

where Cu_{Ads} is the amount of copper adsorbed onto PCEAC at the equilibrium (mg L^{-1}) ; Cd_{eq} is the concentration of Cd(II) in the solution at the equilibrium (mg L^{-1}) ; Cd_{Ads} is the amount of Cd(II) adsorbed onto PCEAC at the equilibrium (mg L^{-1}) ; Cu_{eq} is the concentration of copper in the solution at the equilibrium (mg L^{-1}).

2.5. Metal ions and pH measurements

For copper adsorption equilibrium, copper was measured by electrochemical measurements using a PHM250 ion analyzer equipped with a copper selective electrode (CSE) (Radiometer-ISE25Cu) and a sulfate reference electrode (Radiometer REF621) to follow free copper in the solutions. Table 2 presents the characteristics of the electrochemical method. The pH was also recorded using a PHM250 ion analyzer equipped with a glass electrode (Radiometer pHG301) and the same sulfate reference electrode.

For the adsorption of copper in the presence of cadmium, Cu(II) and Cd(II) were analyzed by ICP-AES [26].

3. Results and discussion

3.1. Characterization of PCEAC and PCEAC/Cu complex

The yield of the monomer was 98%, and its purity was tested by FTIR. The characteristic bands of synthetized EAC are presented in Table 3 and compared to those of commercial EAC [27]**.** All characteristic theoretical bands are recovered.

CH_2 and CH_3 groups of the ethyl function were clearly identified in ^1H NMR spectra of pure PCEAC (results not shown) by the presence of a quadruplet at 4.00 ppm and a triplet at 1.06 ppm respectively. The other hydrogen atoms were observed over the expected range (from 1.43 to 2.95 ppm) in good agreement with previous H-NMR characterization of PCEAC [28]. Because of PCEAC/Cu complexes insolubility the comparison could not be performed with the ^1H NMR spectra.

By comparing EAC and PCEAC IR spectra, the disappearance of symmetric and asymmetric stretching vibrations ($\upsilon_{N\text{-}H}$ respectively at 3 342 cm^{-1} and 3 446 cm^{-1}) let suppose that the amine group is involved into hydrogen bond (Cf. Figure 1). The same observation is made for PCEAC/Cu complex suggesting that the amine group interacts by a dative bond with copper. The complexation of copper by PCEAC was established by the appearance of a medium asymmetric stretching vibration at 1 608 cm^{-1} (Figure 2) characteristic of copper carboxylates [29] and the disappearance of intensive band of carboxylate ions at 1 557 cm^{-1}. This result was checked by Uv-Visible spectroscopy (Figure 3) with a band at 702 nm specific of square pyramidal copper complexes [29]. The 201 cm^{-1} difference measured by FTIR between the asymmetric and the symmetric stretching vibration 1 407 cm^{-1} (observed for both PCEAC and PCEAC/Cu complex) suggested that the coordination of carboxylate groups to copper ions took place in a bridge form [15, 30].

pKa values for the same groups are 5.60 and 9.33 (Figure 4) what is in good agreement with previous results [31]. The rate of amine and carboxylic groups were respectively 53±3% and 47±3% what suggests the equimolar ratio between acidic and basic groups and confirms the chemical structure of PCEAC presented in Figure 1.

3.2. Adsorption isotherms

The experimental and predicted adsorption isotherms of Cu(II) from aqueous solutions onto PCEAC are presented in Figure 5 and values of the Langmuir constants are presented in Table

4. The values of determination coefficient (R^2) presented in Table 4 indicate that there is a strong positive evidence that the adsorption of Cu(II) onto PCEAC follows the Langmuir isotherm.

The favorable nature of adsorption can be expressed in terms of dimensionless equilibrium parameter R_L (equation 6) [32]:

$$R_L = \frac{1}{1 + K_L C_0} \quad (5)$$

where C_0 is the highest initial concentration of adsorbate in solution (mg L^{-1}).

The RL values presented in Table 4 confirm the favorable asdorption equilibrium as far as we know that a favorable equilibrium is demonstrated by R_L comprised between 0 and 1 [22].

We also observed that the values of Langmuir parameters increase (Qm increases from 20.9 to 253 mg g^{-1}) with pH increase (from 3 to 6). But no linear correlation appears what differs from previous results obtained for another PCBet [33]. A very high Qm is observed at pH = 4 (250 mg g^{-1}). This result indicated that the pH of solutions is an important parameter controlling Cu(II) sorption on PCEAC. The particular behavior at pH = 4 is discussed below in §3.3.

The maximal adsorption capacities observed in Table 4 confirmed an interesting effectiveness for copper removal from water compared to other materials of interest (208 mg g^{-1} for chitosan for example) [34]. A comparison of adsorption capacities of copper onto PCBets, natural and synthetic materials was previously presented and our results are in good agreement [14].

Adsorption isotherms were built for pH = 5 at 25°C, 35°C and 45°C and the adsorption free energy were calculated from isotherm constants at each temperature as described in Eq 2. The results obtained for $\Delta G°_{Ads}$ are presented in Table 4. Negative values of $\Delta G°_{Ads}$ indicate the feasibility of the process and spontaneous nature of the copper adsorption. The observed increase in negative values of $\Delta G°_{Ads}$ with increasing pH confirms that the adsorption become more favorable at higher pH value. This is due to larger amounts of COO^- groups in the polymer chains available to complex copper. Here again a lower $\Delta G°_{Ads}$ is observed at pH = 4 suggesting a less favorable adsorption of Cu(II) at the pH.

The values of thermodynamic parameters (ΔH^0_{Ads} and ΔS^0_{Ads}) were obtained from Eq. 3 and are presented in Table 5. Positive value of ΔH^0_{Ads} points out the endothermic nature of the process, while positive value of ΔS^0_{Ads} reveals the affinity of PCEAC for copper adsorption and suggests some structural changes in adsorbate and adsorbent [32].

3.3. PCEAC behavior in solution

The presence of both acid and basic groups among the polymer chain offers specific properties to PCEAC. Depending on pH, the macromolecules change from cationic specie (C-PCEAC) at low pH to anionic macromolecules (A-PCEAC) at high pH (Figure 6). Zwiterionic specie (Z-PCEAC) exists in a pH range from 3.5 to 11.5 in equilibrium with a neutral specie.

As previously reported for other PCBets, the reduced viscosity of PCEAC is a function of pH [33]. Figure 7 shows that it increases with pH and confirms the tendency already observed for such material [28]. This change in viscosity with pH in the specific range tested (from 3 to 6) is linked to the ability pf PCEAC to exist in cationic, zwiterionic species. If repulsive electrostatic forces take place between cationic species and can explain the very low reduced viscosity at low pH, many kind of electrostatic interactions can take place between zwiterionic species (or between cationic and zwiterionic species) : intragroup, intrachain, interchain [35] (Figure 8).

The same explanation can also describe the evolution of maximal adsorption capacity (Qm) with pH increase. As observed from Table 4, a particular high Qm was recorded at pH = 4. Viscosity measurements reveal that this particular behavior is correlated to the particular conformation of PCEAC at pH = 4 (Figure 9). A model of PCEACs' conformations in copper solutions is proposed in Figure 8.

Thus, it is suggested that in the pH range 3 to 6: 1) At low pH < 4, PCEAC is mainly present in its cationic form and interactions with copper are few resulting from equation 6 leading to intergroup interactions (Figure 8b); at higher pH, PCEAC appears in its zwitterionic form and interactions with copper are numerous and can result from equation (6, 7, 8). Various conformations can take place in this last case (Figure 8a, c, d and d'). As previously said, the very high Qm and viscosity observed at pH = 4 is due to a particular conformation that could be explained by Figure 9d' where interchains interactions take place with copper.

$$AH_2 + Cu^{2+} = CuAH + H^+ \quad (6)$$

$$AH + Cu^{2+} = CuAH \quad (7)$$

$$AH + Cu^{2+} = CuA + H^+ \quad (8)$$

3.4. Copper removal

The removal of Cu was very few at pH=3 and increases with pH increase. This observation is in good agreement with results obtained from adsorption isotherms. As far as the maximal adsorption capacity (Qm) increases with pH increase, the amount of copper removed from solution also increases. As shown in Figure 10, for most of the tested pH, copper removal

decreases with the increase of copper concentration. This confirms the finite number of identical sites inherent to the Langmuir adsorption mode [36]. The removal of copper remains in between 88% and 97% at pH = 6 confirming that higher pH ensures better PCBets' performances for copper removal, due to larger amounts of COO^- groups available to complex copper by dative bonds.

3.5. PCEAC and Cu(II) interactions in presence of Cd(II)

The results show that depending on the amount of cadmium added to copper and PCBets' solutions, some copper desorption favoring cadmium adsorption occurs (Figure 11). The initial concentration of copper was fixed at 318 mg L^{-1} and varying concentrations of cadmium were added (ranging from 28 mg L^{-1} to 11 g L^{-1}). In previous study no desorption of copper in favor of nickel, manganese, zinc, calcium, magnesium ($0 < R < 10$) or cobalt complexation ($0 < R < 50$) was observed [15], what suggested a strong selectivity of PCEAC. In this study, results differ in presence of Cd(II). Without Cd, the removal percentage of copper by PCEAC was around 35 ± 2% while it decreases to 11% ± 6% with the biggest amount of Cd (R=20). It is suggested that at low cadmium concentration (R<1), it adsorbs to copper/PCEAC complexes while at high concentration (R>1) copper desorption occurs favoring cadmium adsorption. This observation is confirmed by the separation factors presented in Table 5. For high concentrations of cadmium, the separation factor indicates selectivity to cadmium rather than copper (about 2 times more selective to cadmium than copper).

These results question previous results concerning PCEAC high selectivity toward copper in presence of nickel, manganese, zinc, calcium, magnesium or cobalt [15]. In this previous study the selectivity was assess using copper desorption measurements by electrochemical methods (copper selective electrodes). No analysis of nickel, manganese, zinc, calcium, magnesium or cobalt were directly performed on liquid samples. The calculation of metal ions adsorbed onto PCEAC was operated using copper desorption measurements. This methodology seems inappropriate since it cannot consider co-adsorption phenomena. In the present study both copper and cadmium were analyzed in the liquid samples by ICP-AES and both phenomena (adsorption/desorption and co-adsorption) could be identified. Thus, it is suggested to adopt this last methodology to further examine PCEAC selectivity toward copper and to reconsider previous results.

4. Conclusion

The adsorption of copper onto PCEAC was tested at various pH and fitted to the Langmuir model. The maximal adsorption capacities were shown to be linked to the pH and different conformations of the polymer were suggested to explain our results. Depending on pH and copper concentration many interactions can occur (intragroup, intrachain, interchain) and this consideration helps to understand copper adsorption capacities. Copper removal was ranging from 2% to 97% depending on pH and/or initial copper concentration. The effect of cadmium on copper adsorption was tested and showed that at low cadmium concentration (R<1), it adsorbs to copper/PCEAC complexes while at high concentration (R>1) copper desorption occurs favoring cadmium adsorption. A deeper study of cadmium adsorption onto PCEAC is recommended and could bring answers for its treatment and recovery. The recovery of PCEAC after copper and/or cadmium adsorption for further uses should also be studied to confirm this property already demonstrated around single copper adsorption.

ACKNOWLEDGMENTS

The authors would like to thank the IFD Program Sciences for the financial support that permitted the collaboration between Technical University of Denmark, EPF Graduate school of engineering and the university Pierre and Marie Curie. EPF is also thanked for the support of a MSc student on this work.

DATA AVAILABILITY

The raw/processed data required to reproduce these findings cannot be shared at this time due to legal or ethical reasons.

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FIGURE CAPTIONS

Figure 1. Monomer and polymer syntheses

Figure 2. IR spectra of PCEAC and PCEAC/Cu complexes

Figure 3. UV-Visible spectra of PCEAC, Cu and PCEAC/Cu complex

Figure 4. Titration of PCEAC 2 g L^{-1} in HCl 0.01 mol L^{-1} by NaOH 0.05 mol L^{-1}.

Figure 5. Experimental data of adsorption isotherms of copper onto PCEAC fitted to the Langmuir model for various pH at 25°C.

Figure 6. Distribution of PCEAC species among pH at 25°C according to acido-basic equilibrium

Figure 7. Effect of pH on the reduced viscosity of PCEAC at 0.5 g L^{-1} at 25°C

Figure 8. Type of interactions between copper and zwiterionic PCBets

Figure 9. Effect of pH on the reduced viscosity (black circles) and maximal adsorption capacity (red squares) of PCEAC solutions at 0.5 g L^{-1} at 25°C with Cu(II) 0.001 mol L^{-1}

Figure 10. Copper removal from aqueous solution by PCEAC 0.5 g L^{-1} at 25°C for various pH

Figure 11. Copper and/or cadmium removal from aqueous solution by PCEAC 0.5 g L^{-1} at 25°C for pH=5

FIGURES

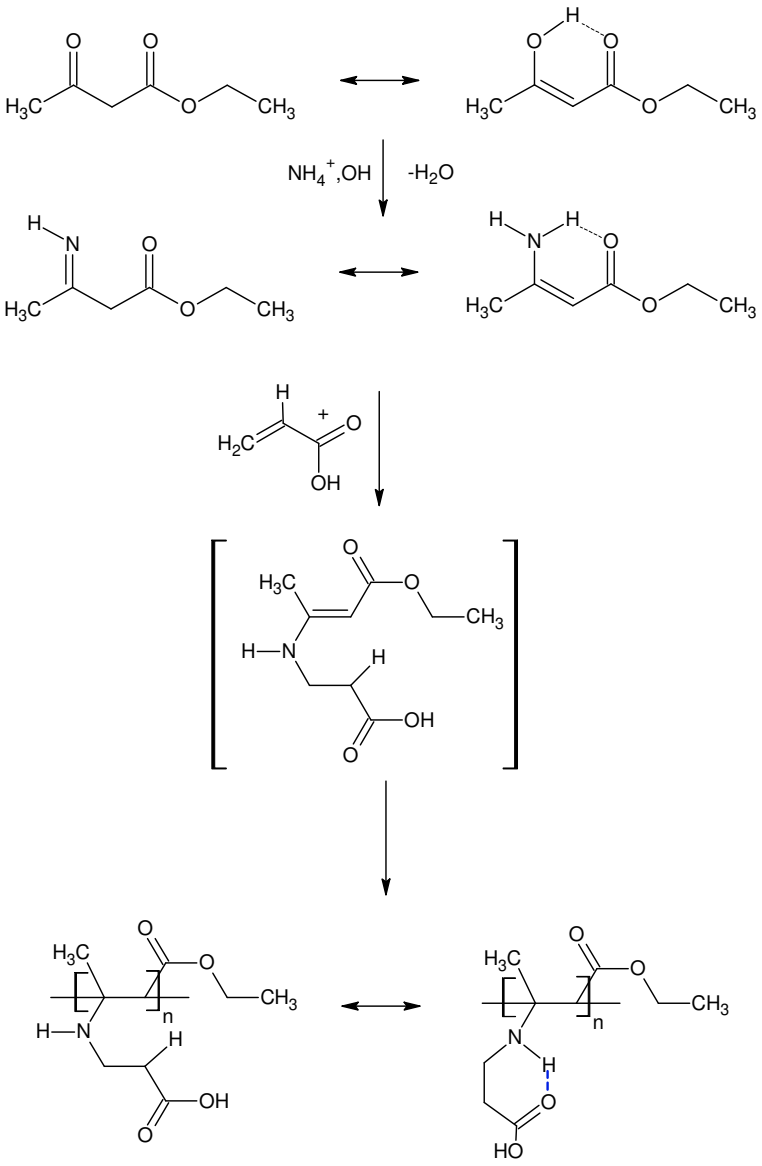
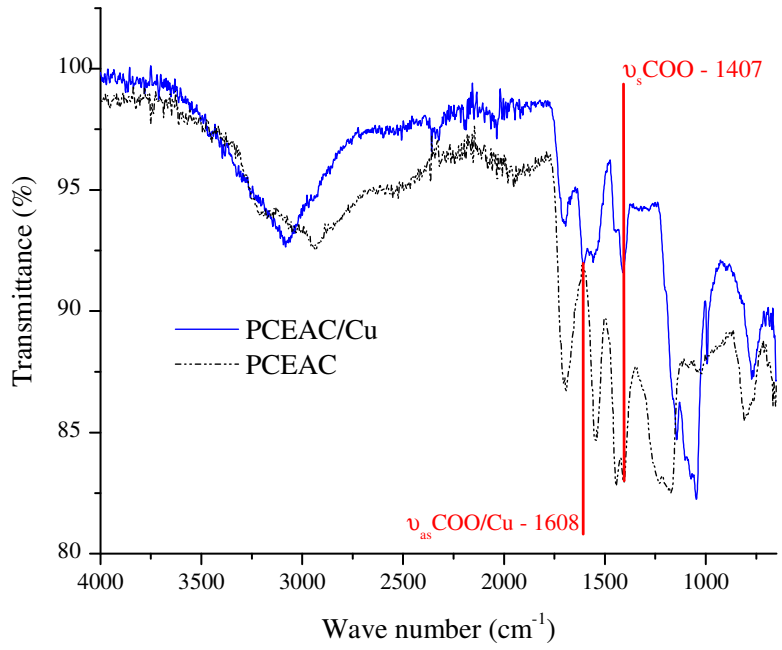


Figure 1.



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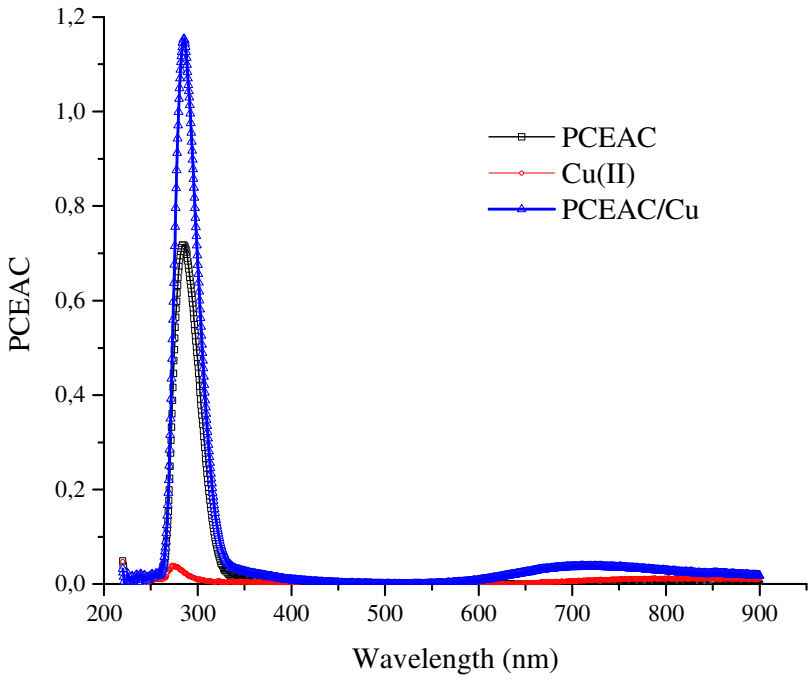

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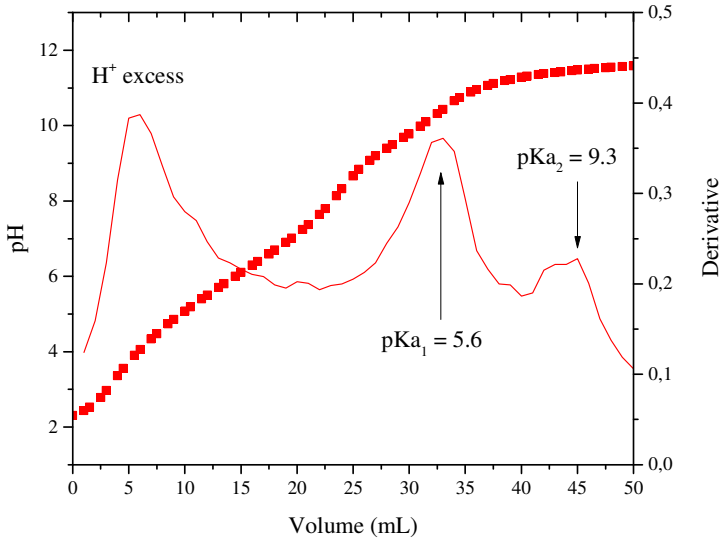

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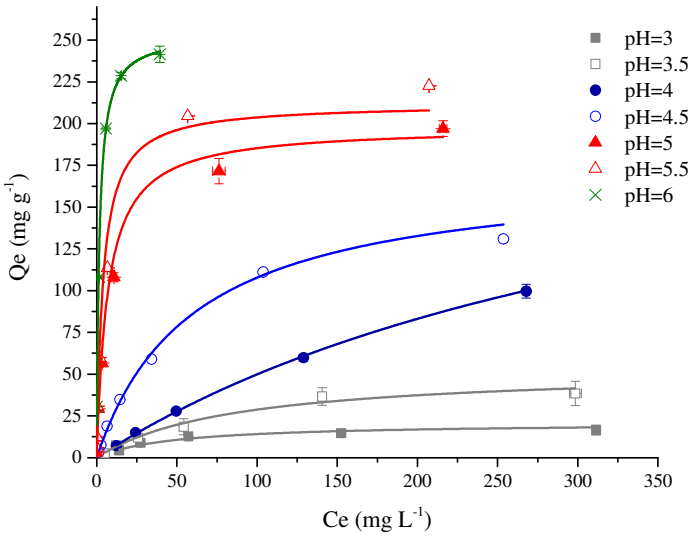

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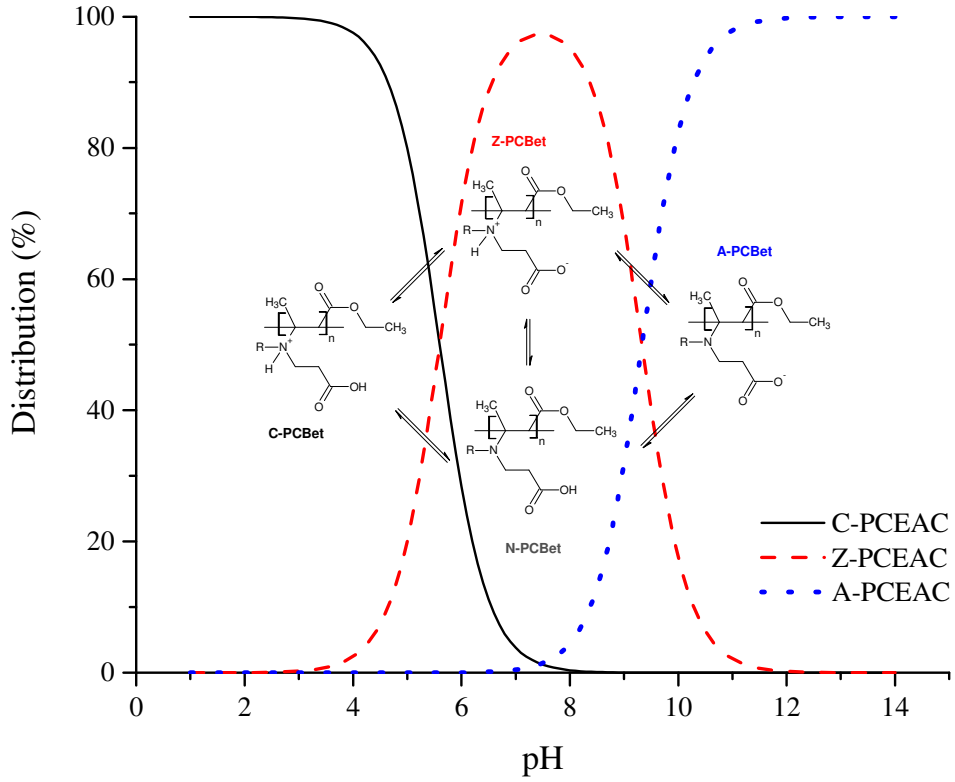

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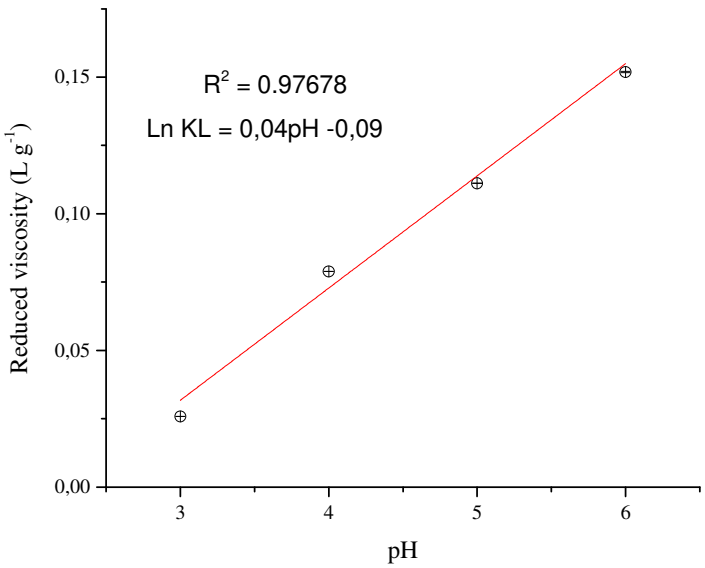

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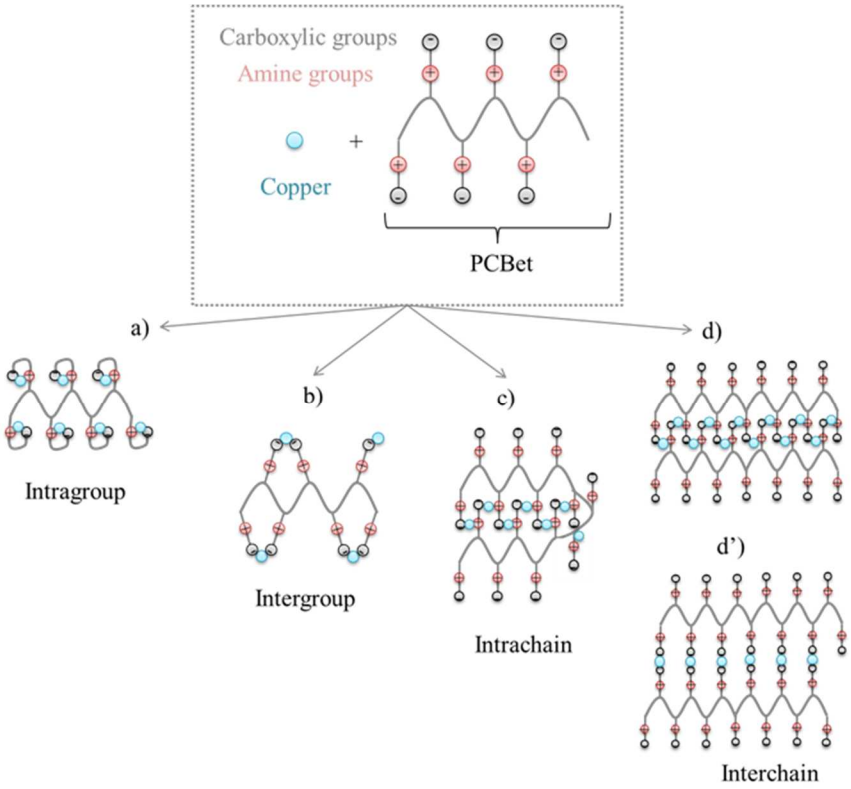

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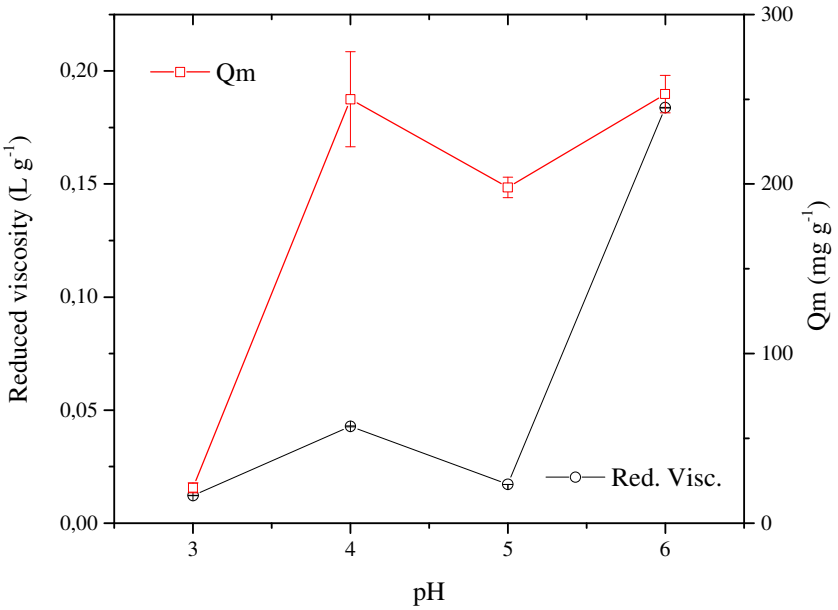

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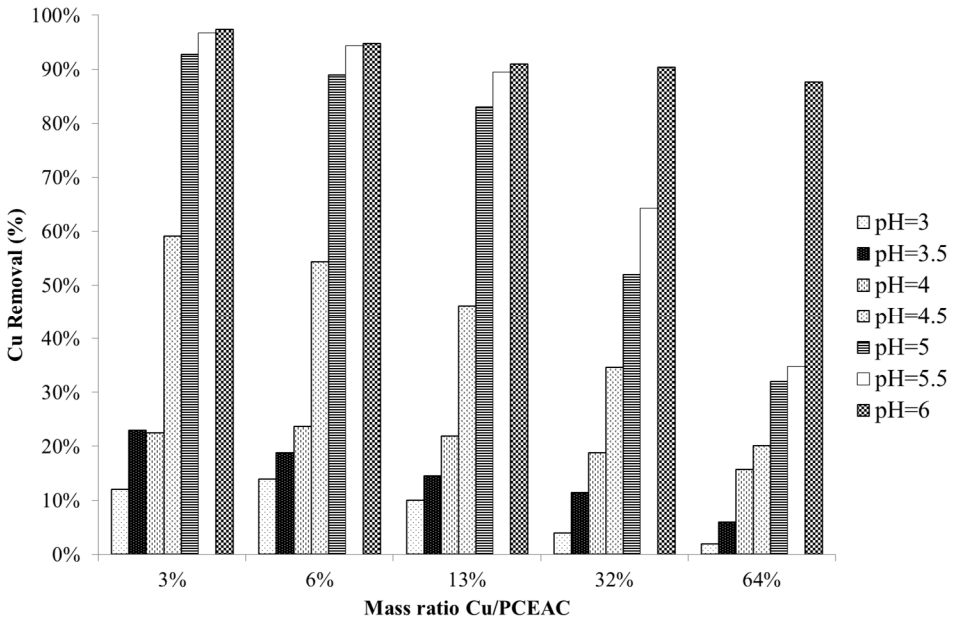

Figure 10.

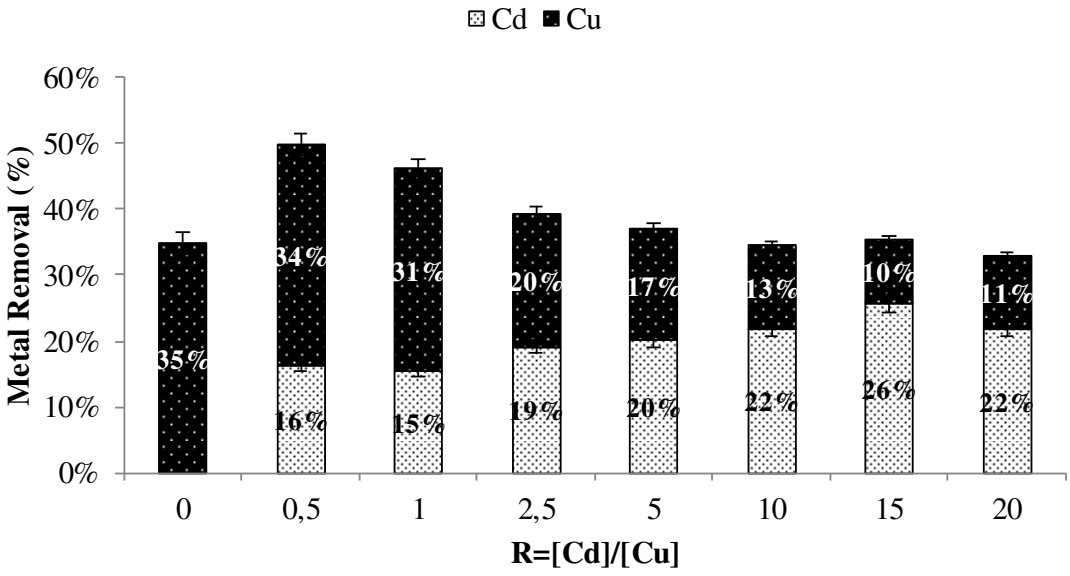

Figure 11.

TABLES

Table 1. Example of water-soluble polymers used for metal ion recovery in typical wastewater treatment processes

Applications	Polymers names	Metal ion	References
Adsorption	Poly(EDGE-MAA-2MI)	Cadmium, Lead	[5]
	HDI-IC-DETA, HDI-IC-PEHA	Cadmium, Cobalt, Chromium, Copper, Nickel	[6]
	Aminophosphine oxide polymer	Palladium	[8]
Flocculation	Mercaptoacetyl chitosan	Copper	[7]
Flotation	Polyvinyl alcohol, polyethylene glycol, chitosan	Cadmium, Lead, Zinc, Nickel, Manganese	[9]
	Butyl xanthate, Di-isobutyl dithiophosphinate, allyl propylthionocarbamate	Copper	[10]
Membranes	Polyethylenimine, polyacrylic acid, Poly(dimethylamine-co-epichlorohydrin-co-ethylenediamine)	Copper	[4, 11]

Table 2. Parameters of the electrochemical analytical method in Na_2SO_4 0.1 mol L^{-1} at various pH

Parameters	pH=3	pH=3.5	pH=4	pH=4.5	pH=5	pH=5.5	pH=6
Slope	27.6±0.3	28.6±0.2	30.1±0.4	29.0±0.3	29.3±0.1	30.1±0.1	30.3±0.2
Intercept	-124±1	-120±1	-118±1	-122±1	-120±1	-119±1	-117±1
R^2	0.9969	0.9992	0.9912	0.9976	0.9960	0.9997	0.9990
Number of points	33	20	60	24	126	24	27
Concentration range	$5x10^{-2}$	$1x10^{-2}$	$1x10^{-2}$	$1x10^{-2}$	$1x10^{-2}$	$1x10^{-2}$	$2x10^{-3}$
(mol L^{-1})	$5x10^{-5}$	$1x10^{-4}$	$5x10^{-5}$	$5x10^{-5}$	$5x10^{-6}$	$5x10^{-5}$	$5x10^{-5}$

Table 3. Characteristic bands (cm^{-1}) of functional groups for commercial and synthetized EAC

Type de vibration	Theorical frequency [27]	Measured frequency
vN-H (as)	3500	3446
vN-H (s)	3400	3342
$vCsp^2$-H	>3000	3235
$vCsp^3$-H (as)	2962	2982
$vCsp^3$-H (s)	2872	2928
vC=O	1715-1730	1692
vC=C	1650-1585	1639
dN-H	1580-1650	1567
$dCsp^3$-H (as)	1450	1448
$dCsp^3$-H (s)	1375	1379
vC-O	1000-1300	1166-1046
vC-N	1250-1340	1291

Table 4. Isotherms parameters of copper adsorption onto PCEAC

pH	Qm ($mg\ g^{-1}$)	K_L ($L\ mg^{-1}$)	$\Delta G°_{Ads}$ ($kJ\ mol^{-1}$)	R_L	R^2
3	20.9±2.9	0.021±0.005	-17,83±	0.130	1.0000
3.5	53.4±6.4	0.012±0.002	-16,38	0.208	0.9998
4	250±28	0.0025±0.0003	-12,55	0.557	0.9999
4.5	173±8	0.017±0.002	-17,26	0.156	0.9996
5	198±6	0.14±0.02	-22,60	0.022	0.9996
5.5	212±16	0.25±0.04	-22,59	0.012	0.9998
6	253±11	0.60±0.11	-26,15	0.005	0.9995

Table 5. Values of thermodynamic parameters of copper adsorption onto PCEAC

Parameters	Average	Standard deviation
Intercept	4.35	0.27
Slope	1355	82
R^2	0.9964	-
ΔH^0_{Ads} (J mol^{-1})	11264	680
ΔS^0_{Ads} (J mol^{-1})	36.2	2.2

Table 6. Values of separation factors ($S_{Cd/Cu}$) for Cd(II) over Cu(II)

R=[Cd]/[Cu]	$S_{Cd/Cu}$
20	2.2
15	2.4
10	1.9
5,0	1.2
2,5	0.9
1,0	0.4
0,5	0.4

FORMATING OF FUNDING SOURCES

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.