Studies on the interaction of olive cake and its hydrophylic extracts with polyvalent metal ions (Cu(II), Eu(III)) in aqueous solutions

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ABSTRACT

The paper presents and discusses the chemical affinity of two different forms of natural organic matter (e.g. in solid (SOM) and soluble form (DOM)) for Cu^{2+} and Eu^{3+} ions. In the this study SOM is represented by olive cake and DOM by its hydrophilic extracts. The investigations were performed in aqueous 0.1 M $NaClO_4$ solutions at pH 6, 23 °C and under atmospheric conditions by means of potentiometry using a copper ion selective electrode and competitions reactions between the two metal ions. The experimental data were evaluated according to an "operational" approach, which is based on the charge neutralization model and the Scatchard approach. Evaluation of the data resulted in the determination of conditional formation constants (β^*), which are a measure for the chemical affinity of natural organic matter for a metal ion. For the olive cake metal ion binding the values of $\log \beta^*$ for Cu(II) and Eu(III) were evaluated to be 5.1 ± 0.3 and 5.4 ± 0.5, respectively, whereas for the hydrophilic extracts the corresponding values for the Cu(II) and Eu(III) complexes were evaluated to be 5.3 ± 0.3 and 6.3 ± 0.5, respectively. The β^* values show that natural organic matter in the two different forms presents almost similar affinity for the Cu^{2+} ion, whereas the affinity of DOM for the Eu^{3+} ion is significantly higher than the corresponding affinity of SOM. This is ascribed to the higher flexibility of DOM, which allows better coordination of its active sites around the Eu^{3+} ion.

1. Introduction

The role of natural organic matter is of fundamental importance in metal ion chemistry as natural organic matter is ubiquitous in natural aquatic systems. Natural organic matter in environmental systems can be found whether in solid (SOM, e.g. biomass by-products) or soluble form (DOM, e.g. humic acid). Depending on its distribution between the aqueous/mobile and solid/stationary phase, natural organic matter can then cause either an enhancement or decrease in metal ion transport and affect the bioavailability of metals. For the quantification of the relevant processes involved, basic knowledge of the binding capacity and the chemical affinity of the two different forms of natural organic matter (e.g. SOM and DOM) for metal ions is essential.

Olive cake is a biomass by-product of the olive oil production and is a very abundant agricultural waste in the Mediterranean region [1–4]. 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. Olive cake disposed in the environment could play, similar to organic matter derived from the decomposition of plant tis-

sues, an important role in the chemical behavior and migration of toxic impurities (e.g. heavy metals) within natural aquifer systems [5,6]. Olive cake (SOM) may increase the retardation of sorbed contaminants, whereas its hydrophylic extracts (DOM), which are soluble in the mobile/aqueous phase, enhance the mobility of pollutants in the geosphere. Olive mill waste waters and leachates from olive cake deposits will potentially percolate into groundwater and together with bounded heavy metals and metalloids they can contaminate groundwater. For the purpose of predicting the potential mobilization of heavy metals from olive cake deposits, the complex formation properties of both, the source material (e.g. olive cake) and the hydrophilic components released by olive cake deposits needs to be known. In this context, one key question is the degree of complexation properties comparability of the source material and its soluble form (e.g. hydrophilic extracts of olive cake).

On the other hand, olive cake could be used as sorbent in wastewater treatment technologies [7–10]. Removal of heavy metals from large volumes of wastewaters requires a cost effective remediation technology [11–14]. Biomasses that are by-products from other commercial processes with little commercial value represent good candidates for the development of inexpensive biosorption processes [15,16]. The major advantage of biomass by-products over microbial systems is that there is no cost of growing a sufficient quantity of bacterial or algae biomass [17].

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This paper deals with the interaction of two polyvalent metal ions (e.g. Cu(II) and Eu(III) ions) with olive cake (SOM) and its hydrophylic extracts (DOM). Cu(II) has been selected, because it can be used as an analogue of Pb(II) and Cd(II) regarding their environmental behavior and because there is extensive literature about the complexation of Cu(II) with soluble natural organic matter (e.g. humic acids) based on a wide spectrum of electrochemical [5,18–21] and spectroscopic methods [22–24]. 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 [5]. Moreover, the Cu(II) ion selective electrode has been chosen because of its stability. The competition investigations involved Eu(III) as competing ionic species, because Eu(III) exists in aquatic solutions for pH < 7 predominantly as Eu(III) aquo-ion and is often used as an analogue for trivalent actinides [25].

The aim of this study was (a) to determine the chemical affinity of olive cake and its hydrophylic extracts for Cu(II) and Eu(III) ions, (b) compare the data obtained with corresponding literature data, (c) understand the sorption mechanism and (d) assess the chemical affinity of the two different types of natural organic matter for the two different metal ions. 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 through underlying aquifers.

2. Materials and methods

All experiments were performed at room temperature ($23 \pm 2\,°C$) under atmospheric conditions in aqueous solutions at constant ionic strength ($0.1\,M\ NaClO_4$) and pH (pH 6, MES Buffer, $C_6H_{13}NO_4S·H_2O$, 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 ($CuSO_4·5H_2O$, Merck) and europium nitrate ($Eu(NO_3)_3·5H_2O$, 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 pre-treated 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 μm was selected for the adsorption experiments and was used without any further purification or other pre-treatment [26].

2.2. Hydrophylic extracts of olive cake

Separation of hydrophilic components from the solid matrix (olive cake) was performed by alkaline extraction using $0.2\,M\ NaOH$. Isolation and purification of the material was carried out by duplicate cycles of flocculation with $1\,M\ HCl$ and dissolution with $0.2\,M$ NaOH. Finally, the protonated flocculate was washed with water and freeze-dried. Tris buffer was obtained from Fluka. All substances were used as delivered and all aqueous solutions were prepared with de-ionized water.

Characterization included: (a) elemental analysis performed by Desert Analytics, (b) Fourier Transform Infra Red (FTIR) spectroscopy (FTIR spectrometer 8900, Shimadzu), (c) UV/Vis spectroscopy (UV 2401 PC, Shimadzu), (d) determination of inorganic impurities by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (7500 Shimadzu) after digestion in 60% nitric acid, (e) molecular mass distribution was carried out by Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) and (f) molecular size distribution by Asymmetrical Flow Field–Flow Fractionation (AFFFF). The data obtained from corresponding measurements are described elsewhere [27]. Generally the size distribution of the DOM particles is very similar to the size distribution of humic acids and extends up to $9000\,g\,mol^{-1}$ with a maximum at $1000\,g\,mol^{-1}$.

2.3. 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/reference solutions of constant ionic strength ($0.1\,M\ NaClO_4$) before and after each measurement.

The Cu(II) interaction with natural organic matter was performed by batch type experiments in PE vessels. Defined amounts of a Cu(II) stock solution ([Cu(II)] = 0.1 M and 1 mmol l^{-1} MES) were added to 25 ml aqueous solutions, which contained $0.1\,g\,l^{-1}$ natural organic matter (e.g. olive cake or hydrophilic extracts of olive cake), had constant ionic strength ($0.1\,M\ NaClO_4$) and were buffered with 1 mmol l^{-1} MES to pH 6. The addition of the Cu(II) stock solution to the 25 ml aqueous solutions resulted in batches of variable total Cu(II) concentration (0.4 mmol l^{-1} < [Cu(II)] < 3.85 mmol l^{-1}) and constant amount (2.5 mg) of natural organic matter. After two days equilibration the concentration of the non-complexed Cu(II) ion was determined by potentiometry using a Cu(II) ion selective electrode. Potentiometric titrations were also performed in blank samples of similar composition with the aqueous test solutions but without natural organic matter and were used as reference/control measurements. All experiments were performed in duplicate and the mean values have been used for data evaluation.

2.4. Competition reactions

Competition reactions between Cu(II) and Eu(III) with natural organic matter were carried out by batch type experiments in PE vessels by addition of a defined amount of a Eu(III) stock solution, to a suspension containing natural organic matter (e.g. olive cake or hydrophilic extracts of olive cake) loaded with Cu(II) ions ($1.6\,10^{-2}$ mol Cu(II) per g natural organic matter). The batch experiments included several mixtures of 25 ml aqueous solution containing constant amount of natural organic matter ($0.1\,g\,l^{-1}$) and variable Eu(III) concentration (0.24 mmol l^{-1} < [Eu(III)] < 2.43 mmol l^{-1}). The aqueous solutions had a constant ionic strength ($0.1\,M\ NaClO_4$) and were buffered with 1 mmol l^{-1} MES at pH 6. After three days equilibration, the pH was measured and the amount of Cu(II) ion exchanged determined.

3. Results and discussion

3.1. Interaction of SOM and DOM with Cu(II)

The binding of metal ions to natural organic matter may occur through non-specific electrostatic interactions and complexation due mostly to carboxylic groups. In contrast to alkali and earth alkali metal ions (e.g. Na$^+$, Ca^{2+}), which interact with natural organic matter mainly through coulombic attraction, d- and f-block element cations are bound to natural organic matter through
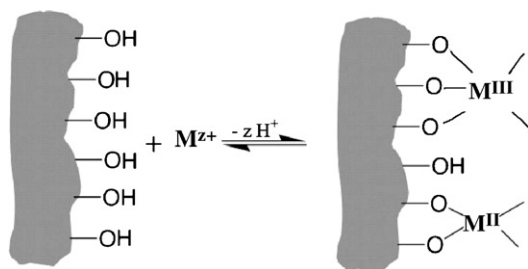
Fig. 1. Schematic illustration of the interaction of M(z) ions with natural organic matter.

inner-sphere complexation due to carboxylic and phenolic groups. The relatively strong binding of the latter indicates polydentate complex formation. The evaluation of experimental data regarding the interaction between metal ions can be performed using sophisticated mechanistical approaches (e.g. NICA-Donnan Model) or simple operational models (e.g. charge neutralization model) [28]. In this study we have used for data evaluation an operational model that combines charge neutralization model and the Scatchard approach, because the experiments were performed at constant pH and amount of natural organic matter. In our approach, we assume charge neutralization of a Cu^{2+} ion by the surface carboxylic groups, that present higher affinity for the metal ion than the perchlorate (ClO_4^-) anion, which is the anion of the background electrolyte.

At pH 6 the Cu^{2+} aquo-ion is the predominant Cu(II) species in solution [25] and interacts with the carboxylic groups of the natural organic matter to form stable complexes [28,29]. The involvement of carboxylic groups in metal binding was confirmed using various spectroscopic methods and by comparing the spectra of the metal ion loaded with natural organic matter with these for the protonated form [28,26]. Schematically binding of metal ion by the natural organic matter surface is illustrated in Fig. 1. Hereby the surface of the natural organic matter particles acts as cation exchanger, which binds a Cu^{2+} ion through two active sites. In terms of a chemical equation, the interaction of the Cu(II) ion with natural organic matter is described by Eq. (1)
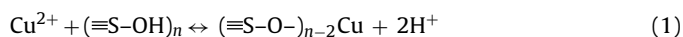
$$Cu^{2+} + (\equiv S\text{–}OH)_n \leftrightarrow (\equiv S\text{–}O\text{–})_{n-2}Cu + 2H^+ \tag{1}$$

and the corresponding equilibrium constant is given by Eq. (2)

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

at constant pH (pH 6) Eq. (2) can be reformulated to Eq. (3):

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

where β^* is the conditional formation constant, $[(\equiv S\text{–}O\text{–})_{n-2}Cu]$ 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 pH (pH 6) is negligible. $[(\equiv S\text{–}OH)_n]$ is defined as the total concentration of active sites on the solid surface minus the complexed active sites ($[(\equiv S\text{–}OH)_n] = [(\equiv S\text{–}OH)_{tot}] - [(\equiv S\text{–}O\text{–})_{n-2}Cu]$). The total concentration of active sites ($[(\equiv S\text{–}OH)_{tot}]$) corresponds to the total number of the surface sites available for complexation (Scatchard approach) and is determined using the Langmuir isotherm. The total concentration of active sites for the olive cake (SOM) is determined to be 0.3 meq g^{-1}, whereas the corresponding value for the hydrophilic extracts (DOM) is found to amount 0.5 meq g^{-1}. The latter value is close to corresponding values given in literature for humic acids [30]. Taking the logarithm and rearranging Eq. (3)

results in Eq. (4)

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

The intercept of the line described by Eq. (4) 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. Fig. 2 presents the experimental data in a $\log([(\equiv S\text{–}O\text{–})_2Cu]/[(\equiv S\text{–}OH)_n])$-$\log[Cu^{2+}]$ diagram. Linear regression analysis of the experimental data obtained at pH 6 based on Eq. (4) shows a good linearity of the experimental data ($R = 0.98$) and results in a slope of 0.95 ± 0.1, which close to 1, proving the theoretical approach.

The values of the $\log\beta^*$ for the binding of the Cu^{2+} ion by the olive cake (SOM) and its hydrophilic extracts (DOM) have been evaluated to amount 5.1 ± 0.3 and 5.3 ± 0.3, respectively, demonstrating almost similar affinities of the two different forms of natural organic matter for the Cu^{2+} ion. This value is very close to the value given in literature for the corresponding humic acid complex ($\log\beta^*_{Cu-HA} = 5.6$) [28,30], indicating that the chemical affinity of olive cake and its hydrophilic extracts for Cu(II) is very similar to the chemical affinity of humic acid for the metal ion and that the interaction between the Cu(II) ions and the different types of natural organic matter occurs via the same type of active sites (e.g. carboxylic groups) and mode of binding [28].

3.2. Interaction of SOM and DOM with Eu(III)—competition reactions between Cu(II) and Eu(III) ions

Competitive experiments between metal ions that can bind differently to natural organic matter could result in data useful to describe and predict metal ion behavior in natural multicomponent systems. In order to investigate and assess the sorption affinity of the two different types of natural organic matter for the Eu(III) ion, ion exchange experiments were performed at pH 6 under defined conditions using the Eu(III) ion as competing cationic species. The advantage of using the Eu(III) ion is that this element is environmentally relevant, because it is used as homologue for trivalent actinides and its aqueous chemistry is extensively investigated and well understood [25,31]. At pH 6, Cu(II) and Eu(III) cations exist predominantly as non-hydrolyzed aquo-ions in solution and bind
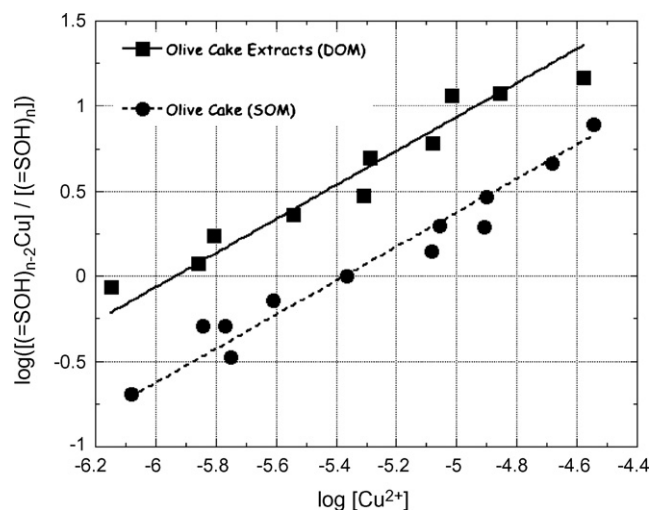

Fig. 2. $\log([(\equiv S\text{–}O\text{–})_2Cu]/[(\equiv S\text{–}OH)_n])$ as a function of $\log[Cu^{2+}]$. Experimental data were obtained from potentiometric measurements in aqueous solutions containing 0.1 g l^{-1} natural organic matter, 0.1 M NaClO$_4$ as background electrolyte and carried out at 23 ± 2 °C under normal atmospheric conditions.
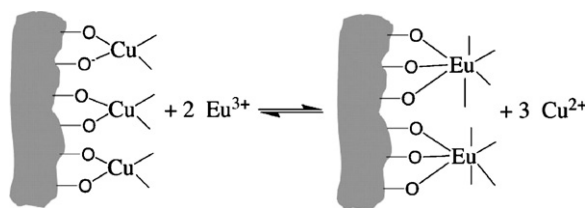
Fig. 3. Schematic illustration of the ion exchange reaction between Cu(II) and Eu(III) on the natural organic matter surface.

to natural organic matter due mostly to carboxylic groups forming inner-sphere complexes [28].

At the beginning of the competition experiment the natural organic matter is loaded with Cu(II), but after stepwise addition of the Eu^{3+} ion, Cu(II) adsorbed is replaced by the competitor metal ion [26,30,32]. This occurs because the amount of natural organic matter ($0.1\,g\,l^{-1}$) and hence the number of complexing sites in the system remains constant. Generally (assuming charge neutralization) a mol Cu(II) is replaced by 2/3 moles of the competitor metal ion. The competition reaction, which is schematically presented in Fig. 3, is a cation exchange reaction described by Eq. (5):

$$((\equiv S-O-)_{n-2}Cu)_3 + 2Eu^{3+} \leftrightarrow 3Cu^{2+} + (\equiv S-O-)_{n-3}Eu)_2 \tag{5}$$
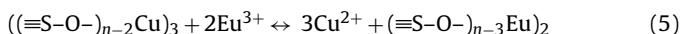
The corresponding constant for the competition reaction is defined as:(6) $K = \frac{[((\equiv S-O-)_{n-3}Eu)_2] \cdot [Cu^{2+}]^3}{[((\equiv S-O-)_{n-2}Cu)_3] \cdot [Eu^{3+}]^2}$ where $[Cu^{2+}]$ and $[Eu^{3+}]$ are the concentrations of the Cu(II) and Eu(III) aquo-ions, respectively, $[(\equiv S-O-)_{n-2}Cu]$ the concentration of the surface sorbed Cu(II) and $[(\equiv S-O-)_{n-3}Eu]$ the concentration of the surface sorbed Eu(III). $[(\equiv S-O-)_{n-3}Eu]$ is assumed to be 2/3 of the concentration of Cu(II) exchanged. Combination of Eq. (5) with (1) results in Eq. (7), which represents the formation equation of Eu(III)–natural organic matter complexes.

$$Eu^{2+} + (\equiv S-OH)_n \leftrightarrow (\equiv S-O-)_{n-3}Eu + 3H^+ \tag{7}$$
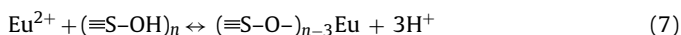
The value of the conditional formation constants for the Eu(III)–natural organic matter complexes (β^*_{Eu}) can be calculated from the competition reaction constant (K) and the conditional formation constant of the Cu(II)–natural organic matter complex ($\log\beta^*_{Cu-SOM}=5.1$ and $\log\beta^*_{Cu-DOM}=5.3$) at pH 6. 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 ion exchange experiments using the logarithmic form of Eq. (8):

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

$$\tag{8}$$

The intercept of the line described by Eq. (8) corresponds to the logarithmic value of the reaction constant ($\log K_{Cu-Eu}$) and the value of the slope corresponds to the stoichiometric factor of Eu^{3+} according to Eq. (8). Fig. 4 shows the experimental data obtained from the Eu(III)–Cu(II) system for the two different forms of natural organic matter in a $\log([((\equiv S-O-)_{n-3}Eu)_2] \cdot [Cu^{2+}]^3/[((\equiv S-O-)_{n-2}Cu)_3]) - \log \cdot [Eu^{3+}]$ diagram. The slope of the curves in Fig. 4 equals to 2, indicating that the complexation and ion exchange scheme suggested is correct. Furthermore, linear regression analysis of the experimental data results in equilibrium constants ($\log K_{Eu-DOM}=-3.3\pm0.3$ and $\log K_{Eu-SOM}=-4.5\pm0.5$) for the competition reactions, which in combination with the conditional formation constant of the Cu(II)
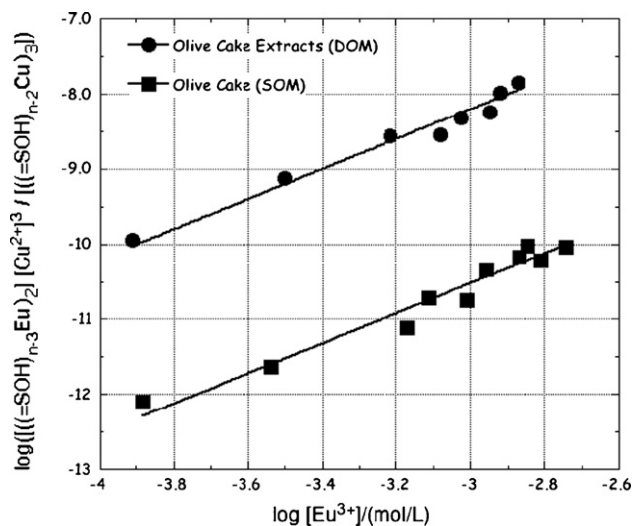

Fig. 4. $\log([((\equiv S-O-)_{n-3}Eu)_2] \cdot [Cu^{2+}]^3/[((\equiv S-O-)_{n-2}Cu)_3]))$ as a function of $\log[Eu^{3+}]$. Experimental data were obtained from potentiometric measurements in aqueous solutions containing $0.1\,g\,l^{-1}$ natural organic matter loaded with Cu(II) ions at different Eu(III) ion concentration, $0.1\,M\,NaClO_4$ as background electrolyte and carried out at $23\pm2\,°C$ under normal atmospheric conditions.

surface complex, leads to the calculation of conditional formations constants $\log\beta^*_{Eu-DOM}=6.3\pm0.5$ and $\log\beta^*_{Eu-SOM}=5.4\pm0.5$ for the Eu(III)–SOM and Eu(III)–DOM complexes, respectively.

The value of $\log\beta^*_{Eu-DOM}=6.3$ is very close to the value given in literature for the corresponding humic acid complex ($\log\beta^*_{Eu-HA}=6.2$) [30,33], indicating that the chemical affinity of hydrophilic extracts for Eu(III) is very similar to the chemical affinity of humic acid for the metal ion. On the other hand the chemical affinity of SOM for the Eu(III) ion is significantly lower and very similar to the affinity of the hydrophilic extracts of olive cake and humic acids for the Cu(II) ion. The higher affinity of the hydrophilic extracts of olive cake and humic acid particles/aggregates (DOM) [34] compared to olive cake (SOM) is ascribed to the flexibility of the former, which allows better coordination of the active sites (e.g. carboxylic groups) around the Eu^{3+} cation, as indicated in Fig. 5.

The relative strong interaction of Cu(II) and Eu(III) cations could have significant implications on the chemical speciation and mobility of these and homologue metal ions in natural systems, particularly if increased amount of natural organic matter is present. In the case of SOM (e.g. olive cake stacks) the interaction with metal ions will result in non-mobile surface complexes retarding their migration. However, in long-term und under certain conditions, which will lead to metal ion release, SOM may become a significant source of metal ion pollution. On the other hand, the ubiquitous presence of the hydrophilic extracts (particularly close to natural organic matter deposits) and their similar or even higher affinity for metal ions will result in the formation of colloidal complexes between DOM and metal ions. These complexes, which are signif-
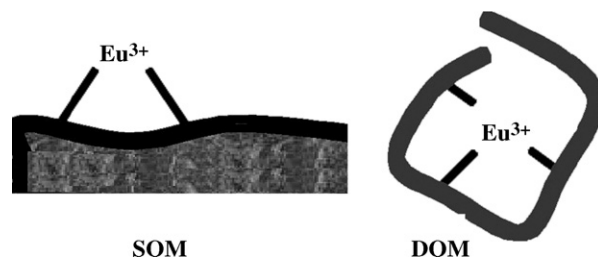

Fig. 5. Schematic illustration of the interaction of SOM and DOM with the Eu(III) ion.

icantly stable and increase the concentration of metal species in solution, will enhance their mobility and bioavailability in natural environments.

Regarding the potential use of natural organic matter (e.g. olive cake) for metal ion uptake beyond laboratory scale, the impact of DOM on the process efficiency must be taken into account. Most probably like most of the available biomass by-products olive cake will require some degree of physical and chemical pre-treatment to enhance its stability and metal-binding capability [35]. Indeed, further experimental work and measurements in real systems are needed to specifically understand and quantify the impact of SOM and DOM on both, the behavior and migration of metal ions in the geosphere, and their removal from wastewaters by natural organic matter-mediated partitioning.

4. Conclusion

In summary, the investigation of the complex formation properties, which was performed in parallel (under similar conditions) for the olive cake and its hydrophilic extracts, has shown that:

(1) The affinity of olive cake and its hydrophilic extracts for the Cu(II) ion is close to one another and similar to the chemical affinity of humic acids for the respective metal ion.
(2) The similar affinity of DOM (e.g. hydrophilic extracts of olive cake and humic acids) and SOM (olive cake) for the Cu(II) ion indicates that the same type of active sites (e.g. carboxylic groups) is responsible for the metal ion binding by various types of natural organic matter.
(3) The hydrophilic extracts (DOM) present higher affinity for the trivalent Eu^{3+} ion than the olive cake (SOM).
(4) The higher flexibility of DOM allows most probably better coordination of its active sites around polyvalent metal ions (increased charge and coordination number).
(5) Because of the similar or even higher affinity of the hydrophilic extracts (DOM) for polyvalent metal ions, DOM will play predominant role in the transport of metal ions from olive cake deposits into the aquatic environment, and determine the efficiency of wastewater treatment technologies based on natural organic matter-mediated separation.

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