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A new water-soluble polycarbobetaine showing high selectivity toward copper

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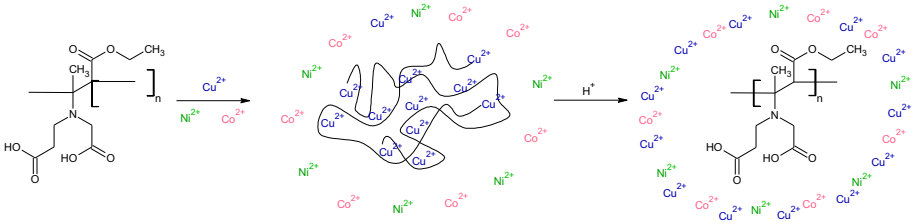
HIGHLIGHTS

- A new pH-sensitive polycarbobetaine was synthetized.
- Adsorption isotherms were built and modeled.
- High adsorption capacities were reached for copper at pH = 5 and pH = 6.
- The selectivity toward copper was indicated in the presence of nickel and/or cobalt.
- The efficiency of copper adsorption was maintained over 5 cycles of polycarbobetaine reuse.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, betaine-type polyampholytes (polycarbobetaines, PCBets) are investigated as complexing agents of metal ions. Because PCBets are pH-sensitive due to the presence of amine and carboxylic acid groups, the complexation of copper was monitored at various pH values (from 3 to 6) by UV–vis spectroscopy and/or electrochemical measurements. The results obtained for the complexation of copper were greatly enhanced as the pH increased and reached 264 ± 11 mg g^{-1} at pH = 6. This maximum adsorption capacity rivals the recent results obtained for molecules of environmental interest, such as chitosan. The selectivity of the target PCBets for copper was indicated in the presence of nickel and/or cobalt and partially accounts for the interest in this material and demonstrated the relevance of using PCBet in environmental applications (such as metal recovery from wastes/wastewaters or environmental sensors). The efficiency of copper adsorption was maintained over 5 cycles of PCBet reuse (91 ± 4%).

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, ultrafiltration, 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

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[3]. Among these techniques, precipitation appears as the most attractive, primarily because of its economical operation. However, one disadvantage exists when treating multi-element samples because all metals are typically precipitated together in sludge without any possibility to valorize them. Selective precipitating agents, such as dithiocarbamate and their ramifications, 2,4,6-tri mercapto-1,3,5-triazine, or dipropyl dithiophosphate, have been studied, but their high cost inhibits their use for different industrial applications [4]. Adsorption is also a well-studied and efficient technique that has been considered more often for metal ion selective treatment [5]. Low-cost natural and synthetic adsorbents have already demonstrated good performances for copper removal from wastewaters [6–9]. Hydrogels are also considered for these applications [10]. However, these techniques are less cost-effective compared with precipitation when considering the clogging/unclogging operational problems in the technology.

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 [11]. This study investigates polycarbobetaines (PCBets) and their interactions with copper to design chemical processes for copper valorization. Cross-linked PCBet hydrogels have been tested for copper adsorption [2,12,13]; however, no literature exists about water-soluble PCBets for similar applications [14], although water-soluble polymers have been suggested to enhance filtration systems [15–17].

2. Theoretical background

The interactions of water-soluble polymers with metal ions are treated as surface phenomena as previously reported [18]. The most appropriate method for assessing sorption capacity is the derivation of a whole sorption isotherm [19]. 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 [20]. This study considers some two parameter isotherms only (Langmuir, Freundlich and Dubinin–Radushkevich). All of the equations and parameters used to model the adsorption isotherms are reported in Table 1 where C_e and Q_e are respectively the concentration of free copper at the equilibrium (mg L^{-1}), and the amount of copper adsorbed (mg) per gram of polymer.

The Langmuir equation is valid for monolayer sorption onto a surface with a finite number of identical sites [21]. It assumes a homogeneous surface and no interaction between the adsorbed species on adjacent active sites [22]. From equation presented in Table 1, one can readily deduce that at low sorbate concentrations it effectively reduces a linear isotherm. Alternatively, at high sorbate concentrations, it predicts a constant – monolayer – sorption capacity [23]. A separation factor or equilibrium parameter (R_L) was defined from this model [24], as:

$$R_L = \frac{1}{1 + K_L * C_0}$$

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

Depending on its value, the isotherm shape can be interpreted as follows: $R = 0$ for the irreversible case, $0 < R < 1$ for favorable equilibrium, $R = 1$ for the linear case, and $R > 1$ for unfavorable equilibrium [24].

The Freundlich equation is characteristic of multilayer adsorption, with non-uniform distribution of adsorption site and affinities over the heterogeneous surface. The magnitude of exponent n gives an indication on the favorability of adsorption. It is generally stated that the values n in the range of 2–10 represent good, 1–2 moderately difficult and less than 1 poor adsorption characteristics [25]. The Freundlich expression is an exponential equation and therefore, assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases. To determine the maximum adsorption capacity (Q_m), it is necessary to operate with constant initial concentration C_0 and variable weights of adsorbent; thus $\ln Q_m$ is the extrapolated value of $\ln q$ for $C = C_0$ as previously reported [26].

Dubinin–Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. The model has often successfully fitted high solute activities and the intermediate range of concentrations data well. The approach was usually applied to distinguish the physical and chemical adsorption of metal ions [20]. The mean free energy (E) can be calculated as follows [27]:

$$E = \left[\frac{1}{\sqrt{2 \times K_{DR}}}\right]$$

The magnitude of free energy is used for estimating the type of adsorption mechanism. When ranging from 8 to 16 kJ mol^{-1}, it indicates an ion-exchange process, beyond 16 kJ mol^{-1} a coordination reaction is expected, and below 8 kJ mol^{-1} physisorption takes place [28]. One of the unique features of the Dubinin–Radushkevich isotherm model lies on the fact that it is temperature-dependent, which when adsorption data at different temperatures are plotted as a function of logarithm of amount adsorbed versus the square of potential energy, all suitable data will lie on the same curve, named as the characteristic curve [29,30].

Thermodynamic data such as adsorption energy can be obtained from Langmuir equation and can be calculated by using the following equation [31]:

$$K_L = e^{\frac{-\Delta G^0_{ads}}{R \times T}}$$

3. Materials and methods

3.1. Materials

Acetoacetic ester (AAE, ⩾99%) and the initiator 2,2′azobisisobutyronitrile (AIBN, ⩾98%) were purchased from Aldrich and used

Table 1
Equations and parameters used to model the adsorption isotherms of copper on PCEGC.

Name	Equation	Parameters
Langmuir	$Q_e = \frac{Q_m * K_L * C_e}{1 + K_L * C_e}$	Q_m = maximum adsorption capacity (mg g^{-1}) K_L = isotherm constant (L mg^{-1})
Freundlich	$Q_e = K_f * C_e^{1/n}$	K_f = isotherm constant (mg g^{-1} (L $mg^{-1})^{1/n}$) n = adsorption intensity
Dubinin–Radushkevich	$Q_e = Q_s * \exp[-\mathrm{Kdr} * \varepsilon^2]$ $\varepsilon = RT * \ln\left(1 + \frac{1}{C_e}\right)$	Q_S = maximum adsorption capacity (mg g^{-1}) Kdr = isotherm constant (mol^2 kJ^{-2})