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BIOSORPTION OF Zn(II) IONS FROM AQUEOUS SOLUTION ONTO MUSTARD WASTE BIOMASS

BY

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Abstract. In this study, the mustard waste biomass, obtained from mustard seeds after oil extraction, was used as biosorbent for removal of Zn(II) ions from aqueous solution. The experiments were performed in batch systems at room temperature, and have follow the influence of initial solution pH, biosorbent dose, initial Zn(II) concentration and contact time, in order to establish the optimal experimental conditions. About 0.125 g of mustard waste biomass was enough to remove 80% of 40.67 $mg\cdot L^{-1}$ Zn(II) ions from 25 mL of aqueous solution in 60 min, at initial solution pH of 5.5, considered to be optimal. The Langmuir and Freundlich isotherm models were used for the mathematical modelling of the equilibrium isotherm, obtained experimentally. The experimental data well fit with Langmuir model, and the characteristic parameters of this model agree with the conditions of favourable biosorption. The pseudo-first order and pseudo-second order kinetic models were used for kinetic modelling of the experimental data. The values of kinetics parameters calculated for both models have shown that the pseudo-second order equation is more adequate. The experimental results indicate that mustard waste

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biomass has a good biosorption capacity for Zn(II) ions, and can be considered a potential biosorbent for the treatment of industrial wastewaters.

Keywords: Zn(II) ions; biosorption; mustard waste biomass; aqueous solution.

1. Introduction

The pollution of environment with metal ions continues to be an important problem worldwide, due to its negative consequences on human life and ecosystems quality (Ahmaruzzaman, 2011; Gautam *et al*., 2014). These consequences are derived from the wide use of metal ions in various industrial activities, from which results high quantities of wastewaters which contains important concentrations of metal ions. Because the metal ions are non-biodegradable, persistent and have an accentuate accumulation tendency (Hadi *et al*., 2014), they have an important contribution to the environment pollution, and from this reason it is necessary to be removed from aqueous effluents.

Though, Zn(II) ions are considered essential microelements for the metabolism of most living organisms (Das *et al*., 2015), their numerous utilizations in industry has determined that large amount of Zn(II) ions to reach the environment. Under these conditions, the pollution with Zn(II) of water sources has become a serious problem, for which is still looking for a solution.

Various methods can be used for the removal and recovery of Zn(II) ions from industrial wastewater effluents, most widely used being chemical precipitation, membrane filtration, ion exchange, electrochemical techniques, flocculation, etc. (Rusten *et al*., 1997; Dabrowski *et al*., 2004; Llanos *et al*., 2010). Unfortunately, most of these methods are inefficient or very expensive, and also can generate high amounts of toxic sludge, which represent another environmental problem (Sciban *et al*., 2007).

Due to its simplicity, biosorption of metal ions from aqueous solution can be considered a promising alternative, which have proved to be very efficient in the removal of metal ions from aqueous effluents (Kumar *et al*., 2006; Montazer-Rahmati *et al*., 2011). In addition, because has the possibility to use various inexpensive materials, such as industrial or agricultural by-products or wastes, the biosorption is considered an economical and eco-friendly method which can be successfully used in environmental decontamination processes (Senthilkumar *et al*., 2000; Krishnan and Anirudhan, 2003).

The utilization of various residual materials from agricultural activities as biosorbents for the removal of numerous metal ions was presented in many studies from literature (Febrianto *et al*., 2009; Qiu *et al*., 2009; Wang and Chen, 2009). Most of these materials have relatively high binding capacities, mainly due to the presence of polysaccharides, proteins or lipids on their cell walls surface. These constituents contain various functional groups (such as hydroxyl, carbonyl, sulphate, phosphates, carboxyl, etc.) which represent the binding sites from metal ions from aqueous solution.

In this study, it was examined the possibility of using mustard waste biomass, obtained from mustard seeds after oil extraction with n-hexane, for the removal of Zn(II) ions from aqueous solution. Experimental parameters which affect the efficiency of biosorption process, such as initial solution pH, biosorbent dose, initial Zn(II) concentration and contact time, were analyzed in batch systems at room temperature. The equilibrium biosorption data were evaluated by Langmuir and Freundlich isotherm models, while for the kinetics modeling pseudo-first order and pseudo-second order models were used. The experimental results included in this study shows that mustard biomass has a good biosorption capacity for Zn(II) ions, and can be considered a potential biosorbent for the treatment of wastewaters.

2. Experimental

2.1. Materials

The mustard waste biomass used in this study as biosorbent was obtained from mustard seeds after oil extraction with n-hexane during of 30 h. After washing several times with distilled water, the mustard waste biomass was dried in air at 70°C for 10 h, and then has been crushed and sieved. The obtained biomass was stored in desiccators for further use.

All chemicals used in this study were of analytical grade and all solutions were prepared using distilled water, obtained from a commercial distillation system. A stock solution of Zn(II) ions containing 677 mg Zn(II)$\cdot L^{-1}$ was obtained by dissolving zinc sulphate (purchased from Chemical Company) in distilled water. Other concentrations within the range 14-190 mg Zn(II)$\cdot L^{-1}$ were obtained by dilution of the stock solution. The initial pH of working solutions was adjusted at required value with 0.1 N HCl or NaOH solutions.

2.2. Methods

Biosorption experiments were performed at room temperature (25 ± 0.5°C) for different pH values of initial solution, biosorbent dosage, initial Zn(II) concentration and contact time. The batch experiments were carried out in 150 mL conical flasks, by adding mustard waste biomass to a solution containing Zn(II) ions with intermittent stirring.

The initial solution pH experiments were carried out at constant biosorbent dose of 5 $g\cdot L^{-1}$ and a constant initial Zn(II) concentration of 54.19 $mg\cdot L^{-1}$, adjusting the pH from 1.0 to 6.0 by adding 0.1 N HCl or NaOH solutions. The biosorbent dose studies were performed by varying the amount of mustard waste biomass between 4 and 40 $g\cdot L^{-1}$, under similar experimental conditions. The influence of initial Zn(II) concentration was examined within 14-190 mg·L^{-1} concentration range. In the kinetic experiments, the same amount of biosorbent (0.125 g) was mixed with 25 mL of aqueous solution containing 54.19 mg Zn(II)·L^{-1}, at various time intervals between 5 and 180 min.

At the end of biosorption procedure, the phases were separated by filtration, and the Zn(II) ions concentration in the aqueous solution analyzed spectrophotometrically with xylenol orange (Digital spectrophotometer S 104 D, λ = 570 nm, 1 cm glass cells) (Dean, 1995) using a prepared calibration graph.

The biosorption capacity of mustard waste biomass for Zn(II) ions was evaluated using amount of Zn(II) ions retained on weight unit of lignin (*q*, [mg·g^{-1}]) and percent of Zn(II) ions removal (*R*, [%]), calculated from experimental results on the basis of the following equations:

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

$$R = \frac{c_0 - c}{c_0} \cdot 100 \tag{2}$$

where: c_0, c are the initial and equilibrium concentration of Zn(II) ions in aqueous solution, [mg·L^{-1}], V is the volume of working solution, [mL] and m is the mass of dry sorbent, [g].

3. Results and Discussions

3.1. Effect of Initial Solution pH

The biosorption of Zn(II) ions onto mustard waste biomass was studied at constant concentration of metal ions (54.19 mg·L^{-1}), biosorbent dose (5.0 g ·L^{-1}) and contact time (24 h), within initial pH interval between 1.0 and 6.0, and the obtained results are presented in Fig. 1.

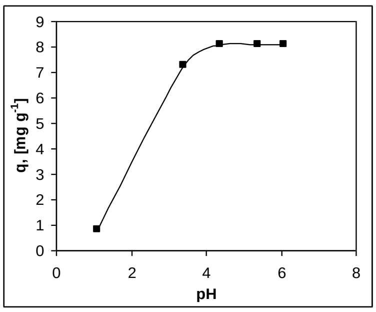

Fig. 1 − Influence of initial solution pH on Zn(II) biosorption onto mustard waste biomass.

It can be observed from Fig. 1 that the biosorption efficiency drastically increases with the increasing of initial solution pH in the pH domain between 1.0 and 3.4, after that remains almost constant (in pH interval between 3.4 and 6.0). On entire pH interval between 3.4 and 6.0, the value of removal percent do not varies significantly (75 ± 1%), and from this reason an initial solution pH value of 5.5 was selected as optimal, and was used in the further biosorption experiments.

The variation of the biosorption capacity as a function of initial solution pH shows that in biosorption system exist a competition between protons and Zn(II) ions for the binding sites from biosorbent surface, and that the retention of Zn(II) ions onto mustard waste biomass is done through electrostatic interactions. In consequence, the ion exchange mechanism may be one of the specific modality through which takes place the Zn(II) uptake from aqueous solution.

3.2. Effect of Biosorbent Dosage

In Fig. 2 is presented the variation of Zn(II) biosorption efficiency as a function of mustard waste biomass dose, at a constant initial pH (5.5), Zn(II) ions concentration (54.19 mg·L^{-1}) and contact time (24 h).

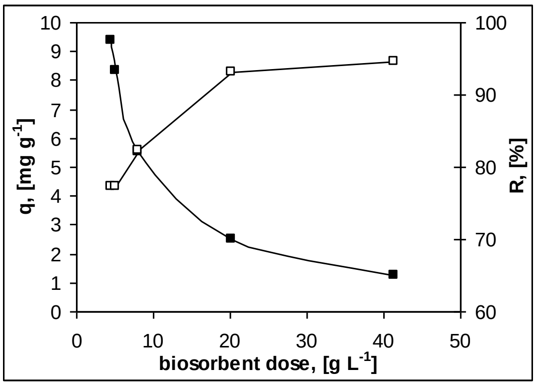

Fig. 2 − Influence of biosorbent dose for Zn(II) biosorption onto mustard waste biomass.

Thus, the increase of biosorbent dose from 4 to 40 g·L^{-1} determined on the hand the decrease of amount of Zn(II) ions retained on weight unit of biomass (from 9.39 to 1.23 mg·g^{-1}), and on the other hand the increase of removal percent (from 77.21 to 94.58%).

Analyzing the opposite variation of these two parameters, it was considered that a biosorbent dose of 5.0 g·L^{-1} is enough for the quantitative removal of Zn(II) from aqueous solution (87.29%), in mentioned experimental conditions, and this value was selected as optimal and used in all subsequent experiments.

3.3. Effect of Initial Zn(II) Concentration

The influence of initial Zn(II) concentration on the biosorption efficiency onto mustard waste biomass was studied in optimal established conditions (initial solution pH of 5.5; biosorbent dose of 5.0 g·L^{-1}, 24 h contact time), by varying the initial concentration between 13 and 190 mg·L^{-1}. The experimental results illustrated in Fig. 3 shows that the biosorption capacity of mustard waste biomass gradually increase with the increasing of initial Zn(II) concentration from aqueous solution.

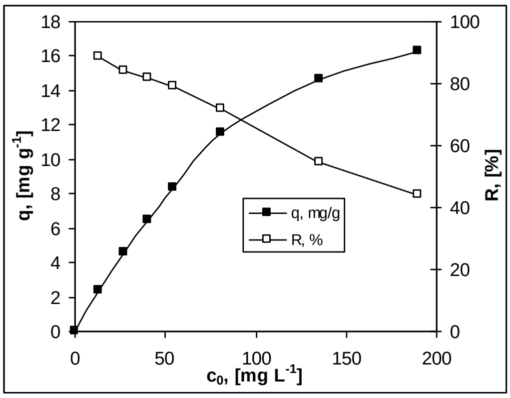

Fig. 3 − Effect of initial Zn(II) concentration on the biosorption efficiency onto mustard waste biomass.

Such variation is considered a typical one for the biosorption systems which use biomasses as biosorbent, and it is determined by the increase of the ratio between initial number of Zn(II) ions and limited number of biosorption sites from biosorbent surface (Krishnan and Anirudhan, 2003).

On the other hand, the removal percent (*R*, [%]) obtained in case of Zn(II) biosorption onto mustard waste biomass decrease from 88.52 to 43.93%, with the increasing of initial metal ions concentration in mentioned interval. The decrease of the removal percent values indicate that after the most available functional groups from mustard waste biomass surface are occupied, the diffusion of Zn(II) ions inside of biosorbent particle is inhibited.

3.4. Effect of Contact Time

The influence of contact time on the Zn(II) biosorption efficiency presented in Fig. 4, shows that with increasing contact time increases the biosorption capacity of mustard waste biomass. As is expected this increase is not a linear one. Initially the Zn(II) biosorption was very fast (up to 60 min), after that the process becomes more slower, near to equilibrium. Once the equilibrium is reached, the biosorption of Zn(II) ions did not change significantly.

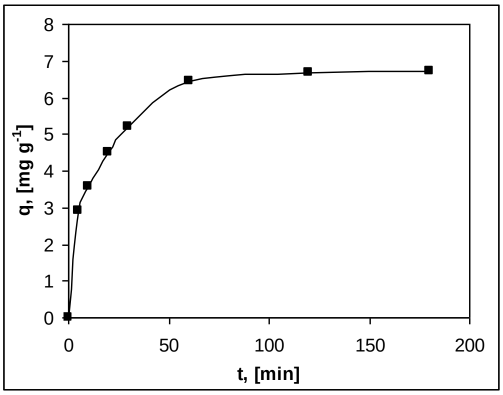

Fig. 4 − Effect of contact time on the Zn(II) biosorption efficiency onto mustard waste biomass.

The shape of dependence from Fig. 4 indicate that the Zn(II) biosorption onto mustard waste biomass occurs by two successive stages: (i) first stage with a very fast biosorption rate – probably determined by the high number of available biosorption sites that can easily interact with Zn(II) ions from aqueous solution, and (ii) second stage, where the biosorption rate is more slower, and the diffusion inside of pores controls the Zn(II) uptake.

Under these conditions, it can be considered that for the efficient biosorption of Zn(II) ions from aqueous solution onto mustard waste biomass, a contact time of minimum 60 min is necessary.

3.5. Modelling of Biosorption Process

Isotherm and kinetic modelling of biosorption process is important for the quantitative evaluation of retention properties of certain biosorbent and also for to elucidate the biosorption mechanism (Chong and Volesky, 1995; Ho and McKay, 1999).

In this study, two isotherm models (Langmuir and Freundlich models) and two kinetics models (pseudo-first order and pseudo-second order models) were used for the modelling of experimental data obtained in case of Zn(II) biosorption onto mustard waste biomass. The mathematical equations of these models and the values of characteristic parameters calculated in this case are summarized in Table 1.

Table 1

Isotherm and Kinetic Models and their Characteristic Parameters Obtained in Case of Zn(II) Biosorption onto Mustard Waste Biomass

Model	Mathematical equation	Calculated parameters
Isotherm modelling		
Langmuir	$\frac{c}{q} = \frac{c}{q_{\max}} + \frac{1}{q_{\max} \cdot K_L}$	$R^2 = 0.9988$ $q_{\max} = 18.02$ mg·g^{-1} $K_L = 0.08$ g·L^{-1}
Freundlich	$\ln q = \ln K_F + \frac{1}{n} \ln c$	$R^2 = 0.9523$ $n = 0.45$ $K_F = 2.37$
Kinetics modelling		
Pseudo-first order	$\log(q_e - q_t) = \log q_e - k_1 \cdot t$	$R^2 = 0.9789$ $q_e = 4.28$ mg·g^{-1} $k_1 = 1.58\ 10^{-2}$ min^{-1}
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e}$	$R^2 = 0.9991$ $q_e = 7.11$ mg·g^{-1} $k_2 = 1.52\ 10^{-2}$ g·mg^{-1}·min^{-1}

where: $q_{\max}$ is maximum adsorption capacity after complete saturation of adsorbent surface; K_L is the Langmuir constant; n and K_F are Freundlich constants; q_e and q_t are the biosorption capacity at equilibrium and at time t respectively; t is biosorption time; k_1 is the rate constant of pseudo-first order kinetic model and k_2 is the rate constant of pseudo-second kinetic model.

As resulted from Table 1, the highest values of correlation coefficients (R^2) are obtained in case of Langmuir isotherm model and pseudo-second kinetic model. In consequence it can be said that the biosorption of Zn(II) onto mustard waste biomass occurs until the formation of monolayer coverage (Ho *et al*., 2002) and the amount of Zn(II) ions required for the formation of this monolayer is 18.02 mg·g^{-1}. Therefore, it is expected that the Zn(II) uptake from aqueous solution onto mustard waste biomass to involve predominantly ion exchange type interactions between metal ions and superficial functional groups of biosorbent.

These observations are also sustained by the kinetic modelling, which shows that the kinetic data are very well described by the pseudo-second order kinetic model (Table 1). Therefore, it can be said that the Zn(II) biosorption onto mustard waste biomass involve predominantly chemical interactions between metal ions from aqueous solution and functional superficial groups of biomass (Ho and McKay, 1999; Pozdniakova *et al*., 2016).

All these observations allow us to say that Zn(II) biosorption onto mustard waste biomass occurs gradually, mainly through ion exchange mechanism, until a complete monolayer coverage is formed at the surface of biomass particles. Such biosorption behavior has practical importance in the conception of treatment systems for industrial wastewater which involve biosorption.

4. Conclusions

In this study, the mustard waste biomass, obtained from mustard seeds after oil extraction, was used as biosorbent for removal of Zn(II) ions from aqueous solution. The experiments performed in batch systems at room temperature, have follow the influence of initial solution pH, biosorbent dose, initial Zn(II) concentration and contact time, in order to establish the optimal experimental conditions. These were found to be an initial pH of 5.5, 5.0 $g \cdot L^{-1}$ biosorbent dose and 60 min of contact time. Under these conditions around 80% of Zn(II) ions are retained from an aqueous solution of 40.67 $mg \cdot L^{-1}$. The modelling of biosorption process was done using two isotherm models (Langmuir and Freundlich models) and two kinetics models (pseudo-first order and pseudo-second order models), and the characteristic parameters of this model agree with the conditions of favourable biosorption. The obtained results have shows that Zn(II) biosorption onto mustard waste biomass occurs gradually, mainly through ion exchange mechanism, until a complete monolayer coverage is formed at the surface of biomass particles. Such biosorption behavior has practical importance in the conception of treatment systems for industrial wastewater which involve biosorption.

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BIOSORBŢIA IONILOR DE Zn(II) DIN SOLUŢII APOASE PE BIOMASĂ DE DEŞEU DE MUŞTAR

(Rezumat)

În acest studiu, biomasa de deşeu de muştar, obţinută din seminţe de muştar după extracția uleiurilor, a fost utilizată ca biosorbent pentru îndepărtarea ionilor de Zn(II) din soluţii apoase. Experimentele au fost realizate în sisteme discontinui, la temperatura camerei, şi au urmărit influenţa pH-ului soluţiei iniţiale, doza de biosorbent, concentraţia iniţială a ionilor de Zn(II) şi timpul de contact, în vederea stabilirii condiţiilor experimentale optime. Aproximativ 0,125 g de biomasă de deşeu de muştar a fost suficientă pentru a îndepărta 80% din 25 mL soluţie apoasă ce conţine 40,67 mg $Zn(II)\cdot L^{-1}$ în 60 min, la un pH iniţial de 5,5, considerat optim. Modelele Langmuir şi Freundlich au fost folosite pentru modelarea matematică a izotermelor obţinute experimental. Datele experimentale sunt cel mai bine descrise de modelul Langmuir, iar parametrii caracteristici acestui model arată că procesul de biosorbţie are loc în condiţii favorabile. Pentru modelarea cinetică au fost utilizate modelele cinetice de ordin pseudo-unu și pseudo-doi. Valorile parametrilor cinetici calculaţi pentru ambele modele au arătat că modelul cinetic de ordin pseudo-doi este mai adecvat pentru descrierea rezultatelor experimentale. Rezultatele acestui studiu arată că biomasa de deşeu de muştar are o capacitate de biosorbţie bună pentru ionii de Zn(II), şi că acesta poate fi considerat un potenţial biosorbent pentru tratarea apelor uzate industriale.