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Kinetic approach to heavy metal mobilization assessment in sediments: choose of kinetic equations and models to achieve maximum information

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Abstract

Studies of trace metal mobilization in sediments are generally performed using sequential extraction schemes at equilibrium. In the present work, a kinetic fractionation of trace metals in sediments has been developed to assess that information. The extraction rate data have been obtained using a single extraction scheme with EDTA and following a protocol previously optimized. Two kinetic equations and two kinetic models were used to fit the experimental data. The *two constants equation* fits well the extraction rate data used in this work but does not present any physico-chemical meaning. The *diffusion model* and the *two first-order reactions model* allow determining which parameter (the reaction between the metal M and the EDTA or the diffusion of the complex M/EDTA) is rate limiting in the trace metal extraction by EDTA. It appears that the *two first-order reactions model* is more efficient than the *diffusion model* to fit the present extraction rate data so it can be deduced that the diffusion of the complex M/EDTA is not the limiting step of the trace metal extraction by EDTA in estuarine sediments. In a second part, relationships between the fraction of metals determined with the two first-order reactions model and the sediments composition were established.

Keywords: EDTA; Heavy metals; Kinetic extraction models; Metal fractionation

1. Introduction

Sediments are usually considered as a sink for trace metals but they can also become a source under certain conditions. Then, trace metals are able to move towards the water column or accumulate in plants and, consequently, contaminate the food chain. The reactivity of trace metals in sediments, in direct relation with their physico-chemical form and localization in different sediment components, is the main parameter ruling their bioavailability and mobility. The determination of the total concentration of metal ions in sediments does not give sufficient information about mobility and bioavailability of trace metals. Therefore, various approaches have been used to quantify the different forms of metals in sediments that can have significance for assessment of the metals mobility.

Sequential extraction schemes are commonly used to describe the distribution of trace metals in soils or sediments [1–3]. These methods consist of using different chemical reagents for the extraction of trace elements in a specific sediment or soil compartment resulting in their quantification in the extraction phase at equilibrium. However, these protocols have been criticized by many authors [4–6] pointing out various pitfalls including the lack of specificity of the reagents used and the occurrence of re-adsorption of metals ions af-

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Table 1
Chemical characteristics of sediments sampled in "Ria de Aveiro"

Sediment	Organic carbon (g/kg)	Organic matter (g/kg)	$CaCO_3$ (g/kg)	Fe (g/100g)	Cu (mg/kg)	Cd (mg/kg)	Pb (mg/kg)
I	51.9	89.3	4	3.94	176.6	9.21	218.2
II	43.4	74.6	6	0.478	29.8	1.08	47.3
III	31.6	54.4	4	2.58	33.8	2.15	53.6

ter release. Furthermore, the reactions in the environment are rarely at equilibrium as is considered in these protocols; instead, they are in a state of continuous change because of the dynamic nature of environmental processes [7,8]. Consequently, methodologies involving kinetic fractionation of trace metals in sediment have been developed.

The kinetic approach is based on the study of the desorption fluxes of the metals from the sediment caused by the action of one specific added chemical reagent. This time-based fractionation highlights the differences in the lability of complexes with similar stability constants. Indeed, mobilization and bioavailability of metal ions depend not only on their concentrations in sediment, but also on the sediment capacity to release those metal ions. The kinetic approach has already been used to study the short-term kinetics of the EDTA extraction of copper and zinc from contaminated sediments [9]. Researchers interested in metal speciation in soils [10,11] and in sediments [12,13] have already preferred the application of kinetic methodologies rather than the traditional sequential extraction schemes. The feasibility of the kinetic extraction of Cd^{2+}, Cu^{2+} and Pb^{2+} from contaminated sediments using EDTA as the complexing agent has been previously studied and an optimized experimental protocol has been proposed [13]. This same protocol has also been used here to obtain the kinetic extraction curves for different metal ions.

The time-based metal extraction curves are commonly used to distinguish two or more fractions of metal based on differences of extraction or desorption rates. Lehman and Harter [14] have directly used the extraction curves without any model fitting to study the copper desorption from enriched sediments. However, kinetic models and kinetic equations have been applied to the metal extraction data in order to identify both qualitatively and quantitatively the various fractions of metals [9,11,15–17]. Nevertheless, it is frequent to find simple fitting equations used as kinetic models, without any associated conceptual support with a physical meaning. Moreover, kinetics models are sometimes used with many inaccuracies namely wrong approximations.

The aim of the present work is to achieve a fractionation of Cu, Cd and Pb in estuarine sediments using time-based extraction experiments with EDTA as the added extractant. Two kinetic models adapted to the sediment system (*diffusion model* and *two first-order reactions model*) and two commonly used empirical kinetic equations are presented and inaccuracies related to their utilization by other authors are pointed out. The EDTA extractions curves of Cu, Cd and Pb were initially fitted using the two kinetic equations. Secondly, the *diffusion model* and the *two first-order reactions model* were applied to the experimental data and the results evaluated in terms of the effective information regarding the mobilization of the studied heavy metals in sediments. Finally, relationships between the fractions of metal determined with the *two first-order reactions model* for the various sediments under study were considered and the influence of the sediment composition on the metals fractionation was evaluated.

2. Materials and methods

2.1. Sampling and sample treatment

Sediments were collected from a contaminated coastal lagoon, "Ria de Aveiro", located in the West Northern coast of Portugal at three different sites (I, II and III) with distinct metal concentrations (site I closer to the discharge of an industrial effluent). A plastic trowel and sampling bags or plastic boxes, previously acid washed, were used to collect samples from the superficial layer (ca. 10 cm) of sediments covered by approximately 20 cm of water. Then, the sediment samples were dried at 50 °C and sieved with a 200 μm mesh sieve. The content in organic carbon measured as the total organic carbon, organic matter, $CaCO_3$, and total Fe, Cu, Cd and Pb of the sediments have been determined in the INRA laboratory (Laboratoire d'Analyse des Sols – Arras, France) and are presented in Table 1.

2.2. Extraction rate data

The extraction rate data of metals from sediments were obtained using the following protocol [13]: several flasks, each containing 6.0 g of sediment and 40.0 mL of the extracting solution (0.05 M EDTA, pH 6.0), were stirred with an end-over-end shaker for different time periods (5 min to 24 h). Samples were then filtered through a 0.45 μm cellulose acetate membrane (Millipore). For longest extractions times, the suspensions were centrifuged for 10 min at 6000 rpm before filtration. The pH was recorded and solutions were stored at 4 °C before analysis by air–acetylene flame-atomic absorption spectrometry (F-AAS). For each sediment, four replicates of the extraction procedure were made. All reagents were of analytical-reagent grade and purchased from Merck. All experiments were performed at room temperature (ca. 20 °C).

2.3. Determination of the concentration of metals

The concentration of metals, Cd, Cu, Pb and Fe, extracted with EDTA, was measured with a Varian (Palo Alto, CA, USA) Spectra 250 Plus FAAS. Instrumental calibration was performed with standard solutions prepared from 1000 ppm Titrisol standards (Merck) and ultra-pure water (Milli-Q system – Millipore).

3. Theorical consideration for metal extraction rate data fitting

According to Martin et al. [18], surface sediments can be considered as a heterogeneous complex mixture of dissimilar particles, generally covered by organic material and Fe-, Mn-, Al- and Si-oxides that provide a high adsorption capacity [19]. Therefore, particulate sediment may be viewed as a loose heterogeneous system. Consequently, studies of trace metal mobility in sediments may have to consider both inter- and intra-particle transfer processes.

From a physicochemical viewpoint, metal ion adsorption/desorption processes are composed of a number of basic steps, namely [20]:

- Transport to or from the adsorbent interface.
- Partial dehydration/hydration reactions.
- Surface association/dissociation reactions.

Other steps may be involved and not all the steps may be relevant in every metal ion adsorption processes.

The overall sorption rate process depends on the path leading from the initial to the final state [21]. In the present case where a porous media is considered, that path includes events that are controlled either chemically or by molecular-level mass transportation [21]. The theoretical aspects of the sorption processes, the mathematics of mass transfer and of sorption kinetics, as well as the applicability of several different approaches to real samples were reviewed by Weber et al. [21]. As these authors pointed out, the simplest way to workout experimental data is by selecting a probable rate determining step, which controls the kinetics of the overall sorption process. However, working with complex systems such as particulate sediments implies to work with very complex mathematical equations.

Various models, which consider the reaction rate or the mass transfer as rate limiting have been proposed by many authors [21]. However, the proposed models are generally very complex and the associated equations are not easily applied. In consequence, the most common models and fitting equations used to fit the extraction rate data are the *diffusion model*, the *model of multiple first-order reactions*, the *Elovich equation* and the *two constants equation* [9,15–17]. A discussion of these models and fitting equations, as well as a detailed description of inaccuracies related to their utilization, is presented in the following sections.

3.1. The diffusion model

The *diffusion model* assumes that the complexation reaction of metals by an added ligand L is fast and that the rate limiting step is the intra-particle diffusion of the complex ML [9,22]. This model is based on the second Fick's law of diffusion.

In most studies, sediment particles are assumed to be spherical [9,23] or cylindrical [16,22,24]. In fact, according to Rao et al. [25], cubic and cylindrical aggregates such as sediment particles might be considered equivalent to spherical aggregates. Therefore, in the present work, sediment particles have been assumed as spherical and the *diffusion model* was applied to the mass transportation of the ML complex from the inner parts of the spherical particle to the solution interface where the ML complex is instantaneously removed to the bulk of the solution by convection (well-stirred solution). Thus, for a spherical system, the Fick's law is mathematically expressed as [26]:

$$\frac{\partial C}{\partial t} = -D\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right) \tag{1}$$

where C is the concentration of the diffusive substance, D the corresponding diffusion coefficient, r the radius of the sediment particle and t the time.

The equations proposed by Crank [26] to describe diffusion phenomena (solutions of Eq. (1)) depend on the boundary conditions that can be associated to the structure and shape of sediment particle considered.

According to Crank [26], the total amount M_t of the complex ML (diffusive substance) entering or leaving a sphere of radius a at time t is given by:

$$\frac{M_\mathrm{t}}{M_\infty} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(\frac{-Dn^2\pi^2 t}{a^2}\right) \tag{2}$$

where M_∞ is the amount of complex ML entering or leaving the sphere after infinite time.

The boundary conditions used were:

$$\begin{array}{lll} C = 0 & r = 0 & t > 0 \\ C = C_0 & r = a & t > 0 \\ C = C_1 & 0 < r < a & t = 0 \end{array}$$

where C_0 is the constant concentration of complex at the surface of the sphere (sediment particle) and C_1 the initial uniform concentration inside the sphere.

Yu and Klarup [9] also used the above equation to fit the extraction rate data of Cu by EDTA in sediments. However, they used this model displaying only the Eqs. (1) and (2) with no indication of the boundary conditions used or any description of the physical meaning of the model. The other main problem related to the presentation of this model by Yu and Klarup [9] is the fact that they did not explain how to obtain the various constants (D, n, a) of Eq. (2). As can be seen, the relation between M_t and t is an infinite series of order n. So, prior to the adjustment of this equation to the experimental data, a finite relation between M_t and t must be found out. In the present work, Eq. (2) has been developed to $n = 10$, using for (D/a^2) the value $1.5 \times 10^{-5}\ \mathrm{min}^{-1}$. This value of (D/a^2)

has been determined by Yu and Klarup [9] and used in the present work as an estimate for typical estuarine sediments. In fact, considering $a = 200\,\mu\text{m}$ (the sediments used in the present work have been sieved with a 200 μm mesh sieve), the D value turns out to be $5.0 \times 10^{-11}\ \text{m}^2/\text{s}$. As the D values found in the literature for copper vary between 2.2×10^{-12} and $1.0 \times 10^{-10}\ \text{m}^2/\text{s}$ [27,28], it can be considered that the D value used here as an example is reasonable. Further, it has been verified that for $n > 8$, the term $1/n^2\ \exp(-Dn^2\pi^2 t/a^2)$ contributes in less than 1% to the overall value of M_t/M_∞. Hence, the following equation was derived:

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2}\left(\exp(-kt) + \frac{1}{4}\ \exp(-4kt) + \frac{1}{9}\ \exp(-9kt) + \cdots + \frac{1}{64}\ \exp(-64kt)\right) \tag{3}$$

where

$$k = \frac{D\pi^2}{a^2}$$

The main advantage of this equation is the need for only one fitting parameter with a clear physical meaning.

The most important inaccuracies found in other approaches of the diffusion model [16,22] appear when the authors consider diffusion in a cylinder sediment particle (parabolic model). According to Crank [26], the equation, which describes the diffusion in and out a cylinder is:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4}{a^2\alpha_n^2}\ \exp(-D\alpha_n^2 t) \tag{4}$$

where α_n represents the positive roots of $J_0(a\alpha_n) = 0$, with $J_0(x)$ being the Bessel function of the first kind of zero order. For small times, this equation can be simplified to:

$$\frac{M_t}{M_\infty} = \frac{4}{\pi^{1/2}}\left(\frac{Dt}{a^2}\right)^{1/2} - \frac{Dt}{a^2} \tag{5}$$

Studying metal desorption from sediments, Chen et al. [22] considered that, for the initial stages of the desorption process, Eq. (5) could be simplified to:

$$\frac{M_t}{M_\infty} = k\sqrt{t} \tag{6}$$

where k is a constant.

Jardine and Sparks [16] have also used Eq. (6) in the study of the kinetics of the potassium–calcium exchange in a multireactive soil system. However, according to Crank [26], Eq. (6) can be used only when the diffusion coefficient is not constant whereas, in their studies, Chen et al. [22] and Jardine and Sparks [16] assumed that D was constant. Moreover, these authors did not present the time range for which these equations were valid.

3.2. The two first-order reactions model

According to previous studies [9,12], the model of multiple first-order reactions gives information with real physicochemical meaning and seems to be efficient to fit extraction rate data. In this model, different first-order reactions are attributed to discrete types of binding sites available in the sediments. Thus, metals are classified into fractions associated to specific compartments of the sediment to which metals were bounded. Hence, it is assumed that there are multiple first-order reactions concurrently taking place and that their rates are independent on each other, i.e. each reaction can be described by:

$$\frac{dQ_i}{dt} = k_i(Q_i^0 - Q_i) \tag{7}$$

where Q_i represents the quantity of desorbed metal from compartment i per gram of sediment at time t, Q_i^0 represents the quantity of desorbed metal per gram of sediment in compartment i at equilibrium ($t = 24\,\text{h}$) and k_i is the rate constant of the first-order reaction for each compartment i. According to Fangueiro et al. [13], 24 h of extractions allows reaching a stationary state that can be considered as an equilibrium state. The model of multiple first-order reactions allows determining the quantity and the extraction rate of metal cations associated to each fraction.

In the present work, the model has been simplified to a *two first-order reactions model* in order to classify the metal cations present in the sediment into three fractions. Therefore, the following equations apply:

$$\frac{dQ_1}{dt} = k_1(Q_1^0 - Q_1) \tag{8}$$

and

$$\frac{dQ_2}{dt} = k_2(Q_2^0 - Q_2) \tag{9}$$

In the present model, it has been assumed that the reactions leading to desorption of each fraction are independent. Integrating Eqs. (8) and (9) for the initial conditions $Q_{1(t=0)} = 0$ and $Q_{2(t=0)} = 0$, and rearranging the solutions yields:

$$Q = Q_1^0(1 - \exp^{-k_1}t) + Q_2^0(1 - \exp^{-k_2}t) \tag{10}$$

The application of the former equation to the metal extraction rate data allows the definition of three fractions characterized as follows:

- Q_1^0 (μg/g), fraction of metal readily extractable, associated to the rate constant k_1.
- Q_2^0 (μg/g), fraction of metal less extractable, associated to the rate constant k_2.
- Q_3^0 (μg/g), fraction of metal not extractable at all. Q_3^0 is obtained by difference between the total concentration of metal in sediment Q_{tot} and the concentration extracted at equilibrium: $Q_3^0 = Q_{\text{tot}} - Q_2^0 - Q_1^0$.

Fig. 1 illustrates the interrelation of these parameters.

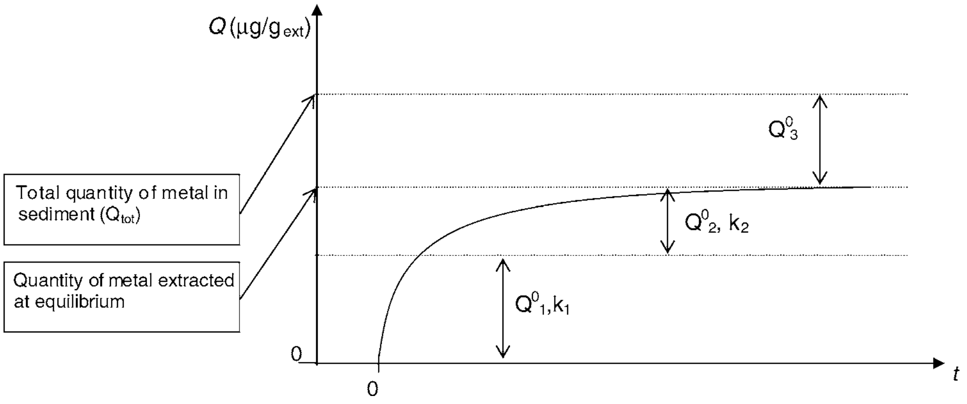

Fig. 1. Fraction of metal obtained using the *two first-order reactions model*.

3.3. Fitting empirical equations

The *two constants equation* [9,15,17,29] and the *Elovich equation* [29–32] are frequently used to fit the extraction rate data.

The *two constants equation* proposed by Kuo and Mikkelsen [15] is written as:

$$C = At^B \tag{11}$$

where C is the concentration of metal in solution, A and B are the constants and t the time. This expression can be easily linearized as follow:

$$\ln C = B \ln t + \ln A \tag{12}$$

The *Elovich equation* applied to metal extraction is expressed as:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = a\,\mathrm{e}^{-bC} \tag{13}$$

where C is the concentration of M in solution at time t, and a and b are constants [33]. This equation is based on the *Elovich model* in which a continuous and specific range of site reactivities are hypothesized [21]. According to Stucki and Lee ([34]), the integrated form of Eq. (13) is:

$$C = \frac{1}{b}\ln(1 + abt) \tag{14}$$

If $abt \gg 1$, then Eq. (14) can be simplified to

$$C = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln(t) \tag{15}$$

Thus, a plot of C versus $\ln(t)$, according to Eq. (15), should be linear with slope $1/b$ and intercept $1/b \ln(ab)$.

In both fitting equations, the meaning of the constants is very unclear. In addition, no physicochemical model is associated to the *two constants equation*. Therefore, the use of those equations is essentially empirical.

4. Results and discussion

4.1. Extraction rate data

Fig. 2 presents the extraction rate data of Cu, Cd and Pb with EDTA for sediment I. The presented results are mean values of four replicates. The curves for all three metals were similar in shape and two regions could be distinguished: a first one for short extraction times ($t < 1$ h), corresponding to faster extraction of metals and a second for higher extraction times ($1 < t < 24$ h) where the extraction kinetics is slower. This sort of extraction rate data with two well-defined extraction stages has been also observed in other studies dealing with metals in sediments [9,22,35]. The metals extracted in the first stage are the fraction easily extracted by EDTA and it is likely that this fraction is composed by the water soluble, exchangeable and weakly adsorbed metals [5,36]. In the second extraction stage, the extracted metals should be involved in complexes needing more time to dissociate.

In terms of environmental significance, the more readily extractable fraction is the most important because it may readily move to the liquid phase (pore water and water column) and contaminate the food chains. Hence, this fraction will be analyzed in more detail in next paragraph.

Table 2 shows that after 1 h, EDTA extracted more than 55% of Cd^{2+} and 70% of Pb for the three sediment samples studied. For Cu, lower extraction percentages were obtained, i.e. only ca. 35% for sediments I and III and 61% for sediment II. Hence, Cu is the slower extractable of all three metals. Differences in the bindings of these three metals should explain this dissimilarity. In a first glance, it can be said that copper establishes less labile bindings with the sediment constituents

Table 2
Percentage of metal extracted with EDTA at 1 h extraction

Metal	Sediment I	Sediment II	Sediment III
Pb (%)	91.6	74.5	73.7
Cu (%)	33.7	60.9	35.9
Cd (%)	56.9	91.3	66.0
Fe (%)	58.2	49.2	37.4

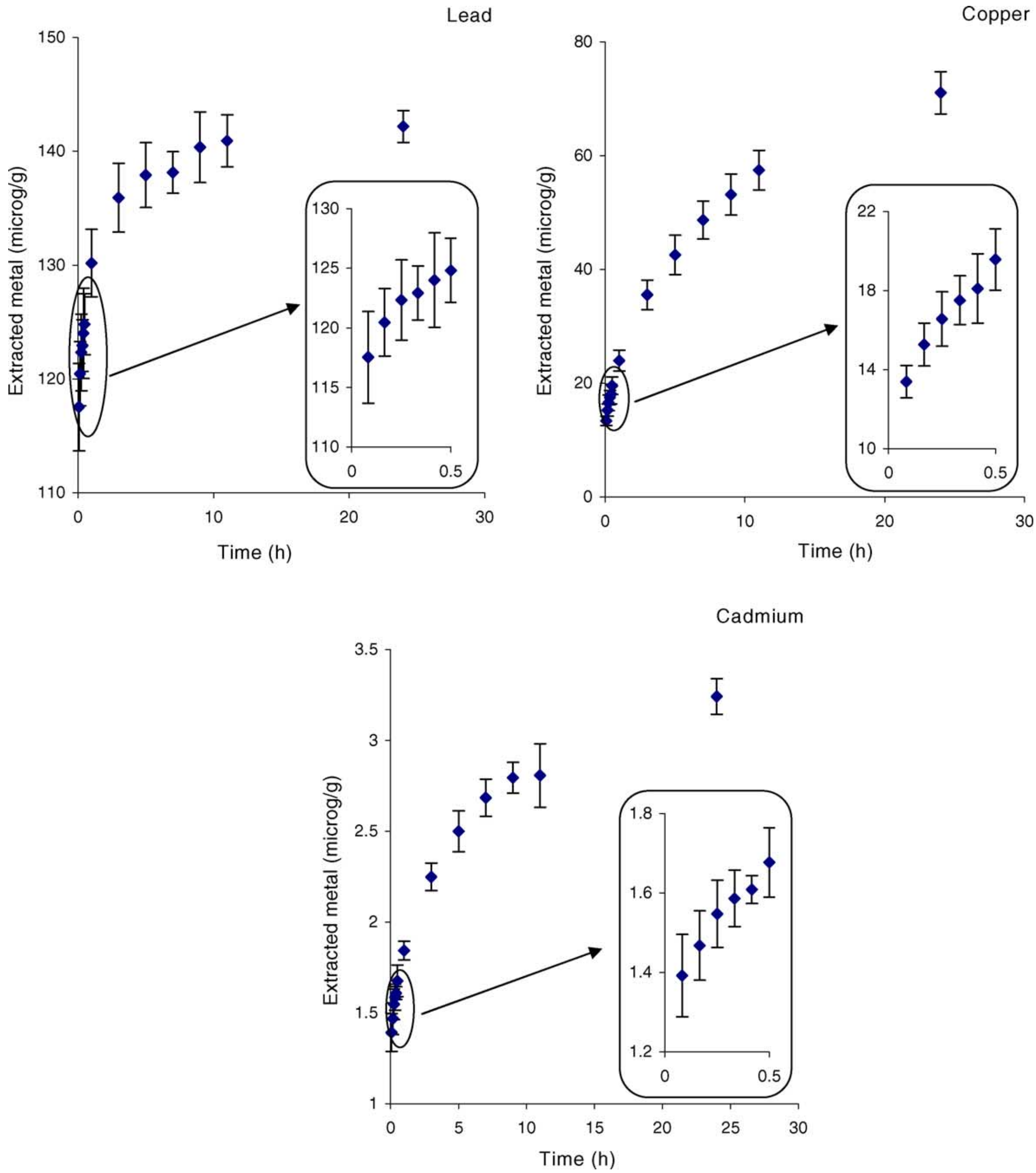

Fig. 2. Extraction rate data of Cu, Cd and Pb from sediment I with EDTA (0.05 M; pH = 6) – mean values and standard deviations of four replicates.

than lead or cadmium. According to Fan et al. [37], Cu can easily form complexes with organic matter due to high stability constants and Pb is mostly associated with the Fe and Mn oxides and carbonate. Cu and Cd can also be complexed by carbonate [38]. On another hand, EDTA is very efficient to extract cations associated to carbonates but hardly extracts metals bounded to Fe-oxide [39].

Important variations of the quantity of metal extracted in 1 h appear between sediments. For sediment II the results displayed in Table 2 are similar to those obtained by Bordas [40] with EDTA (10^{-2} M), i.e. %Cd > %Pb > %Cu. Fangueiro et al. [13] using HNO_3 as extractant also obtained identical results in sediment samples with similar quantities of organic matter and Fe as in sediment II. It is still to notice that the quantities of lead extracted by EDTA in the first hour are similar in sediments II and III but lower than in sediment I, in which more than 90% of lead was extracted. In the case of sediments I and III, copper and cadmium are less efficiently extracted than in sediment II.

It can be concluded that the efficiency of the EDTA extraction of metals in sediments depends both on the metal and on the sediment composition.

Table 3
Coefficient of correlation (r) and standard error of estimate (S.E.) associated to the *two constants* and *Elovich equations* for Cu, Cd and Pb extraction by EDTA in sediments I, II and III

Sediment	Parameter	Equation	Pb	Cu	Cd
I	r	*Two constants*	0.952	0.992	0.987
		Elovich	0.953	0.965	0.980
	S.E. (μg/g)	*Two constants*	2.77	2.45	9.87×10^{-2}
		Elovich	1.11	5.13	12.1×10^{-2}
II	r	*Two constants*	0.989	0.995	0.878
		Elovich	0.962	0.987	0.744
	S.E. (μg/g)	*Two constants*	0.444	0.292	3.88×10^{-2}
		Elovich	0.750	0.309	1.20×10^{-2}
III	r	*Two constants*	0.810	0.968	0.964
		Elovich	0.800	0.933	0.956
	S.E. (μg/g)	*Two constants*	2.18	1.05	3.74×10^{-2}
		Elovich	1.09	1.38	2.08×10^{-2}

P value was always lower than 0.0001.

4.2. Fitting of the extraction rate data

Each of the kinetic equations and models previously described was used for fitting the extraction rate data of Cu, Cd and Pb from the estuarine sediments. The statistical parameters used to access the quality of the fitting process were the standard error of estimate (S.E.), the coefficient of correlation (r), and the P value. A relatively high value of the coefficient of correlation and low values of P and of S.E. were used as criteria for the best fit. The fitting of the extraction rate data has been performed using the Sigma-Plot® software. For each sediment, the fitting parameters were calculated using the whole set of extraction data (four replicate values for each extraction time).

4.2.1. Comparison of the fitting results obtained with the kinetic equations

The *two constants equation* and the *Elovich equation* were used to fit the kinetic curves of EDTA extractions of Cu, Cd and Pb in the three sediments studied. The values of r and S.E. are presented in Table 3.

For the *two constants equation*, the mean value of r was equal to 0.948 and most values are higher than 0.95. On the other hand, with the *Elovich equation*, the mean value of r was equal to 0.920. For both equations, the P values were always lower than 0.0001. Concerning the standard error of estimate, it can be seen in Table 3 that the values of S.E. associated to the *Elovich equation* are close to the values associated to the *two constants equation* but no conclusion can be reached considering this parameter. Fig. 3 shows the experimental extraction rate data and the fitted curves obtained with the *two constants equation* and the *Elovich equation* for Cu, Cd and Pb in sediment I. It can be seen in Fig. 3 that there is a good agreement between the fitted and the experimental results for all metals in sediment I when the *two constants equation* is used in accordance to the low values of S.E. (see Table 3). However, with the *Elovich equation*, experimental and fitted results are well correlated only in two cases. Similar results have been obtained for the others sediments.

Comparing the values of r, S.E. and P obtained with the *two constants equation* and with the *Elovich equation,* it can be concluded that those two equations are quite comparable in terms of efficiency in the fitting process the curves of metal extraction by EDTA even if higher values of r were obtained with the *two constants equation*.

However, the utility of these kinetic equations has not been demonstrated. Considering that they have no clear physical meaning, they should be used only to predict the quantity of metal extracted at times not studied experimentally. Hence, the usefulness of these equations remains questionable.

4.2.2. Diffusion model

The equation of the *diffusion model* used in this work allows to determine $k = D\pi^2/a^2$, thus the coefficient of diffusion D could be calculated only if the value of the radius of the sediment particle a is known. In this work, the diffusion model has been used to fit the extraction rate data and test if diffusion of the complexe M/EDTA is the determining rate of metal extraction by EDTA in sediment.

As can be seen in Table 4, the values of r obtained with this model were generally low; the mean value for all metals and sediments studied is 0.740. Nevertheless, in all cases, the P value was always lower than 0.0001. On another hand, the standard error S.E. obtained was especially high in the case of sediment 1 and Fig. 4 clearly shows the lack of cor-

Table 4
Coefficient of correlation (r) and standard error of the estimate (S.E.) of diffusion model for Pb, Cu and Cd extraction by EDTA in sediments I, II and III

Sediment	Parameter	Pb	Cu	Cd
I	r	0.522	0.979	0.868
	S.E. (μg/g)	7.74	3.87	0.310
II	r	0.662	0.911	0.514
	S.E. (μg/g)	2.23	1.16	0.07
III	r	0.442	0.922	0.837
	S.E. (μg/g)	3.35	1.63	0.08

P value was always lower than 0.0001.

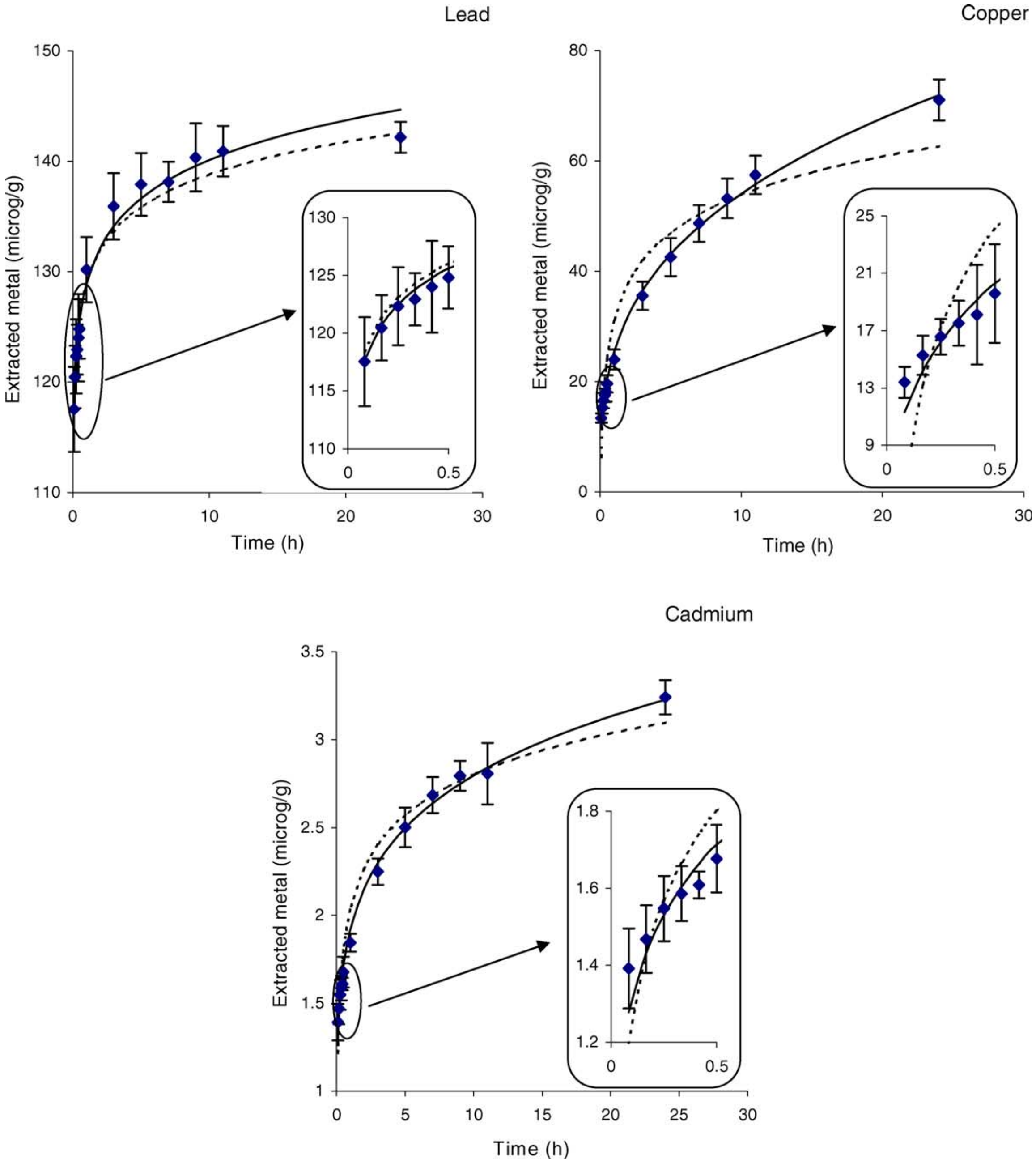

Fig. 3. Experimental (◆) and fitted extraction rate data of Cu, Pb and Cd from sediment I. *Two constants equation* (-----) and *Elovich equation* (- - - -).

relation between experimental and fitted results. Hence, it can be concluded that, in the studied sediments, the *diffusion model* is not adequate to describe the EDTA extraction of Cu, Cd and Pb in the all range of extraction times (0–24 h). Yu and Klarup [9] used the same model in a study of Cu, Zn, Fe and Mn extraction from contaminated sediments with a shorter time range (0–10 h). They showed that, in this time range, the *diffusion model* fits well only to the Fe extraction rate data.

In a previous section, it has been demonstrated that one fraction of metals was quickly extracted within the first hour. Taking this into account, the extraction curves of Cu, Cd and Pb were re-calculated for $t < 1$ h (see Fig. 5). Table 5 presents the values of r, S.E. and P. Low values of S.E. were obtained but the values of r are low too. However, the P value was in most cases lower than 0.05. The results show that, for $t < 1$ h, the *diffusion model* fits correctly the EDTA extraction rate data in most cases; exceptions are lead in sediment II and cadmium in sediment III. Consequently, it can be concluded that diffusion of the complex M/EDTA may be the rate limiting step for the extraction of metals by EDTA for short times. However, it is necessary to keep in mind that a good fitting

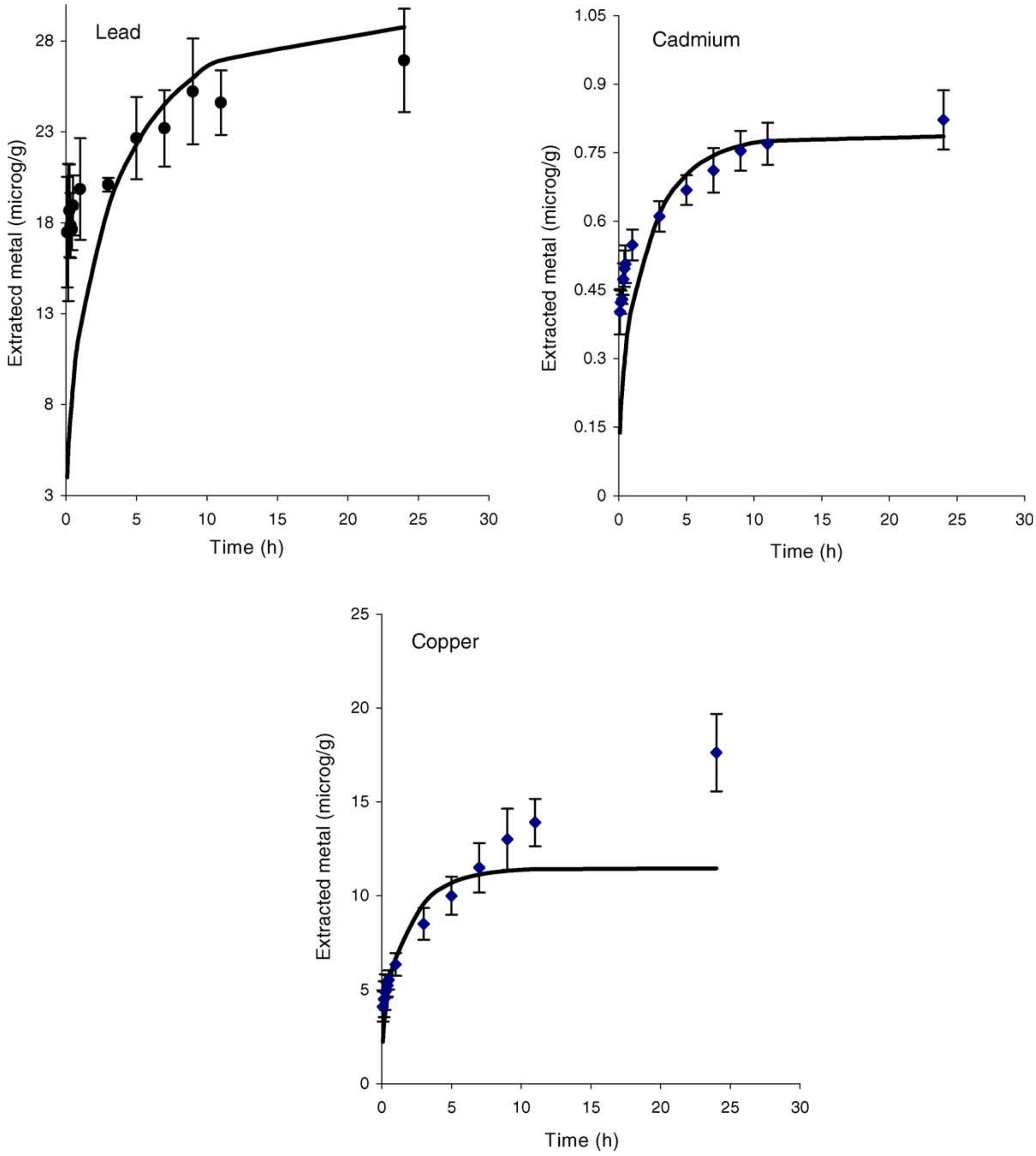

Fig. 4. Experimental (◆) and fitted (—) extraction rate data of Cu, Pb and Cd from sediment III – *diffusion model*.

is not enough evidence for the suitability of the proposed model.

4.2.3. *Two first-order reactions model*

The *two first-order reactions model* precludes two stages of metal extraction: a first one corresponding to metal quickly extracted and a second one corresponding to metal slowly extracted. As described previously, the extraction rate data present two distinct regions most probably corresponding to fractions extracted with different rates. Therefore, the extraction rate data should be well fitted with this model.

Table 6 presents the parameters Q_1^0, Q_2^0, the coefficient of correlation r and the standard error of estimate S.E. for Cu, Cd and Pb in sediments I, II and III. The values of Q_1^0 and Q_2^0 had all relative standard deviations values (R.S.D.) lower than 10% (except for Q_2^0 (Cd) in sediment II). The P value associated to each fit was always lower than 0.0001 and, as shown in Table 6, the coefficient of correlation was always higher than 0.95 (except for Cd in sediment II). The values of S.E. were low if compared with values obtained with the *diffusion model*. Fig. 6 shows representative curves calculated from the *two first-order reactions model* that fits

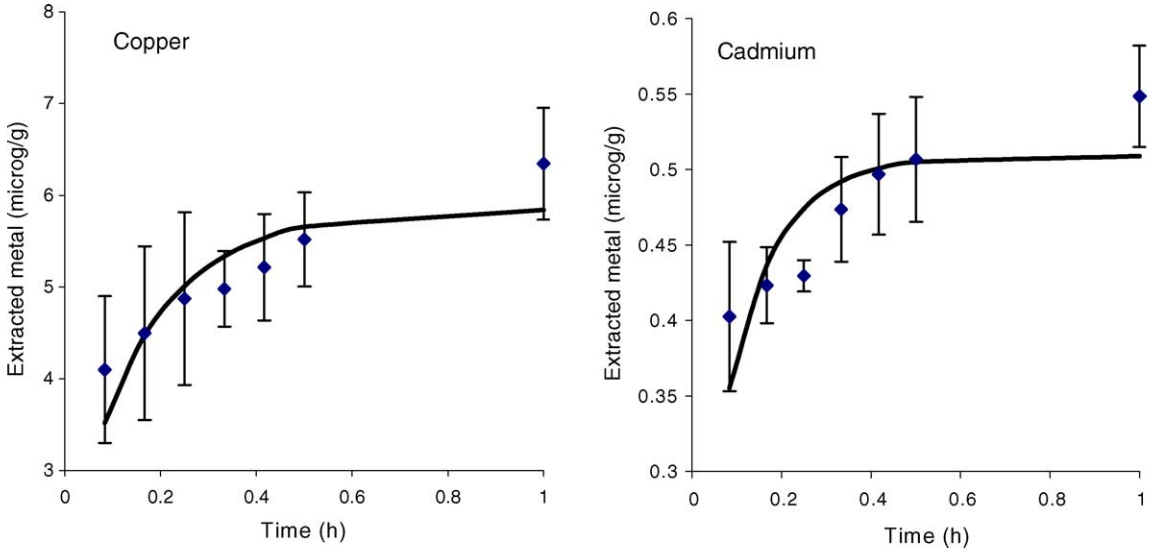

Fig. 5. Experimental (◆) and fitted (—) extraction rate data of Cu and Cd from sediment III in the time range (0–1 h) – *diffusion model*.

Table 5
Coefficient of correlation (r), standard error of the estimate (S.E.) and P value of *diffusion model* for Pb, Cu and Cd extraction by EDTA for extraction times lower than 1 h in sediments I and III

Sediment	Parameter	Pb	Cu	Cd
I	r	0.543	0.853	0.668
	S.E. (μg/g)	3.997	1.824	0.066
	P	0.0034	<0.0001	0.0001
II	r	0.136	0.629	0.674
	S.E. (μg/g)	2.236	0.737	0.044
	P	0.4903	0.0003	0.0002
III	r	0.728	0.870	0.326
	S.E. (μg/g)	0.654	0.481	0.038
	P	<0.0001	<0.0001	0.1115

well the extraction rate data of all metals. In conclusion, the two first-order reactions model can be used to describe the EDTA extraction of Pb, Cu and Cd in all studied estuarine sediments.

4.3. Interpretation of the results obtained with the two first-order reactions model

The *two first-order reactions model* allows the classification of the metals present in sediments in three fractions characterized by the rate of extraction and quantified by Q_1^0, Q_2^0 and Q_3^0. In order to facilitate the comparison of the value of Q_1^0, Q_2^0 and Q_3^0 obtained for different metals in different sediment samples, those values were re-calculated as fractions F_1, F_2 and F_3 of the total content, i.e.:

$$F_1 = Q_1^0 \frac{100}{Q_{\text{tot}}} \% \qquad (16)$$

Table 6
Q_1^0, Q_2^0 (μg/g), coefficient of correlation (r) and standard error of estimate (S.E.) (μg/g) of *two first-order reactions model* for Pb, Cu and Cd extraction by EDTA in sediments I, II and III

Sediment	Parameter	Pb	Cu	Cd
I	Q_1^0	119.6 ± 1.1	15.88 ± 0.58	1.512 ± 0.032
	Q_2^0	20.78 ± 1.22	57.50 ± 1.69	1.686 ± 0.062
	r	0.954	0.992	0.986
	S.E.	2.767	2.446	0.104
II	Q_1^0	17.69 ± 0.14	7.217 ± 0.121	0.764 ± 0.008
	Q_2^0	7.993 ± 0.343	7.043 ± 0.20	0.178 ± 0.018
	r	0.984	0.990	0.864
	S.E.	0.539	0.403	0.042
III	Q_1^0	16.83 ± 1.27	4.496 ± 0.343	0.457 ± 0.011
	Q_2^0	7.999 ± 0.433	13.63 ± 1.25	0.364 ± 0.019
	r	0.968	0.992	0.959
	S.E.	0.890	1.447	0.040

P value was always lower than 0.0001.

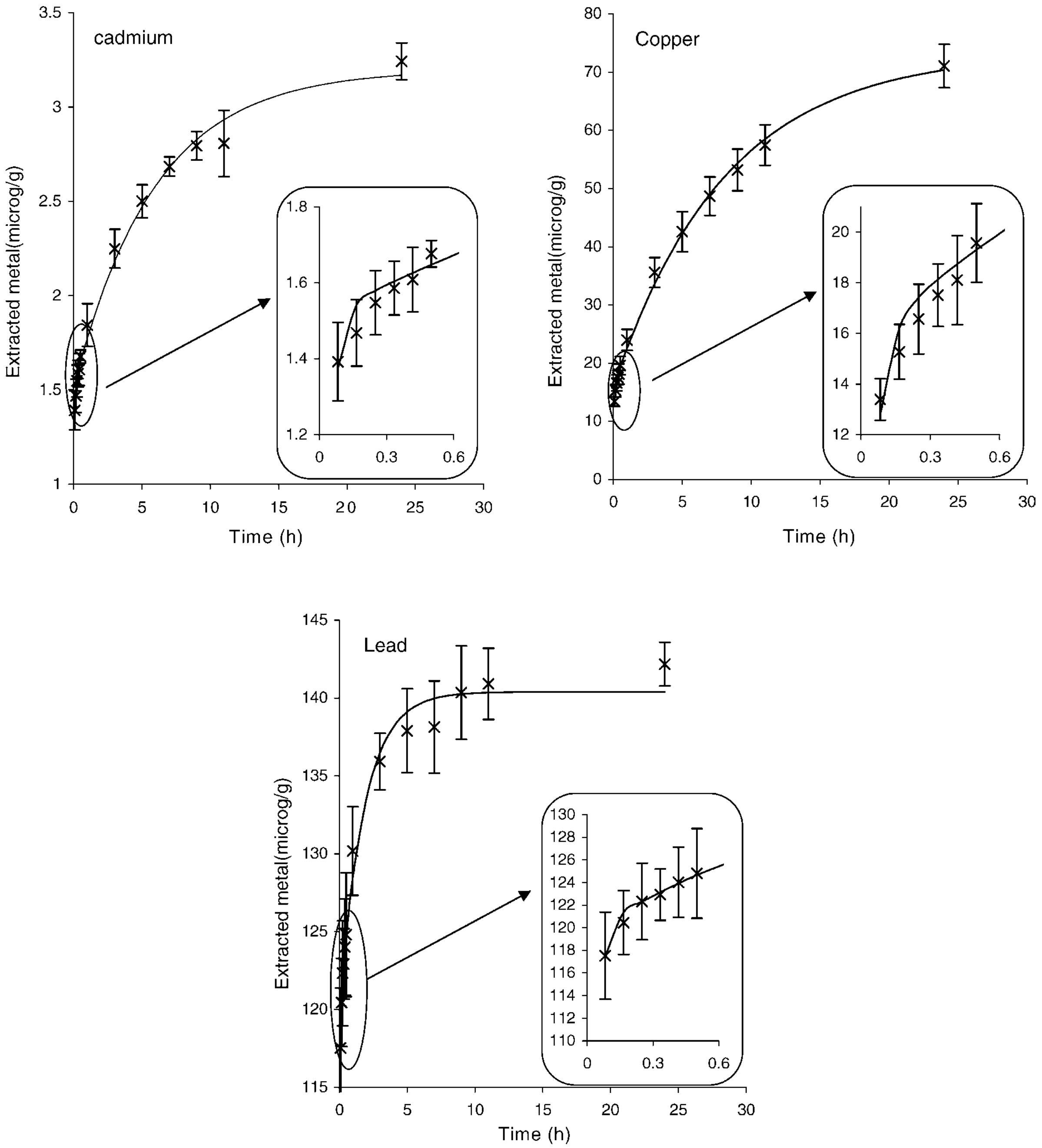

Fig. 6. Experimental (◆) and fitted (—) extraction rate data of Cu, Pb and Cd from sediment I – *two first-order reactions model*.

$$F_2 = Q_2^0 \frac{100}{Q_{\text{tot}}} \% \quad (17)$$

$$F_3 = Q_3^0 \frac{100}{Q_{\text{tot}}} \% \quad (18)$$

with Q_{tot} = total content of metal. The sediments used in this study have distinct quantities of organic mater, carbonate and Fe (see Table 1). In the next sections the distribution of Cu, Cd and Pb between the different fractions is analyzed and the influence of the amount of organic matter and Fe on the mobility of metals is considered.

4.3.1. Distribution of Cu, Cd and Pb between F_1, F_2 and F_3 in the sediments studied

As shown in Fig. 7, copper has the same distribution between F_1, F_2 and F_3 in all sediments: F_1 and $F_2 < F_3$. Furthermore, fraction F_3 always represented ~50%. So it can be inferred that, in all cases, copper is slowly extracted by EDTA and only about one half of the total content is extracted.

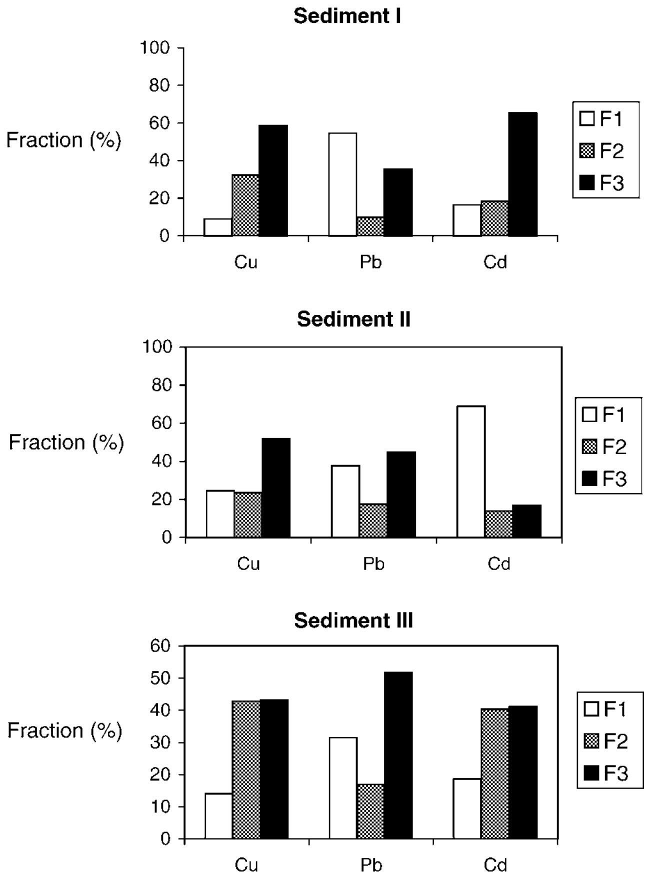

Fig. 7. Distribution of copper, lead and cadmium between F_1, F_2 and F_3 in sediments I, II and III.

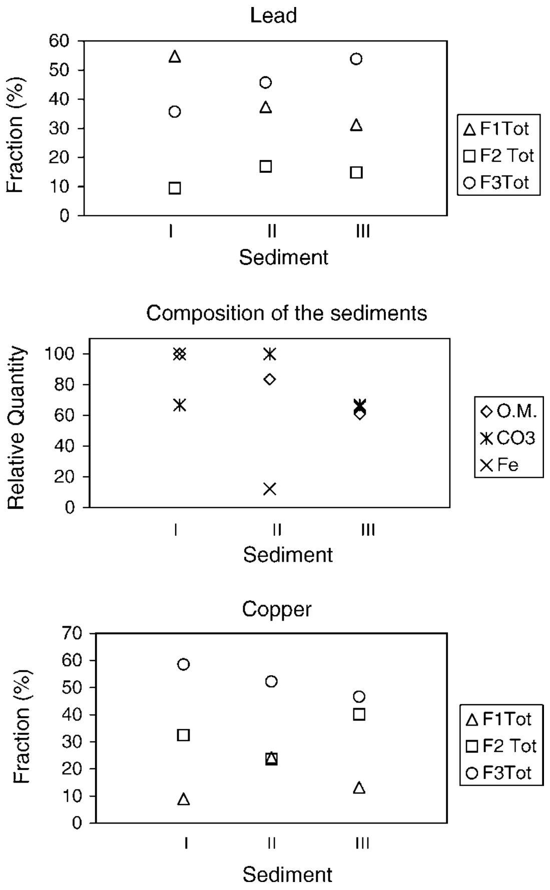

Fig. 8. Influence of organic matter, carbonate and Fe on the mobilization of Cu and Pb by EDTA; the fraction Fn are expressed in % and the total amounts of metal. Organic matter (OM), carbonate CO_3 and Fe are expressed relative to their highest amounts.

The fraction F_2 of lead was always lower than F_1 or F_3 and the fraction F_3 represented between 36 and 53% of the total contents. Consequently, the extraction of lead by EDTA is faster than that of copper (F_2 very low). The results for cadmium do not allow any general conclusion because the distribution in sediment II is much different from the ones obtained for the other two sediments. In fact, cadmium is usually considered as an easily extractable metal due to the low stability constants and high lability of the complexes formed with various natural ligands [41]. Thus, the distribution observed in sediment II seems to be the more “usual”.

In all three sediments studied, F_1 (Cu) was always lower than F_1 (Cd) or F_1 (Pb) and F_2 (Cu) is always higher than F_2 (Cd) or F_2 (Pb). Therefore, Cu is the metal more slowly extracted by EDTA. In terms of bindings, it may be assumed that copper is more strongly bounded to the sediment than lead or cadmium. Polyák and Hlavay [42] reached the same conclusion by comparing the bindings of copper and lead to sediments.

4.3.2. Influence of the sediment composition on copper and lead extraction by EDTA

Organic matter, carbonate and Fe-oxide can complex or adsorb metals in sediments and consequently have a direct influence on their extraction by a complexing agent such as EDTA. Relationships between the distribution of Cu, Cd and Pb between F_1, F_2 or F_3 and the amount of organic matter, carbonate or Fe in sediments may be established. The results obtained in this work allow considering only the case of Pb and Cu.

4.3.2.1. Case of Pb. The distribution of Pb between F_1, F_2 and F_3 and the relative concentrations of organic matter, carbonate and Fe (relative to the highest value of each parameter) are plotted in Fig. 8 for each sediment.

Some correlations can be made. For instance, when the amount of organic matter decreases, F_3 increases and F_1 decreases. Therefore, F_1 is directly correlated to the amount of organic matter while F_3 is inversely correlated. Concerning F_2, this fraction is apparently correlated directly to the carbonate content and inversely correlated to the Fe content. Consequently, EDTA readily extracts Pb in sediments rich in organic matter but with low concentrations of carbonate and Fe-oxides.

These considerations suggest that the fraction F_1 includes mainly Pb complexes with organic ligands, and that the fraction F_2 consists of Pb bounded to carbonate.

It has been already shown that Pb is strongly adsorbed by Fe-oxide [37]. So, it may be assumed that fraction F_3 includes Pb species with that type of bindings, i.e. Pb bounded to Fe-oxides, even though no immediate correlation between F_3 and the amount of Fe could be established.

4.3.2.2. Case of Cu. The distribution of Cu between F_1, F_2 and F_3 were also plotted in Fig. 8. For this metal cation, the fraction F_1 is inversely correlated to the Fe content and directly correlated to that of carbonate. Therefore, it can be presumed that the fraction F_1 is mainly composed by Cu bounded to carbonate. It is still to notice that in Section 4.2.2, it has been seen that in sediments I and III, the extraction of Cu by EDTA is rate limited by diffusion of the complex M/EDTA in the first hour of extraction that corresponds to the fraction F_1 of metal. This suggests that the break Cu-carbonate binding is fast enough to be not the rate limiting step of the extraction. The fraction F_1 and F_2 are inversely correlated so, the fraction F_2 is directly correlated to the Fe content and inversely correlated to that of carbonate. Consequently, the fraction F_2 should be mainly composed by Cu bound to Fe-oxides.

On the other hand, the fraction F_3 is directly correlated to the amount of organic matter suggesting that the fraction F_3 is mainly composed of Cu bound to organic matter. This conclusion is in accordance with published data [37].

5. Conclusion

Kinetic extractions of metals from estuarine sediments appear to be an efficient tool to study trace metals fractionation. Generally, two stages are distinguishable: one, for short extraction times, corresponding to faster metal extraction and a second where the extraction kinetics is lower.

The *two constants* and *Elovich* equations have been used to fit the experimental data obtained for the Cu, Cd and Pb extraction with EDTA. Both equations allow a good fitting of experimental data. However, their utility is still questionable.

The *diffusion model* has been used to fit the extraction rate data and determine if diffusion of the complex M/EDTA is the limiting rate of the extraction. It can be concluded that for some sediments, the extraction of metals is rate determined by diffusion in the first hour of extraction. However, when all the range of extraction times is considered this model did not fit correctly the extraction rate data obtained for the three metals studied.

The *two first-order reactions model* allows fitting efficiently Cu, Cd and Pb data obtained in a wide range of concentrations. This model presents the advantage to divide the metals present in sediment in three fractions characterized quantitatively and qualitatively. Furthermore, it can be considered as a powerful tool to study the trace metals mobilization in sediments. Taking into account that the metals more easily extracted are the more mobile in the sediment, it could be possible to estimate the mobility of metals in sediments using this model: the higher the quantity of metal belonging to the first fraction “readily extractable”, the higher the mobility of this metal in the sediment.

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