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REMOVAL OF Zn(II) IONS FROM AQUEOUS SOLUTION BY ADSORPTION ON MUSTARD HUSKS

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ABSTRACT. Removal of Zn(II) ions by adsorption on a low-cost material, namely mustard husks, was examined in this study. The batch experiments were performed as a function of initial solution pH, adsorbent dose, initial Zn(II) concentration and contact time, at room temperature (25 ± 0.5°C), in order to establish the optimum conditions of adsorption process. The experimental results have shown that 5.0 g/L of mustard husks is sufficient to remove 73.16% of 54.20 mg/L Zn(II) from 25 mL of aqueous solution, in 60 min of contact time and at initial solution pH of 5.5. The adsorption data fitted well the Langmuir isotherm model, with a maximum adsorption capacity of 12.99 mg/g, while the kinetics of adsorption process is described by pseudo-second order model. The results of this study highlight that the mustard husks can become an efficient and economical alternative for the removal of Zn(II) ions from aqueous effluents.

Keywords: *adsorption, Zn(II) ions, mustard husks, isotherm, kinetics*

INTRODUCTION

Pollution of environment with heavy metals is an important issue in many industrialized regions around the world. Their large utilization and industrial importance have determined the serious pollution of many ecosystems with such pollutants, that unlike organic pollutants are not biodegradable, tend to accumulate in living organisms, and many of them are known to be toxic or carcinogenic.

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Zinc is an important element for many growing industrial sectors, such as metallurgical industry, electroplating industry, mine drainage, galvanization industry, wood preservative industry, alloy industry, ceramics, batteries manufacturing, etc. [1, 2]. The rapid development of these economical activities have increase the quantities of waste water that contains significant amounts of Zn(II) ions that are directly or indirectly discharged into environment, and that drastically affects its quality. It is well known that zinc is a trace element that is essential for human health, due to its importance in psychological function of living tissues and many biological processes. Nevertheless, too much zinc can cause several serious health problems, such as gastric cramps, skin irritation, vomiting, nausea and anemia [3]. This is the reason why the permissible limit for Zn(II) ions in drinking waters is only 0.5 mg/L [4].

The most common methods involved in the removal of Zn(II) ions and other heavy metals from various types of industrial effluents include chemical precipitation [5, 6], membrane filtration [6, 7], ion exchange [8, 9], electrochemical techniques [10], etc. Unfortunately, most of these methods have several important limitations, such as generation of high quantities of toxic sludge that required further treatments, high cost of operation, high energy consumption, long treatment time and poor selectivity.

Among the conventional methods, the adsorption of heavy metal ions can be considered an inexpensive, eco-friendly and efficient method that have received a special attention during of last years, mainly because is effective in recovery and recycling of retained metal ions, have a low sludge production and is easy to operate. Activated carbon is a well-known conventional adsorbent hat has been widely employed in the wastewater treatment. Unfortunately, its utilization is not feasible due to high price and costs associated with the regeneration as a result of high-degree losses in decontamination processes [11].

Adsorbent materials derived from agricultural wastes have been intensively used as substitutes for such conventional adsorbent. These wastes are usually composed by polymers, especially different types of lignino-celluloses, and are particularly attractive for the removal of environmental contaminants because are cheap, available in large quantities and contains in their structure numerous functional groups that could represent binding sites for metal ions [12]. From these reasons, many studies from literature have reported the utilization of various agricultural wastes, such as: jack fruit peel, mango bark sawdust [13, 14], sawdust [15], rice straw [16], lemon shells [17], etc., for the removal of Zn(II) ions, in various experimental conditions.

The mustard is an annual plant that is intensively cultivated in many regions of the world, mainly due to their widely utilizations in food industry, and recently for the biodiesel production. After harvesting, the mustard seeds are peeled and selected, and the obtained husks together with low quality seeds are considered a non-value waste that is discharged or incinerated. However, various functional groups, such as carboxyl, hydroxyl, carbonyl, amine, etc. [18] are present in the structure of this low-cost material, suggesting that mustard husks can be a potential adsorbent for the removing of metal ions. In recent studies, we report the ability of such adsorbent material to remove Pb(II) and Cd(II) ions from aqueous solution [18, 19]. The mustard husks were assessed as adsorbent for the removal of some toxic metal ions (such as Cd(II), Pb(II), Cr(VI), Cu(II)) [20-22]), but to the best of our knowledge, this is the first report on the removal of Zn(II) on mustard husks.

In this study, the removal of Zn(II) ions from aqueous solution using mustard husks as low-cost adsorbent was investigated. The influence of the most important experimental parameters that affects the efficiency of adsorption process (initial solution pH, adsorbent dose, initial Zn(II) concentration and contact time) has been examined in batch experiments. Two adsorption isotherm models (Langmuir and Freundlich) and two kinetic models (pseudo-first order and pseudo-second order models) have been used to determine the best fitting model for experimental data. The parameters for each model have been also calculated for the adsorption of Zn(II) onto mustard husks.

RESULTS AND DISCUSSION

In order to characterized the adsorptive performances of mustard husks for Zn(II) removal from aqueous solution, three aspects must be considered, namely: (a) optimization of process parameters; (b) modeling of adsorption isotherms and (c) modeling of adsorption kinetics.

1. Optimization of adsorption process parameters: Many studies from literature have shown that the adsorption of metal ions occurs with maximum efficiency only in well defined experimental conditions [23 24]. Therefore, the first goal of batch adsorption experiments should be to establish the optimum values of most important parameters that affect the adsorption process, such as initial solution pH, adsorbent dose, initial Zn(II) concentration and contact time.

1.1. Effect of initial solution pH: The initial solution pH significantly affects both the dissociation degree of functional groups from adsorbent surface and the speciation and solubility of metal ions in aqueous solution. From this reason, the value of this parameter should be optimized first.

In this study, the influence of initial solution pH on Zn(II) adsorption efficiency onto mustard husks was examined in the pH range between 1.0 and 6.5, and the obtained results are presented in Fig. 1. It can be observed that at initial solution pH higher than 3.5 the removal percent attain the maximum value and remains almost constant (69 – 73%) on entire pH range.

This represents an important advantage in the utilization of mustard husks for removal of Zn(II) ions from aqueous solution, since it does not require a rigorous correction of solution pH in order to attain a high efficiency of adsorption process. In addition, the experimental results illustrated in Fig. 1 indicate that Zn(II) adsorption on mustard husks occurs predominantly by ion exchange interactions. In these interactions are involved the mobile ions from adsorbent structure (Ca^{2+} or Mg^{2+}) and these do not depend by the dissociation degree of functional groups from adsorbent structure. In consequence, the maximum adsorption efficiency is obtained in a wide range of initial solution pH.

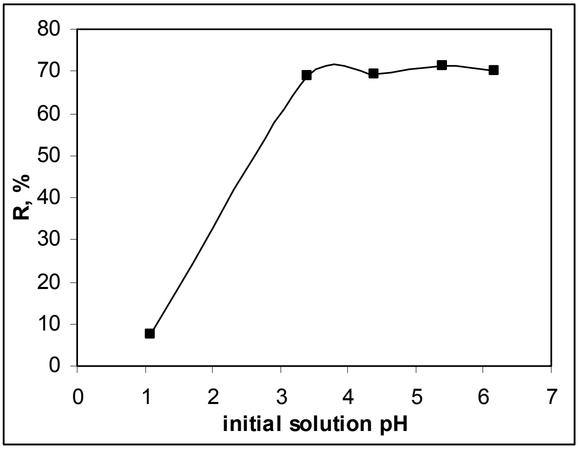

Figure 1. Effect of initial solution pH on Zn(II) adsorption onto mustard husks (c_0 = 54.19 mg/L, adsorbent dose = 5 g/L, contact time = 24 h, t = 25°C).

In strong acid media (pH = 1.5) the adsorption of Zn(II) ions is poor (7.65%), and this is probably due to the fact that the high proton concentration in aqueous solution drastically restricted the interactions between Zn(II) ions and functional groups of adsorbent.

Based on these observations, the optimum initial solution pH for Zn(II) adsorption onto mustard husks was considered to be 5.5 (when 73.16% of Zn(II) ions are removed from aqueous solution), and all further experiments were performed at this pH value.

1.2. Effect of adsorbent dose: The influence of adsorbent dose on the Zn(II) adsorption efficiency was studied using different amounts of mustard husks, in the range of 4.0 – 40.0 g/L, and experimental results (Fig. 2) showed that the adsorption process is highly dependent on this parameter.

Therefore, by increasing the adsorbent dose from 4.0 to 40.0 g/L, the adsorption capacity of mustard husks drastically decrease from 8.23 to 1.09 mg/g. In the same adsorbent dose range, a relatively slow increase in the percent of Zn(II) removal (R,%) from 79.19 to 96.14% was also obtained. Further increase in the adsorbent dose does not change significantly the values of adsorption parameters.

The observed variation is a typical one and can be explained by the increase of the binding sites number as the adsorbent dose rise, until a saturation point is reached, after which no further Zn(II) adsorption occurred [24].

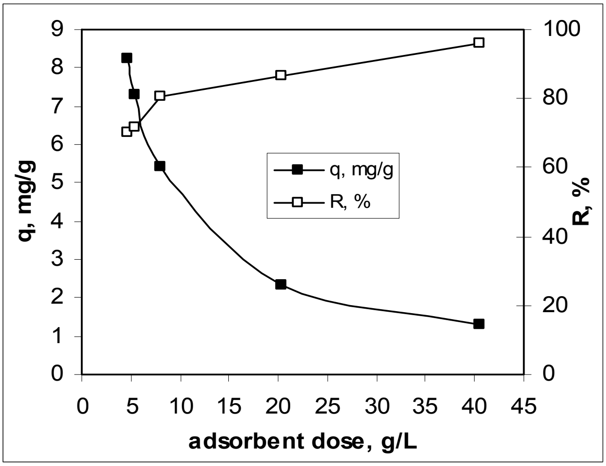

Figure 2. Effect of adsorbent dose on Zn(II) adsorption onto mustard husks (c_0 = 54.19 mg/L, initial solution pH = 5.5, contact time = 24 h, t = 25°C).

Therefore, the optimum adsorbent dose was selected to be as 5.0 g/L, and was used for further experiments.

1.3. Effect of initial Zn(II) concentration: The influence of initial Zn(II) concentration on its adsorption onto mustard husks is presented in Fig. 3. The increase of the initial Zn(II) ions concentration from 13.54 to 189.69 mg/L increased the adsorption capacity of mustard husks from 2.11 to 12.72 mg/g. In the same concentration range, the values of removal percent decrease from 81.26 to 33.68%, with increase of initial Zn(II) concentration.

The opposite variation of the adsorption parameters (q and R) was previously reported [3, 11, 12, 25] and seems determined by the fact that an increase of initial metal ions concentration provide higher driving forces to overcome all mass transfer resistances between solid adsorbent and aqueous solution, and this make that the values of q parameter to increase. However, at higher initial concentration of metal ions, the superficial functional groups of adsorbent are already occupied, and consequently the diffusion of Zn(II) ions appear to be inhibited. In consequence the values of Zn(II) removal percent (R, %) will decrease with increasing of initial metal ions concentration.

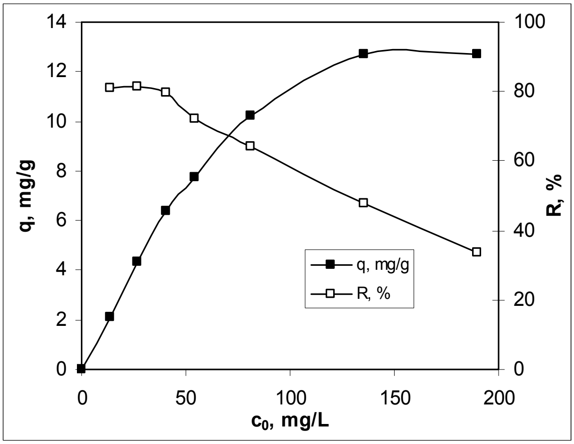

Figure 3. Effect of initial Zn(II) concentration on its adsorption onto mustard husks (initial solution pH = 5.5, adsorbent dose = 5.0 g/L, contact time = 24 h, t = 25°C).

The obtained experimental results have shown that the most efficient removal of Zn(II) ions onto mustard husks occurs when initial Zn(II) concentration is lower than 20 mg/L. In this concentration range (0 – 20 mg/L), the Zn(II) concentration in effluent solution is lower than the value of maximum permissible limit (1.0 mg/L) [26] and mustard husks can be considered an efficient adsorbent in the treatment of wastewater. When initial Zn(II) concentration is higher than 20 mg/L, in order to reduce the metal ions concentration below the permissible limit, are necessary two or more adsorption steps.

1. 4. Effect of contact time: The experimental results (Fig. 4) showed that the adsorption capacity of mustard husk for Zn(II) increase with increasing of contact time. Initially the adsorption process occurs very fast, therefore in the first 30 min more than 63% of Zn(II) ions were retained, after that the rate becomes slower near to equilibrium, which is obtained after 60 min. Once the equilibrium state was reached, the adsorption of Zn(II) ions onto mustard husks did not change significantly.

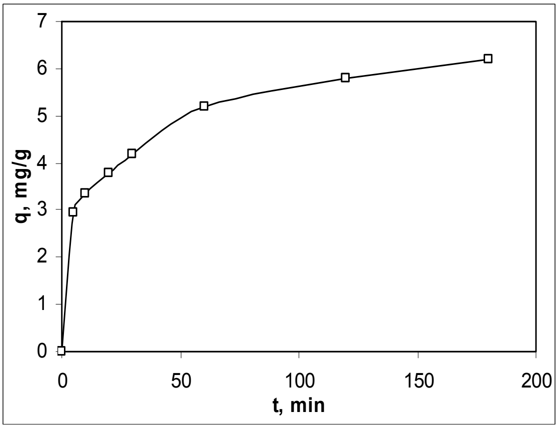

Figure 4. Effect of contact time on Zn(II) adsorption onto mustard husks (c_0 = 54.19 mg/L, initial solution pH = 5.5, adsorbent dose = 5.0 g/L, t = 25°C).

The shape of dependence illustrated in Fig. 4 suggest that the adsorption process of Zn(II) ions from aqueous solution onto mustard husks is the result of two successive stages: (a) first stage where the adsorption rate is very high (first 30 min) which is predominantly determined by the easy of interaction between Zn(II) ions and adsorbent sites that are available in high number, and (b) second stage where the adsorption capacity is almost constant and corresponds to the equilibrium of adsorption process. In the second stage, the number of available sites from adsorbent surface is more reduced, and the diffusion process becomes more important in the binding of Zn(II) ions.

Therefore a contact time of at least 60 min is necessary for the efficient removal of Zn(II) ions from aqueous solution using mustard husks, in mentioned experimental conditions.

2. Adsorption isotherm modeling: Adsorption isotherms are essential for practical design of adsorption system, because their parameters express the surface properties and affinity of adsorbent for a given metal ion. In order to estimate the potential utilization of mustard husks for Zn(II) ions removal from aqueous solution, two isotherm models (Langmuir and Freundlich) were employed to evaluate the adsorption properties of this low-cost adsorbent.

The Langmuir model is the most widely applied model for monolayer adsorption, and is based on the following assumptions: (i) the number of adsorption sites is fixed, (ii) all sites are equivalent, (iii) each site can retain only one metal ion until a complete coverage of adsorbent surface, and (iv) the retained metal ions do not interact after adsorption [27, 28]. Unlike Langmuir model, the Freundlich isotherm model is used to describe the multi-layers adsorption on heterogeneous surfaces or surfaces supporting sites of different affinities [27, 29]. The linear mathematical equations of these two isotherm models are presented in Table 1.

Table 1. Quantitative characterization of Zn(II) adsorption of mustard husks on the basis of Langmuir and Freundlich isotherm models

Isotherm model	Mathematical equation	Calculated parameters
Langmuir model [27, 28]	$\frac{c}{q} = \frac{1}{q_{max} \cdot K_L} + \frac{c}{q_{max}}$	R^2 = 0.9939 q_{max} = 12.9907 K_L = 0.0301
Freundlich model [27, 29]	$\log q = \log K_F + \frac{1}{n} \log c$	R^2 = 0.9141 1/n = 0.5283 K_F = 9.9186

Notation: q_{max} – maximum adsorption capacity (mg/g); K_L – Langmuir constant; K_F and n – constants of Freundlich isotherm model.

The parameters of Langmuir and Freundlich isotherm models have been evaluated from the slopes and intercepts of corresponding linear plots (c/q vs. c for Langmuir model, and log q vs. log c for Freundlich, model respectively – Fig. 5), and the obtained values for Zn(II) ions adsorption onto mustard husks are also summarized in Table 1.

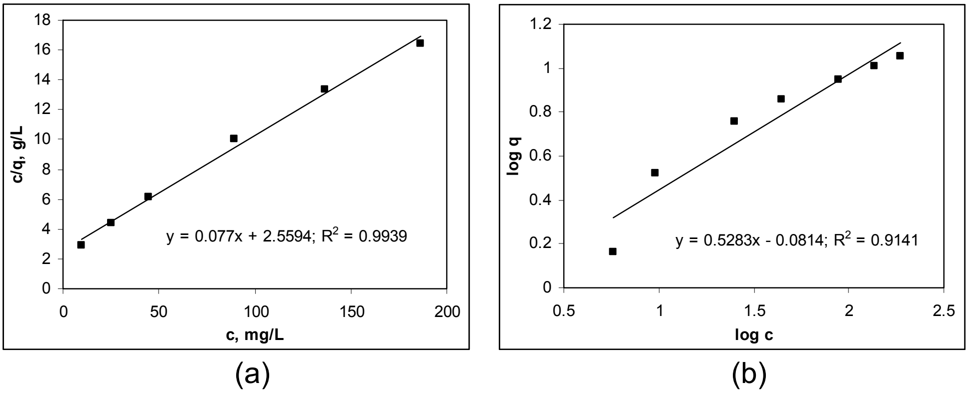

Figure 5. Graphical representation of Langmuir model (a) and Freunslich model (b) for the adsorption of Zn(II) ions onto mustard husks.

The values of correlation coefficients (R^2) shows that the equilibrium isotherm data obtained in case of Zn(II) ions removal onto mustard husks are very well represented by Langmuir isotherm model. In consequence, the surface of mustard husks is considered to present made up of homogeneous adsorption and demonstrate the formation of monolayer coverage of Zn(II) ions on the other surface of adsorbent. The maximum adsorption capacity (q_{max}, mg/g) calculated from this model, is comparable with the Langmuir capacities of other agricultural wastes tested as low-cost adsorbents for Zn(II) ions removal from aqueous solution (Table 2).

Table 2. Comparative values of Langmuir adsorption capacities for Zn(II) removal on various types of agricultural wastes

Adsorbent	pH	q_{max}, mg/g	Reference
Palm tree leaves	5.5	14.60	[30]
Maize cobs	7.5	5.77	[31]
Tea factory waste	5.5	8.9	[32]
Mango peel	-	28.21	[33]
Sugarcane bagasse	5.0	31.11	[34]
Lignin	5.5	11.25	[35]
Mustard husks	5.5	12.99	This study

The Freundlich isotherm model is employed to evaluate the adsorption intensity of Zn(II) ions onto mustard husks. The fractional value of 1/n parameter shows that the adsorption of Zn(II) is a favorable process. However, the value of R^2 coefficient obtained for this model is lower than that obtained in case of Langmuir model (Table 1), which indicate that Freundlich isotherm model is not so adequate to describe the adsorption of Zn(II) ions onto mustard husks.

3. Kinetic modeling: In order to analyze the kinetics of adsorption process of Zn(II) ions onto mustard husks, the pseudo-first order and pseudo-second order kinetic model were used. These models are based on the linear equations that are presented in Table 3.

Table 3. Kinetic characterization of Zn(II) adsorption onto mustard husks.

$q_{e,\,exp}$		6.4192
Kinetic model	Linear equation	Calculated parameters
Pseudo-first order model [36, 37]	$\log(q_e - q_t) = \log q_e - k_1 \cdot t$	$R^2 = 0.9734$ $q_e = 3.4127$ $k_1 = 0.0079$
Pseudo-second order model [36, 37]	$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} t$	$R^2 = 0.9963$ $q_e = 6.4935$ $k_2 = 0.0237$

$q_{e,\,exp}$ – adsorption capacity at equilibrium, obtained experimentally (mg/g),
q_e and q_t - adsorption capacities of Zn(II) at equilibrium and at time t, respectively (mg/g), k_1 - the rate constant of pseudo-first order kinetics equation (min^{-1}), k_2 - the pseudo-second order rate constant (g/mg min).

The kinetics parameters of the pseudo-first order and pseudo-second order kinetics models, calculated from their linear representation ($\log(q_e-q_t)$ vs. t and t/q_t vs. t, respectively) (Fig. 6) are given in Table 3, together with corresponding correlation coefficients (R^2).

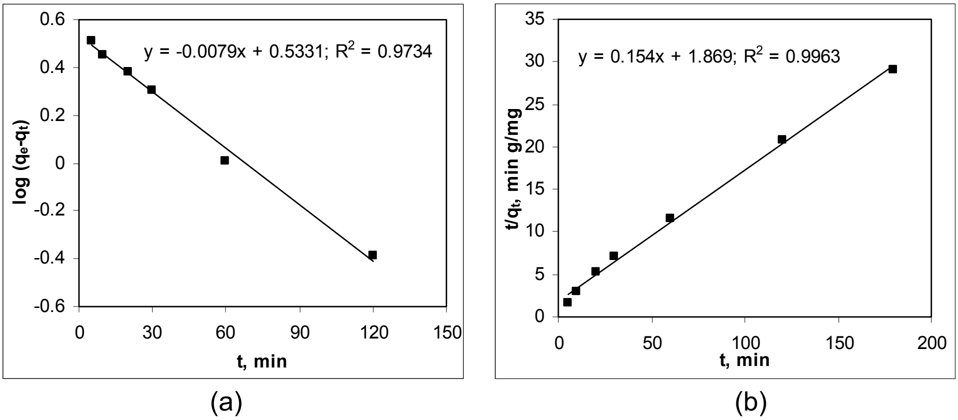

Figure 6. Linear representation of the pseudo-first order kinetic model (a) and pseudo-second order kinetic model (b) for Zn(II) adsorption onto mustard husks.

It can be observed that the correlation coefficient (R^2 = 0.9963) for the pseudo-second order kinetic model is higher in comparison with the value obtained form the pseudo-first order kinetic model, and the calculated value of adsorption capacity at equilibrium (q_e, mg/g) from the pseudo-second order kinetic model is very close to those obtained experimentally ($q_{e,\,exp}$ = 6.4192 mg/g). These observations clearly indicate that the pseudo-second order kinetic model is more adequate to describe the adsorption kinetic of Zn(II) ions onto mustard husks.

The pseudo-second order kinetic model is based on the assumption that in adsorption process, the rate limiting step is the chemical interaction between metal ions from aqueous solution and functional groups from adsorbent surface [37]. Similar behaviors have been reported for the removal of Zn(II) ions on various types of agro-waste materials [30-34].

CONCLUSIONS

In this study, the removal of Zn(II) ions from aqueous solution by adsorption onto mustard husks was investigated. The experiments were performed in batch systems, as a function of several experimental parameters (such as initial solution pH, adsorbent dose, initial Zn(II) concentration and contact time), in order to establish the optimum experimental conditions.

The experimental results have shown that the highest adsorption capacity of mustard husks was obtained at initial solution pH of 5.5, 5.0 g/L adsorbent dose and a minimum 60 min of contact time, when for an initial Zn(II) concentration lower than 20 mg/L, this material can be considered an efficient adsorbent in the treatment of wastewater.

The Langmuir isotherm model best-fit the equilibrium data for the adsorption of Zn(II) ions onto mustard husks, and the maximum adsorption capacity was 12.99 mg/g. The analysis of kinetic data showed that the adsorption of Zn(II) ions onto mustard husks followed the pseudo-second order kinetic model, and this means that the rate controlling step is chemical interaction (most probable ion exchange type) between superficial functional groups of adsorbent and Zn(II) ions from aqueous solution.

The results presented in this study indicate that mustard husks can be an efficient alternative adsorbent for the removal of Zn(II) ions from aqueous media.

EXPERIMENTAL SECTION

1. Adsorbent material: The mustard husks used as adsorbent in this study was obtained from Faculty of Agriculture (USAMV Iaşi, Romania), from their own production. The agricultural waste was washed several times with double distilled water to remove impurities and dried in air at 65 – 70°C for 24 hours. The obtained material was crushed and sieved to a particle size of 1.0 – 1.5 mm, stored in desiccators and was directly used as adsorbent, without any pre-treatment. The chemical composition of mustard husks was determined using a Bruker EDX spectrometer, and was found to be: 50.41% C, 41.25% O, 1.18% P, 2.23% S, 2.11% N, 1.53% Ca, 0.59% Mg and others 0.71%.

2. Chemical reagents: All chemical reagents were of analytical degree and were used without further purifications. In all experiments, diluted solutions were prepared using fresh double distilled water, obtained from a commercially distillation system.

A stock solution of 680 mg Zn(II)/L was obtained by dissolving zinc nitrate (purchased from Reactivul Bucharest) in double distilled water. All other concentrations, which varied between 13.54 and 189.69 mg/L were prepared by dilution from stock solution. The initial solution pH was obtained by adding small volumes of 0.1 M HNO_3 or NaOH solutions.

3. Adsorption experiments: The adsorption experiments were performed using by batch technique, adding a constant amount of mustard husks (0.125 g) to a volume of 25 mL of solution of known Zn(II) concentration in 150 mL conical flasks, with intermittent stirring for a required period of time.

The effect of initial solution pH was examined at room temperature (25 ± 0.5°C), adjusting the pH values between 1.0 and 6.5. The influence of adsorbent dose on Zn(II) adsorption was also investigated by mixing adsorbent samples between 4.0 and 40.0 g/L with 25 mL of Zn(II) solution (54.20 mg/L) at pH 5.5. The effect of initial Zn(II) concentration on mustard husks adsorption efficiency was studied within 13.54 – 189.69 mg/L concentration range. In case of kinetics experiments, the same amount of adsorbent (0.125 g) was mixed with 25 mL of 54.20 mg/L Zn(II) solution at various time intervals, between 5 and 180 min.

After adsorption procedure was complete, the two phases were separated through filtration, and Zn(II) concentration in filtrate was analyzed spectrophotometrically using xylenol orange (Digital Spectrophotometer S104D, λ = 570 nm, 1 cm glass cell, against blank solution) [38].

The adsorption efficiency of mustard husks for Zn(II) ions from aqueous solution was quantitatively evaluated using the following parameters:

- adsorption capacity (q, mg/g):

$$q = \frac{(c_0 - c) \cdot (V/1000)}{m} \qquad (1)$$

- percent of Zn(II) removed (R,%):

$$R = \frac{c_0 - c}{c_0} \cdot 100 \qquad (2)$$

where: c_0, c are the initial and equilibrium concentration of Zn(II) ions from aqueous solution (mg/L); V is volume of solution (mL) and m is the mass of adsorbent material (g).

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