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Sorption of Cu(II) and Eu(III) ions from aqueous solution by olive cake

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Abstract The sorption of Cu(II) on olive cake, a biomass by-product of olive oil production, has been investigated by potentiometry at pH 6, I = 0.1 M $NaClO_4$, 25 °C and under atmospheric conditions. Numerical analysis of the experimental data supports the formation of surface complexes and allows the evaluation of the corresponding formation constant, which is found to amount $\log\beta = 5.1 \pm 0.4$. This value is close to corresponding values given in literature for Cu(II)-humate complexes, indicating that the same type of active sites (e.g. carboxylic and phenolic groups) is responsible for the Cu(II) binding by olive cake. Addition of a competing metal ion (e.g. Eu(III) ion) in the system leads to replacement of the Cu(II) by Eu(III). Evaluation of the potentiometric data obtained from competition experiments indicates on a ionexchange mechanism. The formation constant of the Eu(III) species sorbed on olive cake is found to be $\log\beta = 5.4 \pm 0.9$. The results of this study are of particular interest with respect to waste water treatment technologies using biomass products as adsorbent material and environmental impact assessments regarding disposal of biomass by products in the geosphere.

Keywords Olive cake · Copper · Europium · Surface complexes · Ionexchange · Formation constants

1 Introduction

Olive cake is a biomass by-product of the olive oil production and is a very abundant agricultural waste in the Mediterranean area. Manufacturing of olive oil yields an aqueous (50%), an oily (30%) and a solid residue—the olive cake or pomace (20%). Generally, the olive cake remains stockpiled close to olive oil mills without actual application because only little amounts are used as natural fertilizer, combustible and additive in animal food (Pagnanelli et al. 2003; Doymaz et al. 2004; Akgun and Doymaz 2005; Alcaide and Nefzaoui 1996). Olive cake disposed in the environment could play, similar to organic matter derived from the decomposition of plant tissues, an important role in the chemical behaviour and migration of toxic impurities (e.g. heavy metals) within natural aquifer systems (Liu and Gonzalez 2000; Calace et al. 2006). However, in contrast to dissolved organic matter (e.g. fulvic and humic acids), which is soluble in the mobile phase and enhances the mobility of pollutants in the geosphere, biomass may increase the retardation of sorbed contaminants.

On the other hand, olive cake could be used as sorbent in wastewater treatment technologies (Pagnanelli et al. 2002, 2003; Gharaibeh et al. 1998; Blazquez et al. 2005; Dakiky et al. 2002). Removal of heavy metals from large volumes of wastewaters requires a cost effective remediation technology (Kalin et al. 2005; Veglio and Beolchini 1997; Gavrilescu 2004; Iyer et al. 2005). Conventional technologies relying on mineral adsorbents or chemical flocculating agents are relatively expensive. Biosorption technologies in which biomass is used to accumulate heavy metals are methods that could replace conventional processes for the remediation of polluted wastewaters (Gavrilescu 2004). Biomasses that are by-products from other commercial processes with little commercial value represent good candidates for the development of inexpensive biosorption processes (Psareva et al. 2005; Chubar et al. 2004). The major advantage of biomass by-products over microbial sys-

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tems is that there is no cost of growing a sufficient quantity of bacterial or algae biomass (Schneegurt et al. 2001).

This paper deals with the sorption and particularly with the mechanism of a heavy metal ion sorption (e.g. Cu(II) ion) on olive cake. Cu(II) has been selected, because it can be used as an analogue of Pb(II) and Cd(II) regarding their environmental behaviour and because there is extensive literature about the complexation of Cu(II) with humic acids based on a wide spectrum of electrochemical (Liu and Gonzalez 2000; Osterberg et al. 1999; Evangelou et al. 1999; Choi et al. 1994; Stevenson and Chen 1991) and spectroscopic methods (Korshin et al. 1998; Frenkel et al. 2000; Alcacio et al. 2001). The investigation was performed by potentiometry using an ion selective electrode. Potentiometry, by means of ion selective electrodes, has the advantage that measurements are performed in-situ and there is no need to separate the complexed from the free metal ion to calculate thermodynamic parameters (Liu and Gonzalez 2000). Moreover, the Cu(II) ion selective electrode has been chosen because of its stability. The ionexchange investigations involved Eu(III) a competing ionic species, because Eu(III) exists in aquatic solutions for $\mathrm{pH} < 7$ predominantly as Eu(III) aquo ion and is often used as an analogue for trivalent actinides (Baes and Mesmer 1976).

The aim of this study is (a) to determine the chemical affinity of olive cake for Cu(II), (b) compare the data obtained with corresponding literature data, (c) understand the sorption mechanism and (d) assess the chemical affinity of the olive cake for the competing ion (e.g. sorption affinity of olive cake for Eu(III)). Knowledge obtained from this study could be of particular interest for wastewater treatment technologies using olive cake as adsorbent material and is of fundamental importance for environmental impact assessments regarding disposal of residues from olive oil production into the geosphere and their effect on heavy metal migration.

2 Experimental

All experiments were performed at room temperature ($25 \pm 2\,^{\circ}\mathrm{C}$) under atmospheric conditions in aqueous solutions at constant ionic strength (0.1 M $\mathrm{NaClO_4}$) and pH ($\mathrm{pH} = 6$, MES Buffer, $\mathrm{C_6H_{13}NO_4S{\cdot}H_2O}$, Merck). All experiments were performed in duplicate and since the variation of the experimental data was within the measurement error, 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 ($\mathrm{CuSO_4{\cdot}5H_2O}$, Merck) and europium nitrate ($\mathrm{(Eu(NO_3)_3{\cdot}5H_2O}$, Aldrich Co).

2.1 Olive cake

The adsorbent used in this study was supplied by a local (Cypriot) olive oil production plant. The material was pretreated by means of hexane extraction and hence was dry and free of oil residues. Hexane extraction is an industrial process applied in order to extract and commercialize oil residues from the “pressed” olive cake. The granulated by-product of the hexane extraction 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 pre-treatment.

2.2 BET surface area

The specific surface area ($\mathrm{m^2\,g^{-1}}$) of the adsorbent was measured by $\mathrm{N_2}$-adsorption at 77 K ($p/p_\mathrm{o} = 0.05$–0.25, Micromeritics Co, ASAP 2000). Outgassing of the samples (0.5 g olive cake) before measurements was done at $90\,^{\circ}\mathrm{C}$ under vacuum ($p = 1.3 \times 10^{-6}$ bar) overnight.

2.3 $\mathrm{NH_3}$ thermal programmed desorption ($\mathrm{NH_3}$-TPD)

The proton exchange capacity of the material which corresponds to the concentration of the adsorbent active sites was determined by $\mathrm{NH_3}$-TPD (thermal programmed desorption of pre-adsorbed $\mathrm{NH_3}$ (Costa et al. 2000).

2.4 Attenuated total reflectance Fourier transform infrared measurements

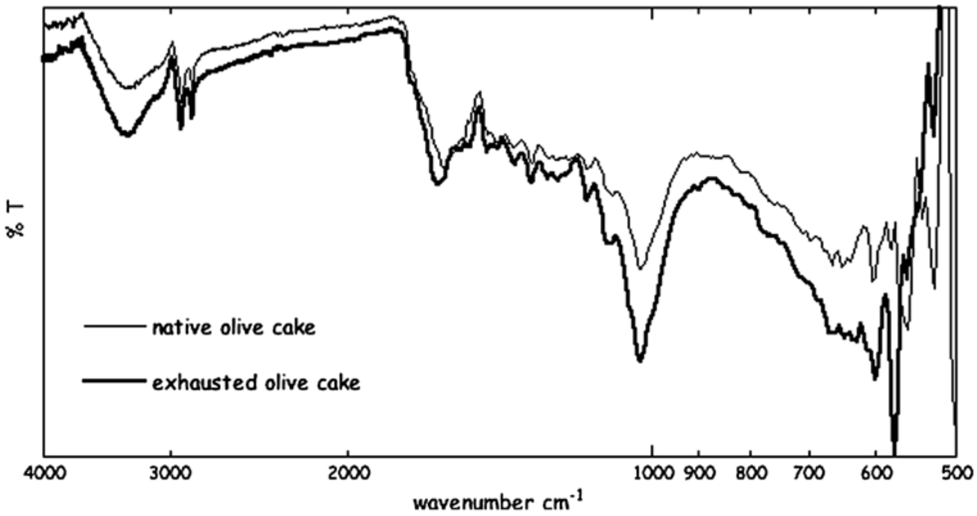
ATR-FTIR analyses onto native and exhausted (after metal sorption) olive cake samples were performed using a Shimadzu FTIR spectrometer 8900 equipped with an horizontal ATR accessory and a ZnSe crystal as the reflection element (PIKE Technologies). For each spectrum, 40 scans were collected at a resolution of 4 $\mathrm{cm^{-1}}$.

2.5 Potentiometric measurements

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 were performed by addition of a Cu(II) stock solution ([Cu(II)] = 0.1 M and 1 mmol MES) to a test solution, which was consisted of 0.1 g olive cake and 1 mmol MES buffer in 25 ml of 0.1 M $\mathrm{NaClO_4}$ aqueous solution. Several mixtures of constant olive cake amount (0.1 g) and variable Cu(II) concentration ($0.4\ \mathrm{mmol\,l^{-1}} < [\mathrm{Cu(II)}] < 3.85\ \mathrm{mmol\,l^{-1}}$) 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 (reference solutions).

Fig. 1 Solid phase ATR-FTIR spectra of native and exhausted (metal ion loaded) olive cake samples



2.6 Competition reactions

Competition reactions between Cu(II) and Eu(III) regarding sorption on olive cake were carried out by addition of a defined amount (50 µl) of a Eu(III) stock solution, to a suspension containing olive cake loaded with the Cu(II)) ion (1.6×10^{-2} mol Cu(II) per g OC). Several mixtures of constant amount of Cu(II) loaded olive cake (0.1 g) and variable Eu(III) concentration ($0.24\ \text{mmol}\,\text{l}^{-1} < [\text{Eu(III)}] < 2.43\ \text{mmol}\,\text{l}^{-1}$) 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) ionexchanged determined.

3 Results and discussion

3.1 Olive cake characteristics

The determination of the specific surface area by N_2-adsorption has shown that olive cake has no internal surface and that all active groups are located on the external surface. The proton exchange capacity of the material, which corresponds to the concentration of the adsorbent active sites, was determined by NH_3-TPD and was found to be 0.59 mmoles g^{-1}. This value is close to the corresponding value given in literature determined by acid/base titration (Pagnanelli et al. 2003). The analysis of the FTIR spectrum (Fig. 1) on solid phase confirms the hypothesis on the nature of these sites by the presence of some characteristic peaks for the native and the exhausted olive cake samples (i.e.: carboxylic: C=O stretching, 1610 cm^{-1}, carboxylic and phenolic: O–H stretching, 3280 cm^{-1} and polyphenolic aromatic ring: C–C stretching, 1510 cm^{-1}). The shift of the C=O stretching band to higher energies in the spectrum of the exhausted olive cake sample indicates on the surface complexation of metal ions by carboxylic groups.

3.2 Sorption of Cu(II) by olive cake

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

The sorption of Cu(II) by olive cake is proposed to occur through the formation of inner-sphere surface complexes. These complexes are formed by the interaction of Cu(II) aquo ion, which is the predominant Cu(II) species under the given conditions in solution (Baes and Mesmer 1976), with the carboxylic and phenolic groups of the olive cake surface. These groups, which act as complexing sites for metal ions, dominate on the solid surface (Gharaibeh et al. 1998). Schematically the sorption of Cu(II) by the olive cake surface is illustrated in Fig. 3. Hereby the olive cake acts as a chelating cationexchanger, which binds a Cu(II) ion through two oxygen containing active sites. These sites correspond basically to carboxylic groups, which are ionized, and phenolic groups, that are predominantly non-ionized at the given pH. Moreover, we assume charge neutralization of Cu(II) by the surface groups, that present by far 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) as competing species as discussed below.

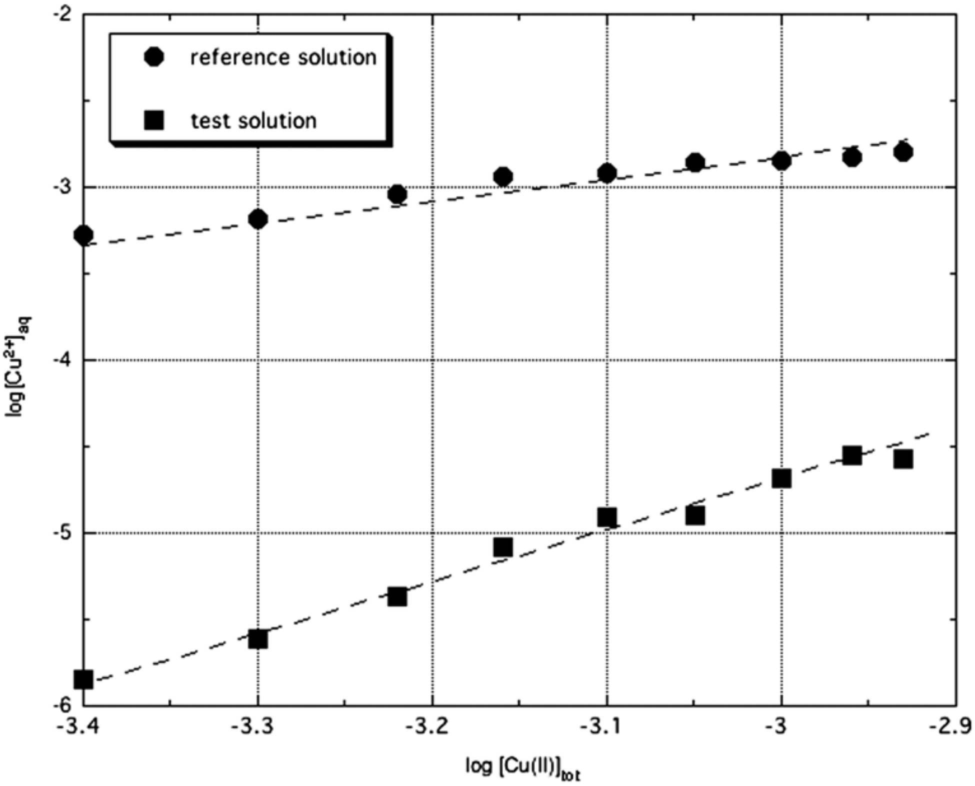
In terms of a chemical equation, the interaction of the Cu(II) ion with olive cake can be described by Eq. 1

$$\text{Cu}^{2+} + (\text{OC}) \leftrightarrow \text{Cu(OC)} \tag{1}$$

and the corresponding formation constant is given by Eq. 2

$$\beta = \frac{[\text{Cu}\{\text{OC(II)}\}}{[\text{Cu}^{2+}] \cdot [\{\text{OC(II)}\}]} \tag{2}$$

Fig. 2 $\log[Cu^{2+}]_{free}$ as a function of $\log[Cu^{2+}]_{tot}$ in OC free and OC containing solutions. Experimental data were obtained from potentiometric measurements in aqueous solutions containing 4 g l^{-1} olive cake, variable Cu(II) concentrations, 0.1 M $NaClO_4$ as background electrolyte and carried out at 25 ± 3 °C under normal atmospheric conditions



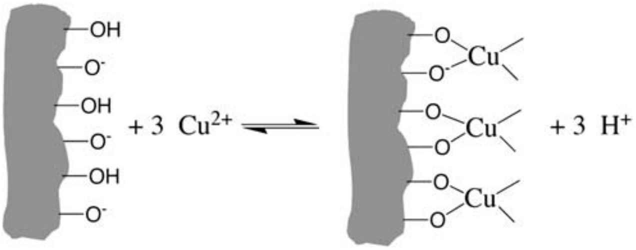


Fig. 3 Schematic illustration of the Cu(II) sorption by olive cake

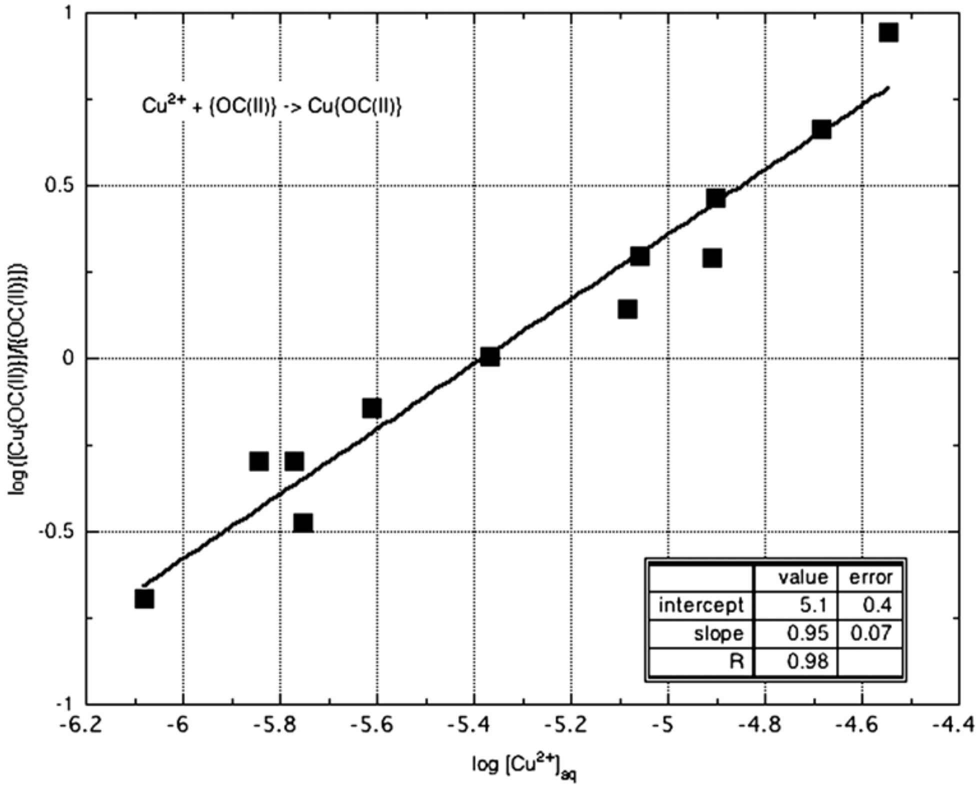
where [Cu(OC)] is the concentration of the complexed Cu(II) ion and equals to the total Cu(II) ion concentration (initial Cu(II) ion concentration) minus the non-complexed $Cu(II)_{free}$ ion concentration determined by potentiometry, since hydrolysis of the Cu(II) ion at the given pH (pH = 6) is negligible. $[\{OC(II)\}]$ is defined as the total concentration of active sites on the olive cake surface minus the complexed active sites ($[\{OC(II)\}_{tot}] - [Cu\{OC(II)\}]$). The total concentration of active sites (($[\{OC(II)\}_{tot}]$) is defined according to the Charge Neutralization Model described by Kim and Czerwinsky (1996) as the proton exchange capacity of the olive cake surface divided by 2 ($[\{OC(II)\}_{tot}] = PEC/2$). Taking the logarithm and rearranging Eq. 2 results in Eq. 3

$$\log\left(\frac{[Cu\{OC(II)\}]}{[\{OC(II)\}]}\right) = \log\beta + n \cdot \log[Cu^{2+}] \tag{3}$$

The intercept of the line described by Eq. 3 corresponds to the logarithmic value of the conditional constant ($\log\beta$) and the value of the slope corresponds to the stoichiometric factor of $[Cu^{2+}]$, which here by definition equals to unity. Figure 4 presents the experimental data in a $\log([Cu\{OC(II)\}]/[\{OC\}]) - \log[Cu^{2+}]$ diagram. Linear regression analysis of the experimental data based on Eq. 3 results in a $\log\beta$ of 5.1 ± 0.4 and in slope of 0.95 ± 0.07. The latter value, which is close to unity, proofs that Eq. 1 proposed for the complexation of Cu(II) by olive cake is consistent. On the other hand, the value for $\log\beta (5.1 \pm 0.4)$ is close to corresponding values given in literature ($5.2 < \log\beta < 5.8$) for similar systems, such as Cu(II) humic acid complexes (Osterberg et al. 1999; Evangelou et al. 1999; Choi et al. 1994; Stevenson and Chen 1991), indicating that in both systems similar characteristic groups are responsible for the metal ion complexation. Indeed, partial dissolution and extraction of olive cake by alkaline aqueous solutions (1 M NaOH) and characterisation of the obtained product has shown that it behaves like humic acid regarding its physical (e.g. size distribution and spectroscopic properties) and complex formation properties (Kolokassidou and Pashalidis 2006).

3.3 Competition reactions between Cu(II) and Eu(III) ions

In order to prove the surface complexation scheme assumed above (Fig. 3) and assess the sorption affinity of olive cake for Eu(III), we performed ionexchange experiments under



	value	error
intercept	5.1	0.4
slope	0.95	0.07
R	0.98	

Fig. 4 log([Cu{OC(II)}]/[{OC(II)}]) as a function of log$[Cu^{2+}]$. Experimental data were obtained from potensiometric measurements in aqueous solutions containing 4 g l^{-1} olive cake, 0.1 M $NaClO_4$ as background electrolyte and carried out at 25 ± 3 °C under normal atmospheric conditions

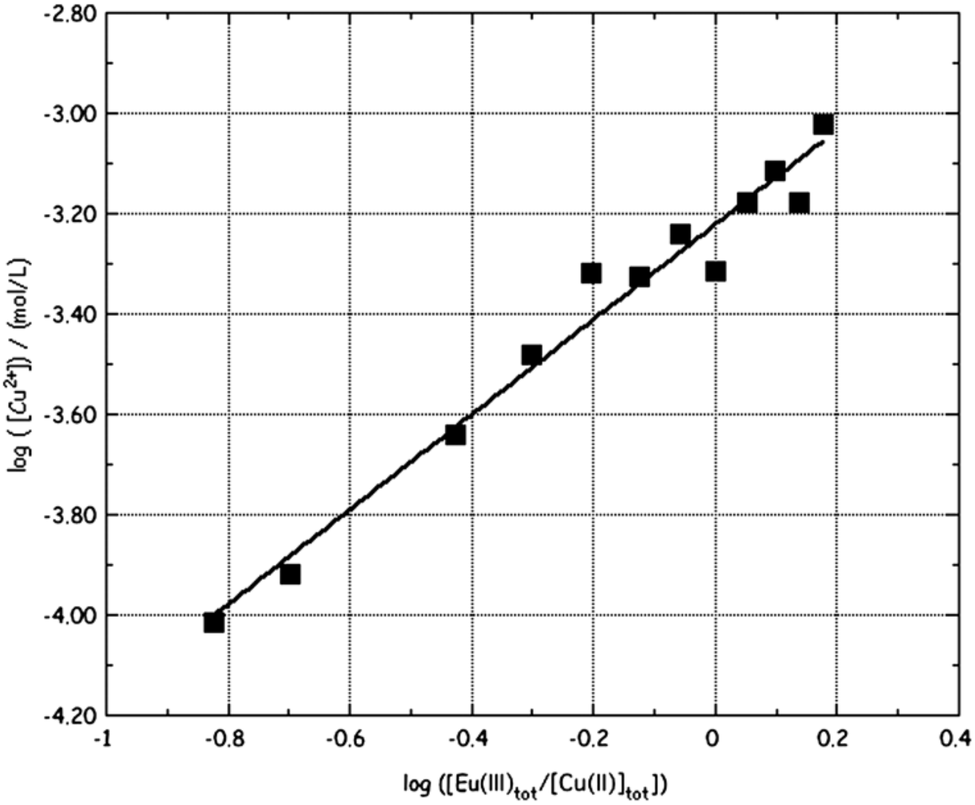


Fig. 5 log$[Cu^{2+}]$ as a function of log([Eu(III)]/[Cu(II)]). Experimental data were obtained from potensiometric measurements in aqueous solutions containing 4 g l^{-1} olive cake loaded with Cu(II) ions at different Eu(III) ion concentration, 0.1 M $NaClO_4$ as background electrolyte and carried out at 25 ± 3 °C under normal atmospheric conditions

defined conditions using Eu(III) ion as competing cationic species. The advantage of using Eu(III) is that its aqueous chemistry is well understood, forms relatively stable complexes with natural organic colloids (e.g. humic and fulvic acids (Baes and Mesmer 1976) and at pH 6 exists predominantly as Eu(III) ion. As shown in Fig. 5, a stepwise addition of the Eu(III) ion leads to an increase of the Cu(II) aquo ion in solution. This effect is attributed to replacement of the complexed Cu(II) ion by the Eu(III) ion.

This competition reaction which results in the replacement of the complexed Cu(II) ion by the Eu(III) ion can be seen as cationexchange reaction (Fig. 6). At the beginning the olive cake surface is loaded with Cu(II), however, after stepwise addition of Eu(III), Cu(II) adsorbed is replaced by Eu(III). This ionexchange reaction is schematically presented in Fig. 6.

The amount of olive cake and hence the number of complexing sites in the system is constant. Assuming charge neutralization, three Cu(II) ions have to be replaced by two Eu(III) ions and hence the corresponding ionexchange reaction can be represented by Eq. 4

$$2 \cdot \mathrm{Eu}^{3+} + \mathrm{Cu}\{\mathrm{OC(II)}\} \leftrightarrow \mathrm{Eu}\{\mathrm{OC(III)}\} + 3 \cdot \mathrm{Cu}^{2+} \qquad (4)$$

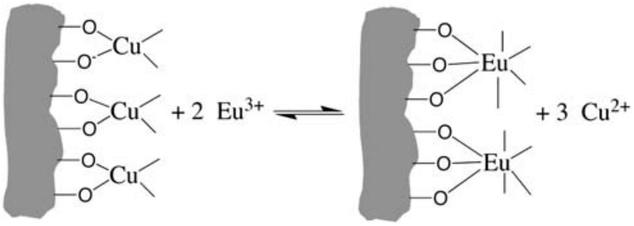


Fig. 6 Schematic illustration of the Ionexchange reaction between Eu(III) and Cu(II) on the olive cake surface

The corresponding conditional constant for the competition reaction is defined as

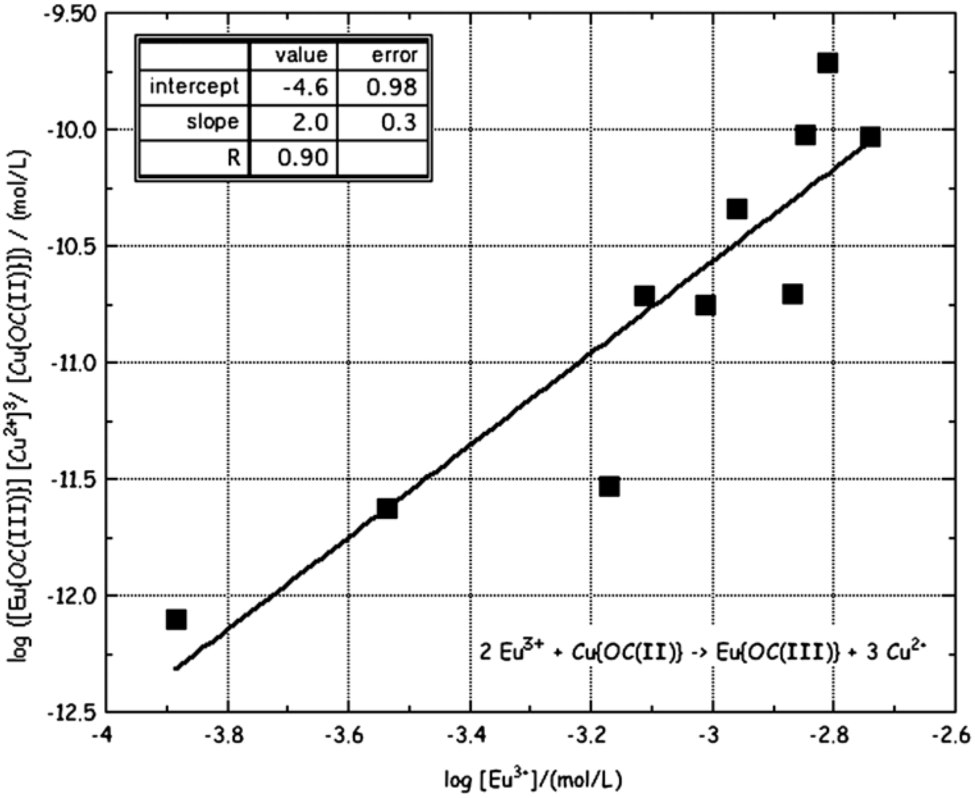
$$\mathrm{K} = \frac{[\mathrm{Eu}\{\mathrm{OC(III)}\}] \cdot [\mathrm{Cu}^{2+}]^3}{[\mathrm{Eu}^{3+}]^2 \cdot [\mathrm{Cu}\{\mathrm{OC(II)}\}]} \qquad (5)$$

where $[\mathrm{Eu}^{3+}]$ is the concentration of the Eu(III) aquo-ion, $[\mathrm{Cu}\{\mathrm{OC(II)}\}]$ the concentration of the surface sorbed Cu(II) ion, [EuOC(III)] the concentration of the of the surface sorbed Eu(III) ion and $[\mathrm{Cu}^{2+}]$ is the concentration of the Cu(II) aquo-ion. $[\mathrm{Eu}\{\mathrm{OC(III)}\}]$ is assumed to be 2/3 of the Cu(II) ion concentration exchanged and $[\mathrm{Eu}^{3+}]$ is given by $[\mathrm{Eu(III)}]_{\mathrm{tot}}$ minus $[\mathrm{Eu}\{\mathrm{OC(III)}\}]$. Combination of Eqs. 4 and 1 results in Eq. 6, which represents the formation equation of Eu(III)-olive cake surface complexes.

$$\mathrm{Eu}^{3+} + \{\mathrm{OC(III)}\} \rightarrow \mathrm{Eu}\{\mathrm{OC(III)}\} \qquad (6)$$

The value of the formation constant for the Eu(III)-olive cake complex (β_{Eu}) can be calculated from the competition reaction constant (K) and the formation constant of the Cu(II)-olive cake complex ($\log \beta_{\mathrm{Cu}} = 5.1$). On the other hand, the conditional constant of the competition reaction (K) as well as the stoichiometry of the competition reaction is determined by linear regression analysis of the potentio-

Fig. 7 $\log \frac{[\mathrm{Eu}\{\mathrm{OC(III)}\}] \cdot [\mathrm{Cu}^{2+}_{\mathrm{aq}}]^3}{[\mathrm{Cu}\{\mathrm{OC(II)}\}]}$ as a function of $\log[\mathrm{Eu}^{3+}]$. Experimental data were obtained from potensiometric measurements in aqueous solutions containing 4 g l^{-1} olive cake 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



metric data obtained from the ionexchange experiments using Eq. 5 in its logarithmic form

$$\log\frac{[\mathrm{Eu\{OC(III)\}}]\cdot[\mathrm{Cu}_{\mathrm{aq}}^{2+}]^3}{[\mathrm{Cu\{OC(II)\}}]}=\log\mathrm{K}+2\cdot\log[\mathrm{Eu}_{\mathrm{aq}}^{3+}] \qquad (7)$$

The intercept of the line described by Eq. 7 corresponds to the logarithmic value of the reaction constant (log K) and the value of the slope corresponds to the stoichiometric factor corresponding to Eu^{3+} according to Eq. 7. Figure 7 shows the experimental data obtain in this study in a $\log([\mathrm{Eu\{OC(III)\}}][\mathrm{Cu}^{2+}]^3/[\mathrm{Cu\{OC(II)\}}]) - \log[\mathrm{Eu}^{3+}]$ diagram.

The linear regression analysis of the experimental data resulted in 2.0 ± 0.3 and 5.4 ± 0.9 for the stoichiometric factor and $\log\beta$, respectively. The slope of the curve in Fig. 7 equals to 2, indicating that the complexation and ionexchange scheme suggested is correct.

4 Conclusions

The sorption of Cu(II) on the olive cake surface takes places through the formation of inner-sphere complexes with the active sites of the surface (e.g. carboxylic and phenolic groups).

The value of the formation constant for the Cu(II)-olive cake complexes (5.1 ± 0.4) is similar to corresponding values obtained for the Cu(II)-humic acid complexes (5.6 ± 0.3), indicating on the predominant role of carboxylic and phenolic groups in the interaction of metal ions with natural organic matter derived from plants.

The competition reaction between Cu(II) and Eu(III) regarding the sorption on olive cake showed that this reaction is based on ionexchange. Furthermore, the results obtained from this study lead to the conclusion that, Cu(II) system can be used as reference in ternary systems in order to study the relative affinity of metal ions to olive cake and other surfaces. Investigations in ternary competition systems may give correct information about the relative affinity of metal ions to humic acid and useful indications about the reaction schemes.

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