KINETICS STUDY OF Pb(II) AND Hg(II) REMOVAL FROM AQUEOUS MEDIA ON RAPESEEDS BIOMASS

STUDIUL CINETIC AL ÎNDEPĂRTĂRII IONILOR DE Pb(II) ŞI Hg(II) DIN MEDII APOASE PE BIOMASĂ DE RAPIȚĂ

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Abstract. *In this study, the removal of Pb(II) and Hg(II) ions from aqueous solution using rapeseeds biomass was examined in batch systems as a funtion of contact time. The results obtained for the removal of each studied metal ion were analyzed using three kinetics models: prseudo-first order, pseudo-second order and intra-particle diffusion, in order to elucidate the mechanism of the removal process. For both studied metal ions, the experimental data are well described by the pseudo-second order kinetics model. These results can be used for to highlight the potential applicability of rapeseeds biomass as low-cost biosorbent in the clean-up of aqueous effleunts, containing toxic heavy metals.*
Key words: metal ions, rapeseed biomass, biosorption, kinetics.

Rezumat. *În acest studiu a fost examinată îndepărtarea ionilor de Pb(II) şi Hg(II) din soluții apoase utilizând biomasă de rapiță, în sisteme discontinui în funcție de timpul de contact. Rezultatele obținute pentru îndepărtarea fiecărui ion metalic în parte au fost analizate utilizând trei modele cinetice: modelul cinetic de ordin pseudo-unu, modelul cinetic de ordin pseudo-doi şi modelul de difuzie intra-particulă, în scopul de a elucida mecanismul procesului de îndepărtare a ionilor metalici. Pentru ambii ioni metalici studiați, datele experimentale sunt cel mai bine descrise de modelul cinetic de ordin pseudo-doi. Aceste rezultate pot fi utilizate pentru a evidenția aplicabilitatea biomasei de rapiță in procesele de îndepărtare a ionilor metalici toxici din efluenți industriali.*
Cuvinte cheie: ioni metalici, biomasă de rapiță, biosorbție, cinetică.

INTRODUCTION

Nowadays anywhere in the world, an important issue is the contamination of environment with heavy metals. This because the heavy metals are not biodegradable and due to their toxic effect and bioaccumulation tendency through food chain, can seriously affect many life forms (Fu and Wang, 2011). The main source of environmental pollution with heavy metals is industrial activities. The wastewaters resulted from various technological processes often contains significant concentrations of heavy metals, and from this reason their discharge into environmental must be done only after a rigorous treatment. Romanian

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legislation impose that the concentration of Pb(II) and Hg(II) ions in industrial effluents which are discharged into natural water sources to not exceeds 0.2 mg/L and 0.05 mg/L, respectively (NTPA 001/2005).

The biosorption of metal ions from aqueous solution has receive considerable attention in the recent years as potential treatment method of industrial effluents containing heavy metals, mainly because it is cost-effective, easy of operate (even at industrial scale) and can use as biosorbents various materials which are considered as waste in other agricultural or industrial activities (Gogate and Pandit, 2004; Barakat, 2011).

The use of various agricultural wastes as biosorbents for the removal of heavy metals from aqueous solution has been extensively studied in literature (Demirbas, 2008; Krika et al., 2016), because these materials are cheap and available in large quantities in many regions. In addition, due to their chemical composition (cellulose, lignin, polysaccharides, etc.), most of agricultural wastes have rather large cation exchange capacities, what makes these materials to be effective biosorbents in the heavy metals removal processes (Demirbas, 2008). The rapeseeds can be such example of biosorbent for heavy metal ions. Cultivated on increasingly large surfaces in our country due to his industrial utilizations, the rapeseeds biomass can be valorized and as biosorbent in the treatment of industrial effluents containing heavy metals.

In this study, the kinetics of Pb(II) and Hg(II) ions biosorption from aqueous solution on rapeseeds biomass was examined. The influence of contact time on the biosorption efficiency was studied in batch systems, under optimal experimental conditions (pH 5.5, 8.0 g biosorbent/L) established previously (Arsenie *et al.,* 2017; Arsenie and Bulgariu, 2017). The experimental results were analyzed using three kinetic models: pseudo-first order, pseudo-second order and intra-particle diffusion model. On the basis of these models, the kinetic parameters were calculated for each case.

MATERIAL AND METHOD

The chemical reagent used for experiments were of analytical grade and were used without further purifications. The stock solutions of Pb(II) and Hg(II) ions (10^{-2} mol/L) were obtained by metal nitrate dissolving in distilled water. All working solutions were then obtained from the stock solutions by dilution. The initial solution pH was adjusted at required value with 0.1 N HNO_3 solution.

The rapeseeds used as biosorbent in this study were purchased form a local farm (Iaşi, Romania). The rapeseeds were first, washed several times with distilled water and dried in air (4-5 days, room temperature), and then crushed and sieved until the particles grain-size was less than 1.0 mm.

The kinetics experiments were performed by batch technique, at room temperature (22 ± 2 °C), mixing biosorbent quantities of 0.2 g with 25 mL of Pb(II) and Hg(II) ions solution, with initial concentration of 0.2 mmol M(II)/L, in 100 mL conical flasks. Each sample was intermittent stirred for various time intervals (from 5 to 180 min), and then filtered on quantitative filter paper. The Pb(II) and Hg(II) ions concentration in filtrate was analyzed spectrophotometric (Digital Spectrophotometers

S104 D, 1 cm glass cell), using an adequate method (Dean, 1995) and a prepared calibration graph.

The biosorption capacity (*q*, mg/g) of rapeseeds biomass for Pb(II) and Hg(II) ions was calculated from experimental results using the equation:

$$q = \frac{(c_0 - c) \cdot V}{m} \qquad (1)$$

where: c_0, c – initial and equilibrium concentration of metal ions in aqueous solution (mg/L), V – volume of aqueous solution (L), m – the mass of biosorbent (g).

RESULTS AND DISCUSSIONS

The kinetics studies are important in the adaptation of a given biosorption process at industrial scale. This because the parameters, calculated from kinetics modeling, provide useful information about how take place the interactions between metal ions from aqueous solution and functional groups from biosorbent surface and the efficiency of biosorption process under well defined experimental conditions (Rao and Khan, 2009). For the kinetics modeling of a biosorption process, the pseudo-first order, the pseudo-second order and intra-particle diffusion models are most widely used to describe the experimental data (Gerente *et al*., 2007), and the mathematical equation of these three kinetics models are summarized in table 1.

Table 1

Mathematical equations of kinetics models used in this study (Ho and McKay, 1999; Gerente et al., 2007)

Kinetics model	Equation	Notations
Pseudo-first order model	$\log(q_e - q_t) = \log q_t - \frac{k_1}{2.303} \cdot t$	q_e, q_t - the biosorption capacity at equilibrium and at time t, (mmol/g); k_1 - pseudo-first order rate constant (1/min)
Pseudo-second order model	$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e}$	k_2 - rate constant of pseudo-second order kinetic model (g/mmol min)
Intra-particle diffusion model	$q_t = k_{dif} \cdot t^{1/2} + c$	k_{diff} - intra-particle diffusion rate constant (mmol/g $min^{1/2}$) ; *c* - concentration of metal ions from solution at equilibrium (mmol/L)

The selection of these three kinetics models for the mathematical analysis of the experimental results is justified by the nature of the information provided by each model. Thus, the pseudo-first order and pseudo-second order kinetics models are based on the assumption the rate limiting step in the biosorption process is the chemical interaction between metal ions from aqueous solution and superficial functional groups of biosorbent, and that the retention of the metal ions on biosorbent surface requires one or respectively two binding sites (Ho and McKay, 1999). Unlike these, the intra-particle diffusion model is generally used to highlights the importance of the elementary diffusion processes in the metal ions uptake onto a considered biosorbent (Gerente *et al.,* 2007). Therefore, the finding of the most adequate kinetics model for to describe the experimental results will also provide an overview on the studied biosorption process.

The experimental results obtained at the study of the effect of contact time on the biosorption efficiency of Pb(II) and Hg(II) ions from aqueous solution on rapeseeds biomass are illustrated in Fig. 1. It can be observed that in considered experimental conditions, the removal efficiency of Pb(II) and Hg(II) ions on rapeseeds biomass increases with increase of contact time.

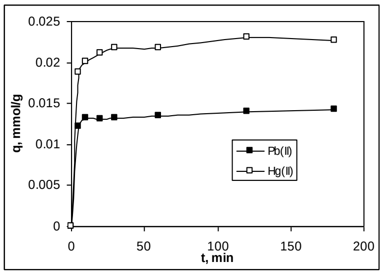
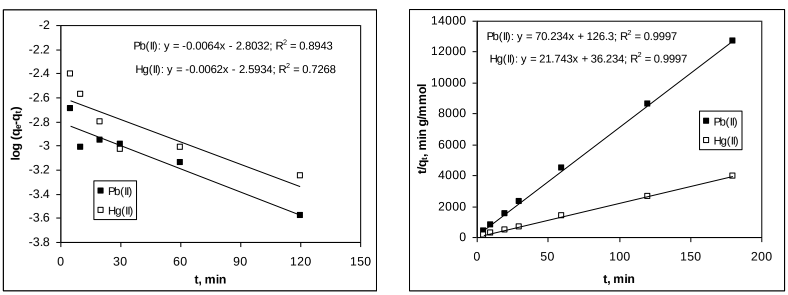


Fig. 1 Effect of contact time on the biosorption efficiency of Pb(II) and Hg(II) ions on rapeseeds biomass

The biosorption process is very fast in the initial step, when in the first 20 min are retained almost 65 % from initial Pb(II) ions and over 89 % from initial Hg(II) ions, respectively. In the second step, the biosorption process becomes slower, and the equilibrium is attained after 30 min, for both metal ions.

The kinetics parameters calculated from the linear representations of the pseudo-first order (Fig. 2a) and the pseudo-second order (Fig. 2b) are summarized in Table 2.



(a) (b)

Fig. 2 Linear representations of the pseudo-first order (a) and pseudo-second order (b) kinetics models.

The compatibility between experimental data and the pseudo-second order kinetics model indicate that the biosorption process is limited by the chemical interactions between metal ions and functional groups of biosorbent, and these interactions involve two binding sites. In addition, the comparison of the kinetics parameters obtained for Pb(II) and Hg(II) ions shows that the Pb(II) ions are more easy removed, while the Hg(II) ions are more efficient retained.

Table 2

Kinetics parameters for the biosorption of Pb(II) and Hg(II) ions on rapeseeds biomass

Metal ion		Pb(II)	Hg(II)
	q_e^{exp}, mmol/g	**0.0141**	**0.0227**
Pseudo-first order kinetic model	R^2	0.8943	0.7368
	q_e, mmol/g	0.0016	0.0025
	k_1, 1/min	0.0028	0.0027
Pseudo-second order kinetic model	R^2	0.9997	0.9997
	q_e, mmol/g	0.0142	0.0249
	k_2, g/mmol min	39.0563	13.0473

The linear representation of the intra-particle diffusion model for Pb(II) and Hg(II) ions biosorption on rapeseeds biomass is presented in fig. 3, and the kinetics parameters calculated in this case are summarized in table 3.

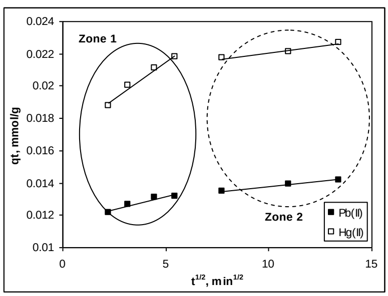


Fig. 3 Linear representation of the intra-particle diffusion kinetic model.

Table 3

Kinetics parameters of the intra-particle diffusion model for the biosorption of Pb(II) and Hg(II) ions on rapeseeds biomass

Metal ion	Pb(II)		Hg(II)	
	Zone 1	Zone 2	Zone 1	Zone 2
R^2	0.9351	0.9933	0.9759	0.9719
k_{diff}, mmol/g $min^{1/2}$	0.0003	0.0001	0.0009	0.0002
c, mmol/L	0.0116	0.0125	0.0169	0.0204

It can be observed from figure 3 that for none of studied metal ions, the linear dependence does not go through the origin, which means that the intra-diffusion particle process is not the rate limiting step, but that the diffusion controls the metal ions biosorption up to a certain degree. In addition, the higher slope of the first zone in comparison with second zone obtained in case of both metal ions (tab. 3), suggests that the active sites are located on the biosorbent surface and are readily accessible for the chemical interactions. The analysis of the results obtained from kinetics modelling shows that the chemical interactions play an important role in the first stage of Pb(II) and Hg(II) ions biosorption on rapeseeds biomass, while the diffusion of metal ions to the pores of biosorbent becomes important in the second stage of biosorption process.

CONCLUSIONS

1. The removal of Pb(II) and Hg(II) ions from aqueous solution using rapeseeds biomass was studied in batch systems as a funtion of contact time.

2. The experimental results were analyzed using three kinetics models: pseudo-first order, pseudo-second order and intra-particle diffusion.

3. For both studied metal ions, the experimental data are well described by the pseudo-second order kinetics model.

4. These results can be used for to highlight the potential applicability of rapeseeds biomass as low-cost biosorbent in the heavy metals removal processes.

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