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Competitive sorption of Cu(II) and Eu(III) ions on olive-cake carbon in aqueous solutions—a potentiometric study

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Abstract The competitive sorption of Cu(II) and Eu(III) ions from aqueous solutions by olive-cake carbon, has been investigated by potentiometry at pH 6, $I = 0.1$ M $NaClO_4$, 25°C and under normal atmospheric conditions. Evaluation of the experimental data supports the formation of inner-sphere surface complexes and results in the calculation of the formation constant of the surface complexes ($(=S–O)_2Cu$), which is found to amount $\log \beta_{Cu} = 5.3 \pm 0.3$. Addition of competing Eu(III) ions in the aqueous system leads to replacement of the Cu(II) by the competitor metal ion. Evaluation of the potentiometric data obtained from competition experiments indicates an ion-exchange mechanism. The formation constant of the Eu(III) species sorbed on olive cake carbon is found to be $\log \beta_{Eu} = 5.1 \pm 0.5$. Comparison of the complex formation constants of the olive-cake carbon with the corresponding complex formation constants for of olive cake and humic acid with the two metal ions, indicates that the same type of active sites is responsible for the metal ion complexation on the surface of the different types natural organic matter (e.g. olive-cake carbon, olive-cake and humic acid).

Keywords Metal ions · Olive-cake carbon · Surface complexes · Competition · Formation constants

1 Introduction

Removal of (radio)toxic metal ions from contaminated waters by adsorption on solid surfaces (minerals and biomass by-products) is compared to other water treatment technologies such as precipitation, ion exchange and reverse osmosis, a cost-effective, simple regarding design and operation, and insensible to toxic substances. Moreover, adsorption water treatment technologies meet environmental protection requirements (Kurniawan et al. 2006).

Activated carbon (AC) is commonly used as an effective adsorbent for the removal of organic micro-pollutants from wastewaters (Mauter and Elimelech 2008). However, activated carbon can remove also metal ions from aqueous solutions (Galiatsatou et al. 2002; Vladimir and Danish 2002). The removal of metal ions is attributed to weakly acidic oxygen groups through surface oxidation of the activated carbon. Nevertheless, a wide application of activated carbon in wastewater treatment is restricted due to its high cost. An economical solution to this problem provides the production of activated carbon from low-cost agriculture biomass by-products (Ioannidou and Zabaniotou 2007).

Several carbonaceous materials such as coal and wood have been used for the industrial production of activated carbons (Ioannidou and Zabaniotou 2007). Recently also agricultural biomass by-products including olive pomace received consideration as lignocellulosic materials for the production of activated carbon (Baccar et al. 2009; Cimino et al. 2005). Olive-waste cakes (olive pomace) is the remaining residue of oil extraction process. The use of this material as precursor for the preparation of activated carbon produces not only a useful adsorbent for the purification of contaminated environments, but contributes also to minimizing the solid wastes (Baccar et al. 2009).

Copper, which is an important metal having many industrial applications and is part of the technical barrier for radionuclides of the high-level nuclear waste, can be toxic in high levels to many organisms and copper contamination of natural systems can cause serious environmental prob-

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lems (Yang et al. 2006). From the experimental point of view the interaction of Cu(II) ions with mineral surfaces (Konstantinou and Pashalidis 2008) and natural organic matter (Kolokassidou and Pashalidis 2006; Konstantinou et al. 2007, 2009; Kolokassidou et al. 2009) is successfully investigated by means of potentiometry using a Cu(II) ion selective electrode. On the other hand europium is used as a non-radioactive analogue for trivalent actinides, because trivalent actinides and lanthanides present similar chemical behaviour in solid and aqueous phase, which is attributed to the fact that the f-elements have almost identical ionic radii (Seaborg 1993).

This paper presents a study on the interaction between Cu(II) and Eu(III) ions with olive-cake carbon by means of potentiometric measurements using a Cu ion selective electrode and competition reactions.

2 Materials and methods

All experiments were performed at room temperature (25 ± 3°C) under atmospheric conditions in aqueous solutions at pH 6 and constant ionic strength ($I = 0.1$ M $NaClO_4$). The experiments were performed in duplicate and the mean values have been used for data evaluation. The preparation of stock solutions was carried out by dissolution of the corresponding salts in de-ionized water e.g. copper sulfate ($CuSO_4 \cdot 5H_2O$, Merck) and europium nitrate ($Eu(NO_3)_3 \cdot 5H_2O$, Aldrich Co). All experiments were performed in polyprolylene tubes since preliminary experiments have shown that metal ion sorption onto the tube walls was negligible.

2.1 Olive-cake carbon

The adsorbent used in this study was supplied by a local (Cypriot) olive-cake carbon production company. The material was sieved and the particle fraction between 200 and 500 microns was selected for the adsorption experiments and was used without any further purification or other pretreatment. The BET surface area was determined by N_2 adsorption and was found to be 135 m^2/g and the average pore diameter 2 nm. FTIR spectra of the olive-cake carbon indicate the presence of carboxylic and phenolic surface-active species.

Potentiometric measurements were carried out using glass or Cu(II) ion selective electrode (Inolap) attached to a pH meter (WTW). The system was calibrated with buffer solutions (pH 2, 4, 7 and 10, Merck) and Cu(II) standard solutions before and after each measurement.

Experiments of the Cu(II) sorption on olive-cake carbon were performed by addition of a Cu(II) stock solution ([Cu(II)] = 0.1 M and 1 mmol MES buffer, $C_6H_{13}NO_4S \cdot H_2O$, Merck, pH = 6) to a test solution, which was consisted of 0.1 g olive-cake carbon and 1 mmol MES buffer in 25 mL of 0.1 M $NaClO_4$ aqueous solution. Several mixtures of constant olive-cake carbon amount (0.1 g) and variable Cu(II) concentration (0.1 mmol L^{-1} < [Cu(II)] < 1.2 mmol L^{-1}) were prepared. After two days equilibration the concentration of the non-complexed Cu(II) ion was determined by potentiometry using a Cu(II) ion selective electrode. For comparison, parallel measurements were made for solutions of similar composition without olive-cake carbon (reference solutions).

Competition reactions between Cu(II) and Eu(III) regarding sorption on olive-cake carbon were carried out by addition of a defined amount (25 mL) of a Eu(III) stock solution, to a suspension containing olive-cake carbon loaded with the Cu(II) ion ([Cu(II) = 1.2 mmol/L). Several mixtures of constant amount of Cu(II) loaded olive-cake carbon (0.1 g) and variable Eu(III) (0.08 mmol L^{-1} < [Eu(III)] < 1.2 mmol L^{-1}) concentration were prepared. The experiments were performed in 50 mL screw capped PE vials. After three days equilibration, the pH was measured and amount of Cu(II) ion exchanged determined.

3 Results and discussion

Figure 1 shows experimental data in the form of a $\log[Cu^{2+}] - \log[Cu(II)]_{tot}$ pointing out that the concentration of the Cu^{2+} aquo ion in the test solution is lower than in the reference solution. This is because of the sorption of Cu^{2+} on the surface of olive-cake carbon particles.

The sorption of Cu(II) by olive-cake carbon occurs most probably through the formation of surface complexes (Frenkel et al. 2000). These complexes are formed by the interaction of the Cu^{2+} aquo ion, which is the predominant Cu(II) species under the given conditions in solution (Baes and Mesmer 1976), with the surface active groups (carboxyl- and hydroxy- groups) of the olive-cake carbon surface (Toles et al. 1999). Schematically the sorption of Cu(II) by the solid surface is illustrated in Fig. 2. Hereby the surface of the olive-cake carbon particles acts as cation exchanger, which binds a Cu(II) ion through two oxygen active sites. Moreover, we assume charge neutralization of Cu^{2+} by the surface groups, that present higher affinity for the cation than the perchlorate (ClO_4^-) anion, which is the anion of the background electrolyte. This assumption is proved by the ionexchange experiments using Eu(III) ions as competing species, as discussed below.

In terms of a chemical equation, the interaction of the Cu(II) ion with olive-cake carbon is described by (1)

$$Cu^{2+} + (\equiv S\text{–}OH)_n \leftrightarrow (\equiv S\text{–}O\text{–})_{n-2}Cu + 2H^+ \quad (1)$$

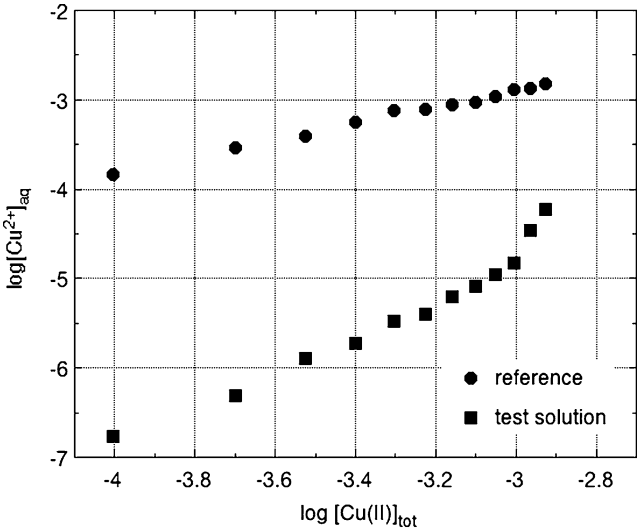

Fig. 1 $\log[Cu^{2+}]_{aq}$ as a function of $\log[Cu(II)]_{tot}$. in solid phase free and olive-cake carbon containing solutions. Experimental data were obtained from potentiometric measurements in aqueous solutions containing 0.1 $g\,L^{-1}$ olive-cake carbon, variable Cu(II) concentrations, 0.1 M $NaClO_4$ as background electrolyte and carried out at 25 ± 3°C under normal atmospheric conditions

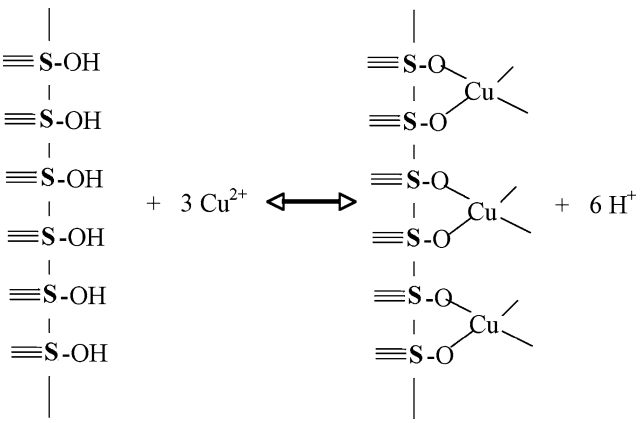

Fig. 2 Schematic illustration of the Cu(II) sorption by olive-cake carbon

and the corresponding equilibrium constant is given by (2)

$$K = \frac{[(\equiv \mathrm{S{-}O{-}})_{n-2}\mathrm{Cu}] \cdot [\mathrm{H}^+]^2}{[\mathrm{Cu}^{2+}] \cdot [(\equiv \mathrm{SOH})_n]} \tag{2}$$

at constant pH (pH = 6) (2) can be reformulated:

$$\beta_{\mathrm{Cu}} = \frac{[(\equiv \mathrm{S{-}O{-}})_{n-2}\mathrm{Cu}]}{[\mathrm{Cu}^{2+}] \cdot [(\equiv \mathrm{S{-}OH})_n]} \tag{3}$$

where, β_{Cu} is the conditional formation constant, $[(\equiv S{-}O{-})_{n-2}Cu]$ is the concentration of the complexed Cu(II) ions and equals to the total Cu(II) ion concentration (initial Cu(II) ion concentration) minus the non-complexed Cu(II) aquo ion concentration determined by potentiometry, since hydrolysis of Cu(II) ions at the given

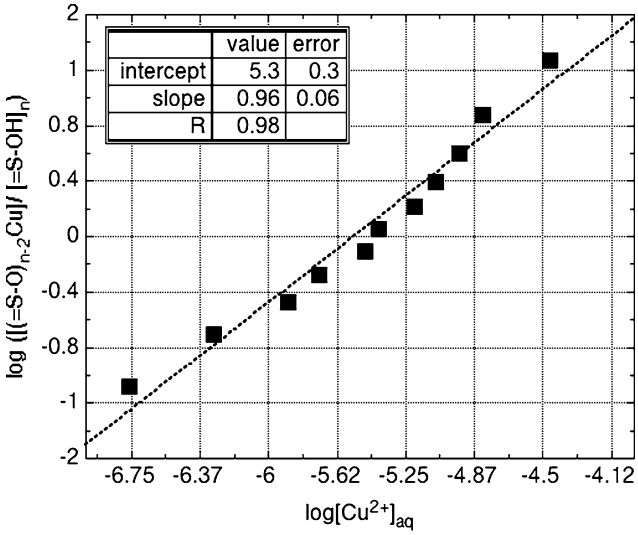

Fig. 3 $\log([(\equiv S{-}O{-})_2Cu]/[(\equiv S{-}OH)_n])$ as a function of $\log[Cu^{2+}]$. Experimental data were obtained from potentiometric measurements in aqueous solutions containing 0.1 $g\,L^{-1}$ olive-cake carbon, 0.1 M $NaClO_4$ as background electrolyte and carried out at 25 ± 3°C under normal atmospheric conditions

pH (pH = 6) is negligible. $[(\equiv S{-}OH)_n]$ is defined as the total concentration of active sites on the solid surface minus the complexed active sites ($[(\equiv S{-}OH)_n] = [(\equiv S{-}OH)_{tot}] - [(\equiv S{-}O{-})_{n-2}Cu]$). The total concentration of active sites ($[(\equiv S{-}OH)_{tot}]$) corresponds to the total number of the surface sites available for complexation and is determined using the Langmuir isotherm. Taking the logarithm and rearranging (3) results in (4)

$$\log\left(\frac{[(\equiv \mathrm{S{-}O{-}})_{n-2}\mathrm{Cu}]}{[(\equiv \mathrm{S{-}OH})_n]}\right) = \log\beta_{\mathrm{Cu}} + n \cdot \log[\mathrm{Cu}^{2+}] \tag{4}$$

The intercept of the line described by (4) corresponds to the logarithmic value of the conditional constant ($\log\beta_{Cu}$) and the value of the slope corresponds to the stoichiometric factor of $[Cu^{2+}]$, which here by definition equals to unity. Figure 3 presents the experimental data in a $\log([(\equiv S{-}O{-})_2Cu]/[(\equiv S{-}OH)_n])$–$\log[Cu^{2+}]$ diagram. Linear regression analysis of the experimental data obtained at pH 6 based on (4) results in a $\log\beta_{Cu}$ of 5.3 ± 0.3 and in slope of 0.96 ± 0.06. The latter value, which is close to unity, proofs that (1) proposed for the surface complexation of Cu(II) by olive-cake carbon is consistent.

In order to prove the surface complexation scheme assumed above (Fig. 3) and assess the sorption affinity of olive-cake carbon surface for Eu(III)), ion-exchange experiments were performed at pH 6 under defined conditions using Eu(III) ions as competing cationic species. The advantage of using Eu(III) ions is that this element is environmentally relevant (analogue for trivalent actinides) and its aqueous chemistry is extensively investigated and well understood (Baes and Mesmer 1976). At pH 6 the Cu(II) and

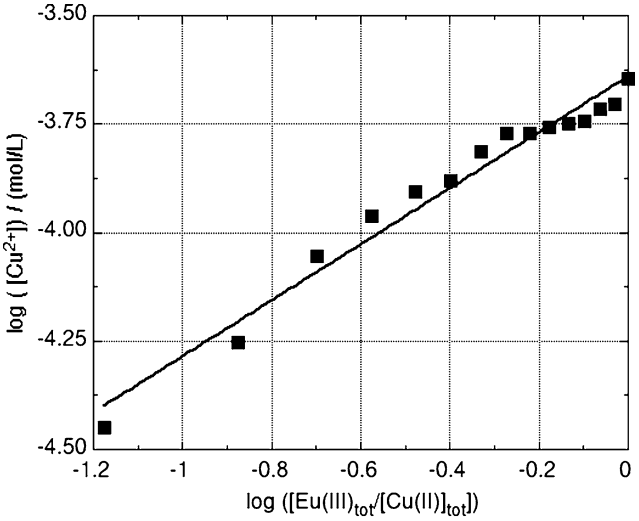

Fig. 4 $\log[Cu^{2+}]$ as a function of $\log([Eu^{3+}]_{tot}/[Cu^{2+}]_{tot})$. Experimental data were obtained from potentiometric measurements in aqueous solutions containing 0.1 g L^{-1} olive-cake carbon loaded with Cu(II) ions at different Eu(III) ion concentration, 0.1 M $NaClO_4$ as background electrolyte and carried out at 25 ± 3°C under normal atmospheric conditions

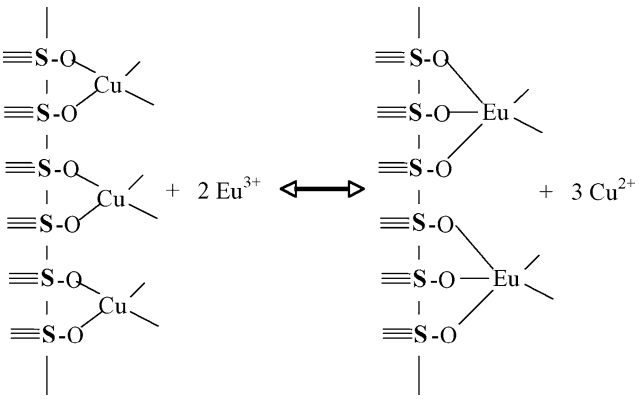

Fig. 5 Schematic illustration of the ion exchange reaction between Cu(II) and Eu(III) on the olive-cake carbon surface

Eu(III) ions exist predominantly as non-hydrolyzed aquo-ions. As shown in Fig. 4, a stepwise addition of the Eu^{3+} ion leads to an increase of the Cu^{2+} aquo ion in solution. This effect is attributed to replacement of the complexed Cu(II) ions by Eu(III) ions.

The competition reaction which results in the replacement of complexed Cu(II) by the competitive metal ions can be seen as cation exchange reaction, which is schematically presented in Fig. 5. At the beginning the solid surface is loaded with Cu(II), however, after stepwise addition of Eu^{3+} ions, Cu(II) adsorbed is replaced by the competitor metal ion.

The amount of olive-cake carbon and hence the number of complexing sites in the system is constant. Generally (assuming charge neutralization) a mol Cu(II) is replaced by 2/3 moles of the competitor metal ion, Eu^{3+}. The corresponding ion-exchange reaction can be represented by (5):

$$((\equiv S\text{–}O\text{–})_{n-2}Cu)_3 + 2Eu^{3+} \leftrightarrow 3Cu^{2+} + ((\equiv S\text{–}O\text{–})_{n-3}Eu)_2 \quad (5)$$

The conditional equilibrium constant for the competition reaction is defined as:

$$K_{Cu-Eu} = \frac{[((\equiv S\text{–}O\text{–})_{n-3}Eu)_2] \cdot [Cu^{2+}]^3}{[((\equiv S\text{–}O\text{–})_{n-2}Cu)_3] \cdot [Eu^{3+}]^2} \quad (6)$$

where $[Cu^{2+}]$, $[Eu^{3+}]$ are the concentrations of the Cu(II), Eu(III) aquo ions, respectively, $[(\equiv S\text{–}O\text{–})_{n-2}Cu]$ the concentration of the surface sorbed Cu(II), $[(\equiv S\text{–}O\text{–})_{n-3}Eu]$ the concentration of the of the surface sorbed Eu(III). $[(\equiv S\text{–}O\text{–})_{n-3}Eu]$ is assumed to be 2/3 equal to the concentration of Cu(II) exchanged. Combination of (5) with (1) results in (7), which represents the formation equations of Eu(III) surface complexes.

$$Eu^{2+} + (\equiv S\text{–}OH)_n \leftrightarrow (\equiv S\text{–}O\text{–})_{n-3}Eu + 3H^+ \quad (7)$$

The value of the conditional formation constant for the Eu(III) surface complexes (β_{Eu}) can be calculated from the competition reaction constant (K) and the conditional formation constant of the Cu(II)-olive-cake carbon surface complex ($\log \beta_{Cu} = 5.3 \pm 0.3$) at the respective pH. On the other hand, the conditional constant of the corresponding competition reaction (K_{Cu-Eu}) as well as the stoichiometry of the competition reaction are determined by linear regression analysis of the potentiometric data obtained from the ionexchange experiments using the logarithmic form of (6):

$$\log\left(\frac{[((\equiv S\text{–}O\text{–})_{n-3}Eu)_2] \cdot [Cu^{2+}]^3}{[((\equiv S\text{–}O\text{–})_{n-2}Cu)_3]}\right) = \log K_{Cu-Eu} + 2 \cdot \log \cdot [Eu^{3+}] \quad (8)$$

The intercept of the line described by (8) corresponds to the logarithmic value of the reaction constant ($\log K_{Cu-Eu}$) and the value of the slopes corresponds to the stoichiometric factors of Eu^{3+} according to (8). Figure 6 shows the experimental data obtained in this study from the Eu(III)–Cu(II) system in a $\log(\frac{[((\equiv S-O-)_{n-3}Eu)_2]\cdot[Cu^{2+}]^3}{[((\equiv S-O-)_{n-2}Cu)_3]})$–$\log[Eu^{3+}]$ diagram. The slope of the curve in Fig. 6 equals to 2 for the Eu(III)–Cu(II) system, indicating that the complexation and ion-exchange scheme suggested is correct. Furthermore, linear regression analysis of the experimental data resulted in equilibrium constants ($\log K_{Cu-Eu} = -5.8 \pm 0.4$) for the competition reactions, which in combination with the conditional formation constant of the Cu(II) surface complex, leads to the calculation of conditional formation constant $\log \beta_{Eu} = 5.1 \pm 0.5$ for the Eu(III) surface complexes, indicating on a relatively high affinity of the olive-cake carbon surface for the Eu^{3+} cation. This affinity is similar to the

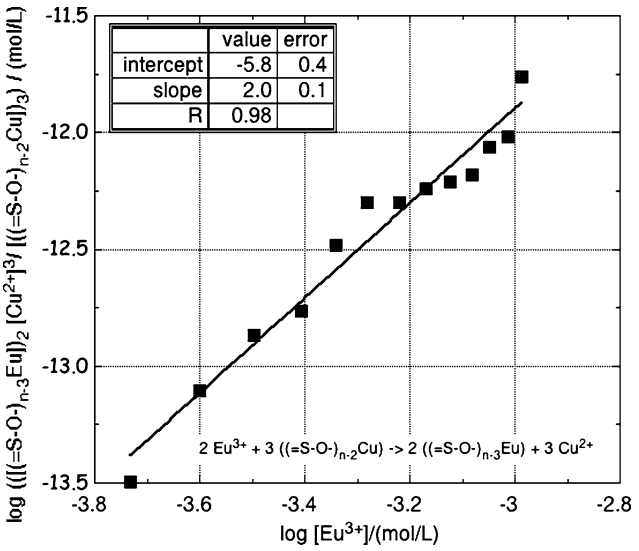

Fig. 6 $\log(\frac{[((\equiv S-O-)_{n-3}Eu)_2]\cdot[Cu^{2+}]^3}{[((\equiv S-O-)_{n-2}Cu)_3]})$ as a function of $\log[Eu^{3+}]$. Experimental data were obtained from potentiometric measurements in aqueous solutions containing 0.1 g L^{-1} olive-cake carbon loaded with Cu(II) ions at different Eu(III) ion concentration, 0.1 M $NaClO_4$ as background electrolyte and carried out at 25 ± 3°C under normal atmospheric conditions

corresponding affinities of olive cake and humic acid, indicating that similar active sites are responsible for the metal ion binding on the olive-cake carbon surface (Kolokassidou and Pashalidis 2006; Kolokassidou et al. 2009; Konstantinou et al. 2007, 2009). The relatively increased surface area (135 cm^2 g^{-1}) and adsorption capacity of the olive cake carbon for Eu(III) ions (37 mg g^{-1}), which is close to the corresponding value given in literature (Gad and Awwad 2007), suggests that olive cake carbon can be considered as a potential adsorbent for Cu(II)- and Eu(III)-ions in water treatment technologies. However, the almost similar chemical affinity of the olive cake carbon for both metal ions indicates that selective adsorption of the metal ions can't be possible.

4 Conclusions

The sorption of Cu(II) on the olive-cake carbon surface takes places through the formation of inner-sphere complexes with the active sites of the surface (e.g. hydroxyl groups). The value of the conditional formation constant for the Cu(II) surface complexes is $\log \beta_{Cu} = 5.3 \pm 0.3$, at pH = 6.

The competition reaction between Cu(II) and Eu(III) ions regarding the sorption on the olive-cake carbon surface showed that this reaction is based on ion-exchange and the surface presents almost similar affinity for Eu(III). The conditional formation constants evaluated for the Eu(III) surfaces complexes on olive-cake carbon at pH = 6, have been evaluated to amount $\log \beta_{Eu} = 5.1 \pm 0.5$.

The affinity of olive-cake carbon for metal ions is similar to the corresponding affinities of olive cake and humic acid, indicating that similar active sites are responsible for the metal ion binding on the olive-cake carbon surface.

Olive cake carbon can be considered as a potential, non-selective adsorbent for Cu(II)- and Eu(III)-ions in water treatment technologies.

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