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Valorization of *Moringa oleifera* seed husk as biosorbent: isotherm and kinetics studies to remove cadmium and copper from aqueous solutions

B. Garcia-Fayos, J.M. Arnal*, J. Piris, M. Sancho

ISIRYM Research Institute, Universitat Politècnica de València, Camino de Vera s/n, Valencia 46022, Spain, email: jarnala@iqn.upv.es (J.M. Arnal)

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ABSTRACT

Moringa oleifera is a plant with multiple uses. Among them, the best-known use of seeds is as natural coagulant for the clarification of turbid water. The process of preparation of the natural coagulant generates different wastes including *Moringa* seed husk. This work studies the use of this waste as biosorbent for cadmium and copper removal. Adsorption studies were performed using batch test and the effects of contact time, temperature, pH, concentration of metal, and concentration of adsorbent were also analyzed. We have also studied the biosorbent structure through SEM and EDX. Experimental results were analyzed using Langmuir and Freundlich isotherms and the adsorption kinetics by pseudo-first and pseudo-second-order equations. The experimental results showed that the maximum removal of Cu and Cd was observed at pH 6, 1 h contact time, 1 mg/L initial concentration of Cd and 2 mg/L of Cu, and 1 g of biosorbent added. The percentages of metal removal were around 90% for both metals studied. Results indicate that the data of Cu and Cd adsorption onto *Moringa* seed husk were best fit by the Langmuir model. The adsorption capacity (q_m) calculated from the Langmuir isotherm was 13.1 mg g^{-1} for both metals, higher than observed for other biosorbents prepared from *M. oleifera*. The results indicate that the adsorption kinetic data were best described by pseudo-second-order model. In summary, *Moringa* seed husk can be considered as potential and promising biosorbent for heavy metals removal from water or wastewater systems.

Keywords: Cadmium; Copper; Adsorption; *Moringa oleifera* husk; Heavy metals removal

1. Introduction

Access to water and sanitation is one of the biggest challenges today. Water scarcity and water pollution are the main problems to address. Heavy metals are, among others, substances responsible for the pollution of water. Arsenic, cadmium, copper, lead, mercury, zinc, and nickel, coming from industrial activity, can be present in surface and ground water and represent a hazard because are toxic to humans.

One of the main problems of heavy metal is the trend of some to bioaccumulate and biomagnificate [1,2], which means they are pollutants that persist in the body, accumulating along trophic chain and

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*Corresponding author.

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causing some pathologies in human being, or even death at high concentrations, due to exposition and ingestion [3,4].

The World Health Organization (WHO) establishes an acceptable maximum concentration of cadmium and copper in drinking water of 0.003–2 mg L^{-1}, respectively [5].

The main techniques of metal ion removal from water are: chemical precipitation, oxidation–reduction processes, ionic exchange, electrochemical treatments, membrane processes, solvent extraction, adsorption, and biosorption [6,7]. Selection of the best treatment for polluted water by heavy metals should be done considering the composition of the water, the flexibility and reliability of the treatment, and its environmental impact. Furthermore, initial investment and operational costs must be taken into account [8].

Biosorption is an alternative process to conventional methods for treating liquid effluents with heavy metals. It is a technique that can be used for the treatment of high volumes of water with low metal concentrations. Some advantages of biosorption with respect to conventional techniques include low cost, possible regeneration of biosorbent, recovery of the heavy metal after regeneration, and low waste production [9,10].

The main factors that affect the effectiveness of biosorption process are: the biosorbent material, particle size, kind of heavy metal, pH, the presence of other metals in the solution, temperature, initial concentration of metal, dose of biosorbent, and contact time between heavy metal and biosorbent.

There are many materials with adsorptive ability both from inorganic origin such as clays (bentonites, kaolinites, etc.), or organic origin such as fruit wastes [11], seeds of different plants [12–14], activated carbons from several types of woods [15,16], etc. Adsorbents of vegetal origin are very efficient, low-cost, and they can be modified with the aim of obtaining greater effectiveness and multiple reuses to improve its applicability [17]. Some of the biosorbents studied for the removal of heavy metals in polluted waters are the ones prepared from different parts of the *Moringa oleifera* tree, although its best-known use is the application of seeds as natural coagulant for turbid water clarification [18].

Table 1 shows different substrates of *M. oleifera* which have been tested as biosorbents for various heavy metals.

As it can be seen in the previous table, there are several studies of biosorption from some components of the *M. oleifera* tree, such as activated carbon prepared from husk, pods or wood, seeds, or even leaves, for the removal of different heavy metals.

In the present work, biosorption ability of *M. oleifera* raw husk without being prepared as activated carbon has been studied. The raw husk has been tested for the removal of cadmium and copper from synthetic water. There are not previous studies of this part of the tree used as raw material for these metals. In comparison to other parts of the tree showed in Table 1, the use of the raw husk as biosorbent does not need processing of the material reducing associated costs and it allows valorization of the waste produced after coagulant extraction from the seed for water treatment purposes.

Independent test for each heavy metal has been performed, estimating the optimal parameters of contact time, pH of the solution, temperature, initial concentration of heavy metal, and biosorbent dose. Results have allowed to determine the maximum adsorption capacity of the biosorbent as a function of the mathematical linear regression following the isothermal models of Langmuir and Freundlich, and the kinetics using pseudo-first and second-order models. This has allowed determining if the biosorption process is suitable for removing heavy metals from contaminated waters.

2. Materials and methods

2.1. Preparation of biosorbent

M. oleifera seeds were collected in Burkina Faso. They were manually dehusked, and then stored for being later conditioned. To remove humidity from the husk, it was dried in a heater (*Digitronic*) at a temperature of 333 K during 24 h. Then, the dried husk was grinded with an electrical mill (*Moulinex Super Junior "S"*) and after, it was washed with distilled water since turbidity values of washed effluent (measured with a turbidimeter D112 DINKO) were lower than 1 NTU. The husk was again dried in the heater, following the procedure described before. Finally, the sample was manually powder and sieved, thus obtaining a fraction of size between 125 and 250 μm of diameter. This fraction was stored for being used later as biosorbent.

2.2. Biosorbent characterization

A Scanning Electron Microscopy (SEM) analysis was performed to observe the morphology of the biosorbent surface prepared as explained before. Micrography picture and microanalysis spectra obtained by energy dispersive X-ray (EDX) were carried out by JEOL JSM–6300 microscopy equipment. Biosorbent was also characterized before and after

Table 1
Biosorption studies using different parts of the tree *M. oleifera* for removing heavy metals in water solutions

Biosorbent	Metal	Refs.
Moringa oleifera seed powder	Cd(II)	[12,14,19]
	Zn(II)	[19]
	As(III)	[20]
	As (V)	
Activated carbon from husk and pods of *Moringa oleifera*	Pb(II)	[21]
Activated carbon from *Moringa oleifera*	Cu(II)	[15]
	Ni(II)	
	Zn(II)	
Activated carbon from *Moringa oleifera* leaves	Cd(II)	[16]
	Cu(II)	
	Ni(II)	
Moringa oleifera biomass	Zn(II)	[22]
Moringa oleifera bark	Pb(II)	[23]
Moringa oleifera tree leaves	Pb(II)	[24]
Moringa oleifera husk	Cd(II)	This study
	Cu(II)	

metal adsorption using Fourier Transform Infrared (FTIR) technique. FTIR spectra were obtained using FTIR spectrophotometer (Model 710, Nicolet, Madison, USA). The analysis was performed using KBr and a spectral range varying from 0 to 4,500 cm^{-1}

2.3. Synthetic water preparation

Biosorption tests were done with synthetic solutions for each heavy metal, with a concentration of 50 $mg\ L^{-1}$ (stock solution). Cadmium solutions were prepared from tetrahydrated cadmium nitrate, $Cd(NO_3)_2 \cdot 4H_2O$ (Panreac, Spain), and copper solutions were prepared from pentahydrated copper sulfate, $CuSO_4 \cdot 5H_2O$ (Panreac, Spain).

The value of pH of each solution was adjusted with chloride acid, HCl (Panreac. Spain) or NaOH (Panreac, Spain), depending on the required value.

2.4. Batch biosorption tests

Biosorption tests were performed with 500 mL of each heavy metal solution, separately. This volume of the metal solution was placed with the biosorbent in an orbital shaker (GFL model 3015), working at a shaking speed of 100 rpm. Two control or blank were included in each experimental set. The blank consisted in the heavy metal solution without biosorbent addition.

The effect of the following parameters was studied: contact time (0–24 h), pH of the solution (2.0–8.0), temperature (3.5–30°C), initial concentration of metal ions (1–40 $mg\ L^{-1}$) obtained by dilution of stock solution, and biosorbent dose (0.05–1 g $(500\ mL)^{-1}$). Each test was repeated twice to improve the reliability of the results.

Samples from each test were filtered and analyzed by atomic absorption spectrophotometry (Perkin Elmer 3100), to determine heavy metal concentrations.

Adsorption capacity of each test was calculated by the following equation:

$$q_e = \frac{(C_0 - C_t)V}{m} \tag{1}$$

where q_e is the adsorption capacity of the biosorbent ($mg\ g^{-1}$), V is the heavy metal solution volume (L), m is the mass of biosorbent used in the test (g), C_0 and C_t are the concentrations of the heavy metal in the solutions ($mg\ L^{-1}$) at the beginning of the test and at a time t, respectively.

The percentage of heavy metal removal for each biosorption test was determined by the following equation:

$$\%\ \text{removal} = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{2}$$

where C_0 and C_t are the concentrations of the heavy metal in the solutions ($mg\ L^{-1}$) at the beginning of the test and at a time t, respectively.

2.5. Adsorption isotherms

The models defined by Langmuir and Freundlich were used for studying the adsorption isotherms.

2.5.1. Langmuir model

This is the non-linear model most used to represent homogeneous adsorption, but it does not show evidences of the process mechanism. In this model, it is assumed that the adsorption process takes place over a homogeneous surface, forming an adsorbate monolayer when saturation is reached. It also assumes adsorption energy is constant and adsorbed molecules keep unmoving. Langmuir model [25] can be described by the following expression:

$$q_e = \frac{X_m b\ C}{1 + b\ C_e} \tag{3}$$

where q_e is the adsorption capacity of the biosorbent (mg g^{-1}), C_e is the equilibrium concentration of the metal ion in solution (mg L^{-1}), X_m represents the maximum capacity of retention of the heavy metal per unit of adsorbent mass (mg g^{-1}), and b is the Langmuir constant that is related with the adsorption energy (L mg^{-1}). This constant shows in a quantitative way the affinity between the biosorbent and the adsorbate, so a high value of this constant means higher affinity.

2.5.2. Freundlich model

Freundlich equation is a classical model to describe heterogeneous adsorption. It is an empirical model with two variable parameters, which does not show a finite removal capacity. The Freundlich model [26] is represented by the following expression:

$$q_e = K_F \cdot C_e^{1/n} \tag{4}$$

where q_e is the adsorption capacity of the biosorbent (mg g^{-1}), C_e is the equilibrium concentration of the metal ion in solution (mg L^{-1}), K_F is the Freundlich equilibrium constant (mg g^{-1}), and n is the constant of affinity between the adsorbate and the sorbent. If $n > 1$, the tendency of adsorption is high at low concentrations of solute in solution.

2.6. Kinetic studies

The results obtained in the tests for determining the optimal contact time were adjusted following linear equations of the kinetic models of pseudo-first and second-orders.

2.6.1. Pseudo-first-order

The mathematical expression of the pseudo-first kinetic order is based on the assumption that each metal ion has a sorption place in the biosorbent material. The Lagergren [27] pseudo-first-order model is represented by the following expression:

$$\ln(q_e - q_t) = \ln(q_e) - K_1 \cdot t \tag{5}$$

where q_e and q_t are the amount of metal adsorbed per biosorbent mass (mg g^{-1}) at the equilibrium and at a time t (min), respectively; and K_1 is the kinetic constant of pseudo-first-order (min^{-1}).

2.6.2. Pseudo-second-order model

The mathematical expression of the pseudo-second kinetic order is based on the assumption that the adsorbate is adsorbed at two places of the biosorbent. The model [28] is represented by the following expression:

$$\frac{t}{q_t} = \frac{1}{K_2 \cdot q_e^2} + \frac{t}{q_e} \tag{6}$$

where K_2 is the pseudo-second-order kinetic constant (g mg^{-1} min^{-1}), and the product $K_2 \cdot q_e^2$ represents the initial speed of adsorption (mg g^{-1} min^{-1}).

3. Results and discussion

3.1. Biosorbent characterization

The material surface bioadsorbent was studied using a scanning electron microscope coupled to an X-ray detector.

3.1.1. Chemical composition by EDX

The spectrum obtained for *M. oleifera* husk is shown in Fig. 1.

Being a naturally occurring organic bioadsorbent, its chemical composition is mostly based on the elements carbon and oxygen, as shown by the spectral peaks.

The percentage of each element that composes bioadsorbent structure is summarized in Table 2.

As shown, the husk structure of *M. oleifera* is mainly formed by carbon and oxygen elements, with 72.580 and 27.220% of weight, respectively.

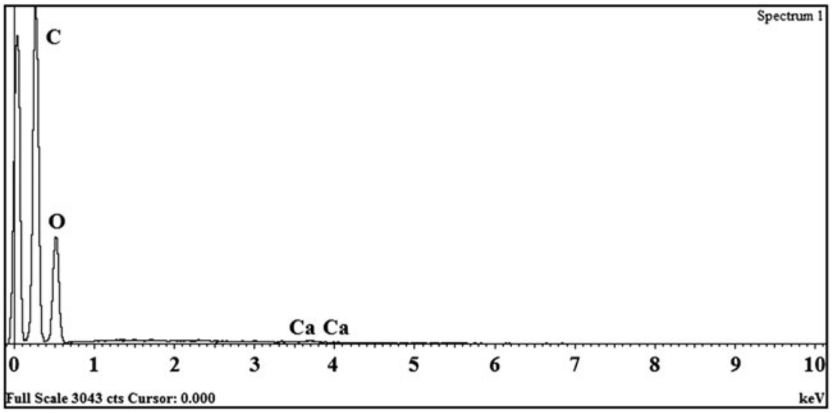

Fig. 1. Spectrum for *M. oleifera* husk after microanalysis by energy-dispersive X-ray.

3.1.2. Functional groups by FTIR

Fig. 2 shows the husk characterization by means of FTIR spectra in order to determine the functional groups responsible of metal binding. The spectra for the raw material and the spectra for the husk after highest results of biosorption of Cu or Cd heavy metals are included.

As it can be observed, the FTIR spectra of the three samples analyzed are similar with slight changes. The following peaks can be emphasized in the raw husk:

(1) one peak at 3,390 cm^{-1}, which is attributed to the stretching of chemisorbed H_2O or more specifically to O–H bond in hydroxyl functional groups.
(2) smaller peaks at 2,970 and 2,920 cm^{-1}, which are due to symmetric and asymmetric C–H stretching vibrations (as CH_3 and CH_2–groups).
(3) peak at 1,640 cm^{-1} can be assigned to $H_2O + C = O$ or $H_2O + NH$ stretching vibrations.
(4) peak at 1,050 cm^{-1} can be originated by C–O bonds.

Table 2
EDX microanalysis to determine the chemical composition of the structure of *M. oleifera* husk

Element	Weight (%)	Atomic (%)	Compd (%)	Formula
C	27.220	33.280	99.720	CO_2
Ca	0.200	0.070	0.280	CaO
O	72.580	66.640		
Total	100.000			

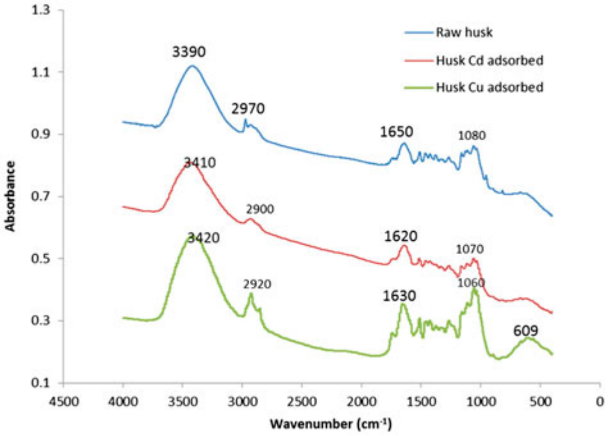

Fig. 2. FTIR spectra of Raw husk, Cadmium-adsorbed husk, and Copper-adsorbed husk.

These peaks observed have shifted to 3,410, 2,900, 1,620, and 1,070 cm^{-1} for Cd and to 3,420, 2,920, 1,630, and 1,060 cm^{-1} for Cu, respectively. For cooper, it is interesting to highlight the shift of the peak from 1,080 (in the raw husk) to 1,060 cm^{-1} (in the husk Cu adsorbed) that seems to be due to the metal–oxygen binding as previously reported [29]. It is also significant the peak observed at 609 cm^{-1} for copper adsorbed husk which indicates the binding of the Cu to O group as a consequence of the adsorption. For Cadmium, shift from 1,650 to 1,620 cm^{-1} and from 1,080 to 1,070 cm^{-1} could indicate metal adsorption through the complexation of Cd(II) with functional groups present in the adsorbent [30]. Therefore, the spectral analysis before and after metal binding confirms that carboxyl, acidic, and hydroxyl groups, are main contributors in metal ion uptake.

3.1.3. Surface morphology characterization by SEM

The SEM picture shows the surface texture and morphology of the biosorbent. The morphology of the surface of the husk of *M. oleifera* is characterized by a filamentous structure (Fig. 3 left). After increasing the resolution (Fig. 3 right), it is found that it is a material with a spongy and irregular structure with a high number of pores that can be work as active adsorption centers. This feature makes the husk surface of *M. oleifera* a suitable natural biosorbent for removing heavy metals.

3.2. Effect of operating conditions

Biosorption test with *M. oleifera* husk as biosorbent allowed to optimize the following parameters: contact time, pH, and temperature of the solution, biosorbent dose and initial concentration of heavy metal.

3.2.1. Contact time effect

Fig. 4 shows the adsorption capacity of cadmium and copper with time. The aim of this test is determining the time needed to adsorb the highest amount of heavy metal by reaching saturation of the biosorbent. Biosorption tests were performed with an initial heavy metal concentration of 5 mg L^{-1}, a dose of 0.2 g biosorbent (500 mL^{-1}), temperature of 293 K and a pH value of 6 units.

In the Fig. 4 adsorption results are shown for samples with biosorbent (Cd, Cu) and the corresponding control or blank without biosorbent (B. Cd and B. Cu, respectively).

The results show a high value in the adsorption capacity for the first time samples, which implies a rapid decrease in the concentration of heavy metal in the solution. After 1 h of contact time, a maximum adsorption capacity is observed, with values of 6.656 mg g^{-1} for cadmium and 3.967 mg g^{-1} for copper, equivalent to a percentage removal of 50.657–55.604%, respectively, for each metal.

The average adsorption capacity for control samples or blank was 0.052 mg g^{-1} for cadmium, and 0.124 mg g^{-1} for copper, equivalent to average percentages of adsorption of 0.436–1.359% for each respective metal. Thus, an optimum value of contact time is estimated around one hour for both metals. This contact time was used as reference time for the following tests.

3.2.2. pH effect

Biosorption tests were performed under the following conditions: 1 h of contact time, temperature 293 K, biosorbent dose of 0.2 g (500 mL^{-1}) and heavy metal initial concentration of 5 mg L^{-1}. pH of the synthetic solutions varied in the range of 2–8 pH units. Fig. 5 shows the adsorption capacity obtained after the biosorption tests with *M. oleifera* husk for cadmium and copper.

As shown in Fig. 5, the adsorption capacity increases when the pH of the solution is increased, obtaining maximum values of 6.774 mg g^{-1} for cadmium and 10.024 mg g^{-1} for copper in the pH range studied. The average adsorption capacity for control samples, with values below pH 6, was 0.489 mg g^{-1} for cadmium, and 0.510 mg g^{-1} for copper, equivalent to average percentages of adsorption of 1.848–2.268% for each respective metal. Comparing the effect of pH from 6 units, a significant increase is observed in the adsorption capacity for both heavy metals. This increase is also

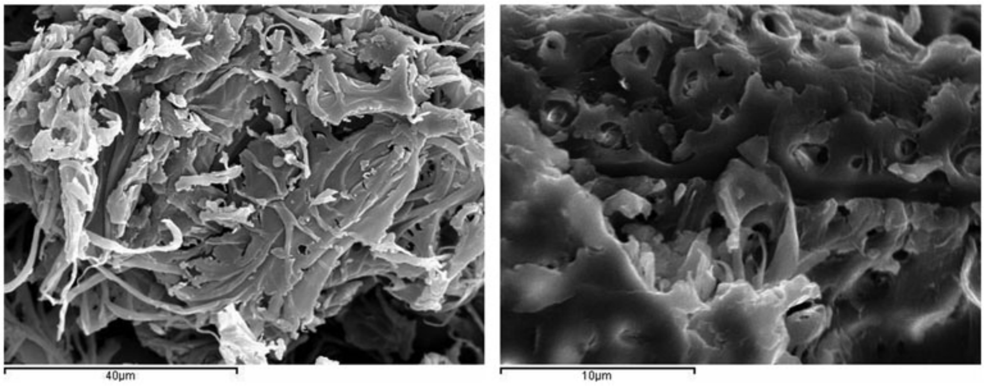

Fig. 3. Left. Scanning electron microscope micrography of *M. oleifera* husk 1500×. Right. Scanning electron microscope micrography of *M. oleifera* husk 5000×.

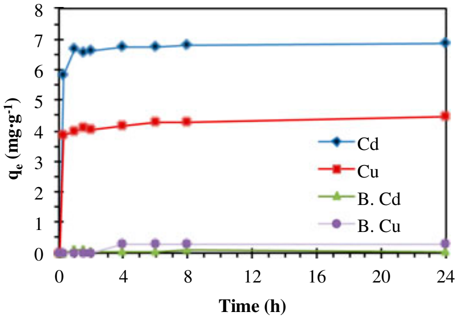

Fig. 4. Effect of contact time on the adsorption capacity of *M. oleifera* husk for heavy metals Cd and Cu.

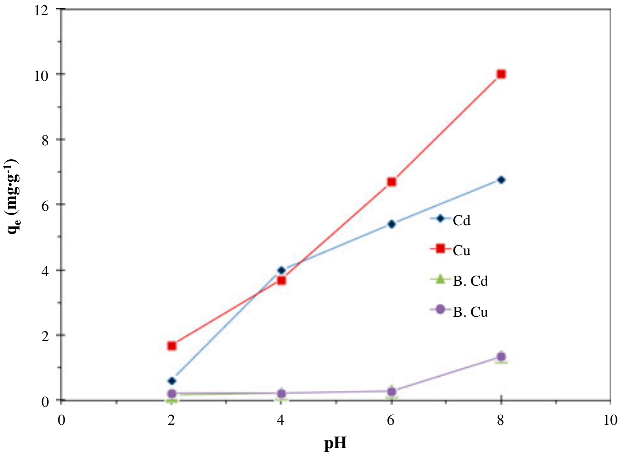

Fig. 5. Effect of pH solution in the adsorption capacity of *M. oleifera* husk for Cd and Cu removal.

reflected in the control samples included in all series. However, this occurs as a result of the precipitation of metal in the form of hydroxide and not to the biosorption process Therefore, it is estimated that the pH of the solution that improves adsorption is 6 units, achieving an adsorption capacity of 5.421 mg g^{-1} for cadmium and 6.694 mg g^{-1} for copper, equivalent to a percentage removal of 50.080–55.985%, respectively, for each metal. This pH value was taken as reference for the following experiments.

3.2.3. Temperature effect

Effect of temperature on biosorption process was studied under the following conditions: 1 h time test, pH of 6 units, biosorbent dose of 0.2 g (500 mL^{-1}), and initial concentration of heavy metal of 5 mg L^{-1}. Biosorption tests were performed for temperature values of 276.5, 293, and 303 K. The effect of this variable in the biosorption process is reflected in Fig. 6, which represents the adsorption capacity vs. test temperature.

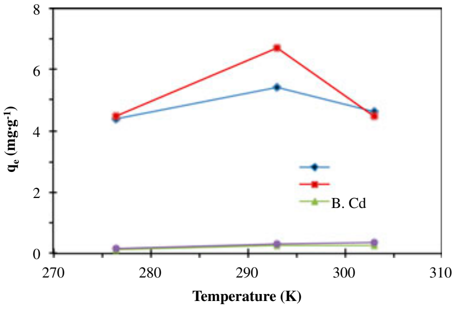

Fig. 6. Effect of solution temperature on adsorption capacity of *M. oleifera* husk for Cd and Cu removal.

As it is shown in Fig. 6, an increase in the adsorption capacity for both metals is observed at temperatures of 293 K while not for control or blank solutions. At temperatures below or above this, the adsorption capacity decreases. The average adsorption capacity for control samples or blanks was 0.210 mg g^{-1} for cadmium, and 0.268 mg g^{-1} for copper, equivalent to average percentages of adsorption of 1.870–2.522%, respectively, for each metal.

For the experimental tests at 293 K, the results obtained are: 5.421 mg g^{-1} for cadmium and 6.694 mg g^{-1} for copper, equivalent to a percentage removal of 50.080–55.985%, respectively. This temperature value (293 K) was taken as reference to perform subsequent experiments.

3.2.4. Effect of biosorbent dosage

In these tests, husk dosage of *M. oleifera* was varied from 0.05 to 1 g. The study of the effect of this variable was performed under the following conditions: 1 h of contact time, pH of 6 units, temperature of 293 K, volume of 500 mL, and heavy metal initial concentration of 5 mg L^{-1}.

Fig. 7 shows the obtained adsorption capacity after biosorption test of *M. oleifera* husk for each heavy metal studied.

Fig. 7 shows that the adsorption capacity decreases with increasing biosorbent dose. This is because the number of active sites is not increased proportionally to the addition of higher biosorbent dose, and as a consequence, adsorption capacity, which is referred to biosorbent mass, decreases [15]. Maximum values in the adsorption capacity are: 7.825 mg g^{-1} for cadmium and 20.588 mg g^{-1} for copper, for husk doses of 0.05 g, equivalent to a percentage removal of 17.191–41.722%, respectively, for each metal.

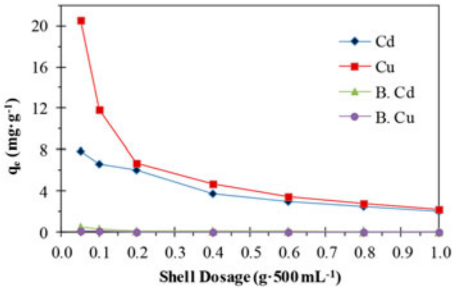

Fig. 7. Effect of biosorbent dosage on the adsorption capacity of *M. oleifera* husk in Cd and Cu removal.

The average adsorption capacity for control samples or blank was 0.137 mg g^{-1} for cadmium, and 0.032 mg g^{-1} for copper, equivalent to average percentages of adsorption of 1.020 and 0.221%, respectively, for each metal.

Fig. 8 shows the evolution of the percentage of heavy metal removal based on the husk dose added.

Fig. 8 shows an increase in the removal percentage when husk dose added to solution is increased. This is because the available surface of biosorbent increases with the dose, and also the availability of active sites, resulting in a higher metal removal rate [31]. The evolution of the percentage of adsorption with the mass of husk added, shows that the highest values are achieved for the higher doses of biosorbent, with values of 87.267% for cadmium and 89.845% for copper, for husk doses of 1 g. This implies that, although at higher biosorbent doses the percentage of removal is higher, the biosorbent is more efficient at lower dosages since adsorption capacity is higher as it has been shown in Fig. 7.

Therefore the range of husk dosages that produces better combination of removal percentage and biosorbent capacity is between 0.1 and 0.2 g 500 mL^{-1}. For this reason, the following tests were performed with a husk dose of 0.2 g in order to be able to compare the effect of biosorption process with the other variables previously studied, which were tested with this husk dosage.

3.2.5. Effect of initial metal concentration

Biosorption experimental tests varying the initial concentration of the synthetic heavy metal solutions from 1 to 40 mg L^{-1} were conducted (in the case of Cu, the range varied from 2 to 40 mg/L, according to the standards fixed by WHO for human drinking water [5]). Assays were performed with a dose of 0.2 g of husk in 500 mL of solution, 1 h contact time, pH of 6 units and temperature of 293 K. The results obtained for the tests with different values of initial metal concentration are shown in Fig. 9.

The average adsorption capacity for control samples was 0.442 mg g^{-1} for cadmium and 0.242 mg g^{-1} for copper, equivalent to average percentages of adsorption of 1.383 and 1.256% for each respective metal. These results are consistent with previous results for control samples.

An increase in the adsorption capacity with an increase in the heavy metal initial concentration, achieving maximum values of 56.408 mg g^{-1} for cadmium and 52.714 mg g^{-1} for copper, for initial concentration of heavy metal of 40 mg L^{-1} can be observed. This is due to an increase in the driving force (concentration gradient) of the adsorption process due to an increase in the initial concentration of the heavy metal [32].

Fig 10 shows the removal percentage achieved depending on the initial concentrations studied.

Maximum removal percentage values are achieved for heavy metal concentrations of 1 mg L^{-1}, in particular 74.042–78.613% for cadmium and copper, respectively. From this concentration, the removal percentage decreases to a minimum value for initial heavy metal concentrations of 10 mg L^{-1}. From this

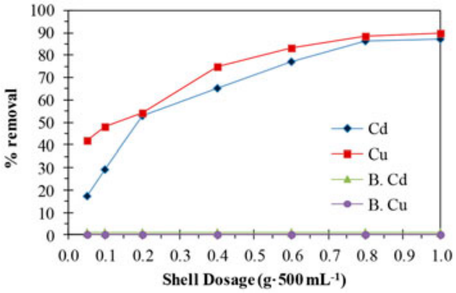

Fig. 8. Dosage effect in the removal percentage of Cd and Cu using *M. oleifera* husk.

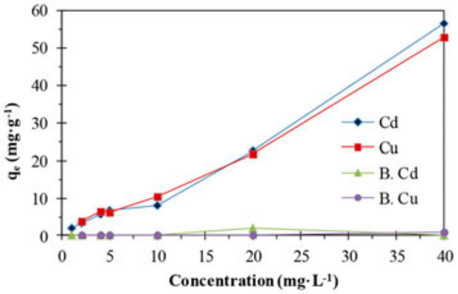

Fig. 9. Effect of the initial metal concentration on the adsorption capacity of *M. oleifera* husk for Cd and Cu.

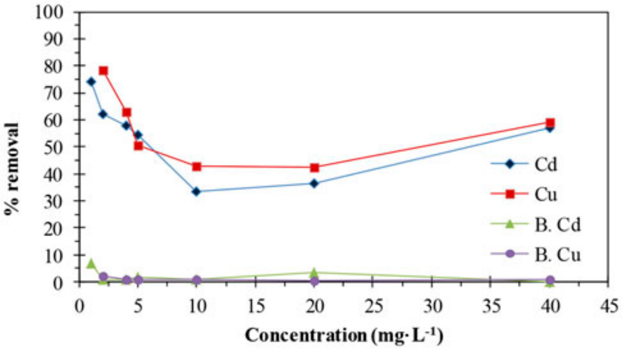

Fig. 10. Effect of the initial metal concentration on the adsorption removal percentage of Cd and Cu.

concentration value, the removal percentage increases again until 57.067% values for Cd and 59.230% for Cu, for initial heavy metal concentrations of 40 mg L^{-1}.

Comparing results of both figures, it is observed that adsorption capacity increases with initial concentration of metal and removal percentage ranges between 35 and 80% for all the concentration tested values. The best values of removal percentage are reached for initial metal concentrations below 5 mg/L.

According to these results, if this biosorbent is going to be used for drinking water treatment, it is recommended low initial metal concentration values in order to reach WHO standards. In the case of Cu, values of initial concentration should be below 4 mg/L of metal for reaching final concentration values below 2 mg/L with only one adsorption stage. In the case of Cadmium, several adsorption stages should be performed in order to reach values below 0.003 mg/L.

For high metal concentrations, as removal percentage is lower, remaining metal concentration in water would be higher. So, if greater purification is needed, several adsorption stages should be applied or a previous treatment (as chemical precipitation), followed by biosorption process.

3.3. Adsorption isotherms

Results from biosorption process were adjusted to linear equations of Langmuir (Fig. 11 left) and Freundlich (Fig. 11 right) mathematical isotherm models.

From the adjustment of each adsorption isotherms, isothermal parameters are calculated in order to select the best model followed by experimental results of biosorption tests. Table 3 shows the isothermal constants for Langmuir and Freundlich models and the mean square error obtained after the results adjustment.

It is observed from the mean square errors of the linear adjustments that the biosorption using *M. oleifera* husk as biosorbent follows better Langmuir adsorption isotherm model. The affinity between the copper metal and the bioadsorbent is greater than the affinity obtained for the metal cadmium as *b* value is double. The maximum adsorption capacity is similar for both metals: 13.123 mg g^{-1} for Cd and 13.089 mg g^{-1} for Cu. Analyzing the Freundlich model, values higher than one are observed for the affinity constant *n*, indicating that the adsorption affinity is greater when lower concentration values of heavy metal are tested.

Table 4 shows the results of different isothermal parameters for different biosorbents prepared from *M. oleifera*, for the removal of cadmium and/or copper of synthetic water.

The values of the Langmuir constant, X_m, obtained in this study are the second best data obtained for the removal of Cd and Cu using biosorbents prepared from *Moringa*. These data indicate a high adsorption capacity of *M. oleifera* husk compared with other published studies with biosorbents prepared from *M. oleifera*. For the comparison of the data, it should be considered the operating conditions of each of the studies since the setting isothermal experimental results depend on them as would be discussed in Section 3.5. Even though it is shown that the results obtained in this study perform higher values in adsorption capacity and affinity constants, which implies that its use is valid for treating water containing heavy metal cadmium and copper contamination.

3.4. Kinetic study

The adsorption kinetics describes speed adsorbate retention, controlling the residence time thereof in the solute interface—dissolution. These settings allow to determine a speed rate at which contaminants are removed from the aqueous medium.

The following figure shows the adjustment results to kinetic expressions of pseudo-first-order (Fig. 12 left) and pseudo-second-order (Fig. 12 right) for both heavy metals after biosorption tests.

From the adjustment of the kinetic models, the kinetic constants are calculated by determining the kinetic model that follows the biosorption tests. Table 5 shows the kinetic constants of the models of pseudo-first and pseudo-second-orders, and the square error obtained after adjusting the results.

From the square errors of each linear adjustment, it is observed that the biosorption process using *M. oleifera* husk fits to a pseudo-second-order kinetic model, obtaining values for R^2 of 1–0.999 for cadmium and copper, respectively.

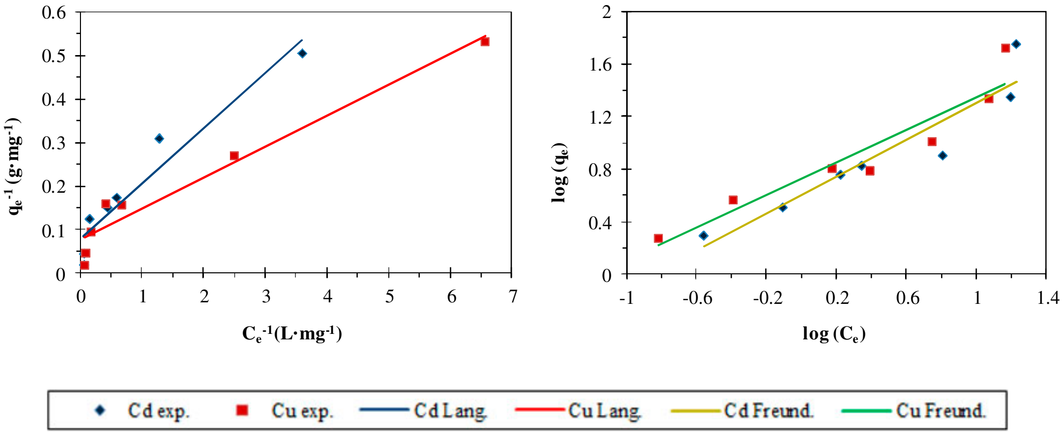

Fig. 11. (left) Mathematical adjustment for Langmuir model for Cu and Cd. (right) Mathematical adjustment for Freundlich model for Cu and Cd.

Table 3
Isothermal constants for Langmuir and Freundlich for Cd and Cu removal using *M. oleifera* husk

	Langmuir constants			Freundlich constants		
Metal	X_m (mg g^{-1})	b (L mg^{-1})	R^2	K_F (mg g^{-1})	n	R^2
Cadmium	13.123	0.560	0.923	3.995	1.433	0.887
Copper	13.089	1.070	0.947	5.322	1.622	0.894

Table 4
Isotherm comparison for different biosorbents obtained from *M. oleifera* for Cd(II) and Cu(II) removal

		Langmuir constants			Freundlich constants			
Biosorbent	Metal	X_m (mg g^{-1})	b (L mg^{-1})	R^2	K_F (mg g^{-1})	n	R^2	Refs.
Moringa oleifera seed	Cd(II)	Non available			3.040	1.370	Non available	[12]
		0.132	4.500	0.940	2.660	1.420	0.970	[14]
		5.770	–0.183	0.982	0.612	–0.318	0.994	[19]
Activated carbon from *Moringa oleifera wood*	Cu(II)	11.136	0.200	0.999	2.912	2.720	0.977	[15]
Activated carbon from *Moringa oleifera* leaves	Cd(II)	171.370	0.037	> 0.99	23.530	3.120	Non available	[16]
	Cu(II)	167.900	0.024	> 0.99	21.230	3.010		
Moringa oleifera husk	Cd(II)	13.123	0.560	0.923	3.995	1.433	0.887	Present study
	Cu(II)	13.089	1.070	0.947	5.322	1.622	0.894	

Table 6 shows the results of the various kinetic constants for different bioadsorbentes prepared from *M. oleifera*, for the removal of cadmium and/or copper of synthetic water.

In accordance with other studies, the kinetics of this study is based on biosorption model pseudo-second-order. There are also many studies which no kinetic analysis of biosorption process is included.

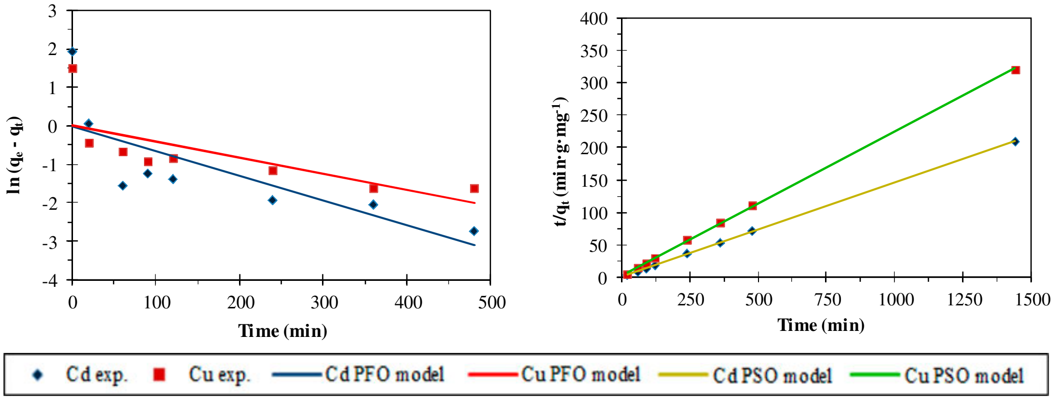

Fig. 12. (left) Mathematical adjustment for pseudo-first-order (PFO) for Cd and Cu removal. (right) Mathematical adjustment for pseudo-second-order (PSO) for Cd and Cu removal.

Table 5
Kinetic constant of pseudo-first and pseudo-second-order model for Cd and Cu removal using *M. oleifera* husk as biosorbent

	Pseudo-first-order model			Pseudo-second-order model		
Metal	q_e (mg g^{-1})	K_1 (min^{-1})	R^2	q_e (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	R^2
Cadmium	0.994	0.007	0.580	6.882	0.032	1.000
Copper	1.057	0.004	0.523	5.305	0.017	0.999

Table 6
Comparison of kinetic constant for different biosorbents from *M. oleifera*, in adsorption studies to Cu and Cd removal

		Pseudo-first-order model			Pseudo-second-order model			
Biosorbent	Metal	q_e (mg g^{-1})	K_1 (min^{-1})	R^2	q_e (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	R^2	Refs.
Moringa oleifera seed powder	Cd(II)	Unavailable			Unavailable			[12] [14] [19]
Activated carbon from *Moringa oleifera wood*	Cu(II)	1.769	0.017	0.725	8.326	0.085	0.999	[15]
Activated carbon from *Moringa oleifera leaves*	Cd(II)	15.240	0.067	0.967	21.570	0.012	0.998	[16]
	Cu(II)	12.860	0.051	0.953	16.590	0.016	0.998	
Moringa oleifera husk	Cd(II)	0.994	0.007	0.580	6.882	0.032	1.000	Present study
	Cu(II)	1.057	0.004	0.523	5.305	0.017	0.999	

Comparing the results of this study, it is observed that the parameters of the adsorption capacity are similar in the case of [15] but lower than the values of [16]. In the case of kinetic constants of the pseudo-second-order model, values obtained in our study are similar to [16] for Cu and different from [15] and from [16] for Cd. These differences should be explained because different parts of the *M. oleifera* tree were used as bioadsorbent (husk or activated carbon form wood or leaves) for removing cadmium and/or copper and also in the different operating conditions of the test performed. Its influence would be discussed in the following section.

Table 7
Comparison of operating conditions in previous biosorption studies using *M. oleifera*

		Operating Conditions								
Biosorbent	Metal	Contact time (min)	pH	T[a] (K)	C_0 (mg L^{-1})	Dosage (g L^{-1})	$q_{\max}$ (mg g^{-1})	Adsorption isotherms	Kinetic studies	Refs.
Moringa oleifera seed powder	Cd(II)	40	6.5	N.A.	25	20.00	3.040	Freundlich[b]	N.A.	[12]
Moringa oleifera seed powder	Cd(II)	120	5.0	313	7	25.00	2.660	Langmuir Freundlich[b] Dubinin–Radushkevich	N.A.	[14]
Activated carbon of *Moringa oleifera wood*	Cu(II) Ni(II) Zn(II)	240	6.0	303	30	2.00	11.530 19.080 17.670	Langmuir[b] Freundlich Dubinin–Radushkevich Temkin	Pseudo-first-order Pseudo-second-order[b]	[15]
Activated carbon from *Moringa oleifera* leaves	Cd(II) Cu(II) Ni(II)	50	5.0	313	40	0.04 a	171.370 167.900 163.880	Langmuir[b] Freundlich	Pseudo-first-order Pseudo-second-order[b] Weber and Morris model	[16]
Moringa oleifera seeds	Cd(II)	60	4.0	303	1	10.00	0.173	Langmuir	N.A.	[19]
	Zn(II)						18.380	Freundlich[b]		
Shelled *Moringa oleifera* seed powder	As(III) As(V)	60	7.5 2.5	N.A.	25	10.00	2.160 1.590	Langmuir[b]	Pseudo-first-order[b]	[20]
Activated carbon from husk and pods of *Moringa oleifera*	Pb(II)	120	5.5	303	30	2.00	1.220	Langmuir[b] Freundlich	Bangham's equation Pseudo-first-order Pseudo-second-order[b]	[21]
Moringa oleifera biomass	Zn(II)	50	7.0	N.A.	50	0.50	52.080	Langmuir[b] Freundlich	Pseudo-first-order Pseudo-second-order[b]	[22]
Moringa oleifera bark	Pb(II)	30	5.0	298	50	0.40	8.600	Langmuir Freundlich[b] Dubinin-Radushkevich Temkin	Pseudo-first-order Pseudo-second-order[b]	[23]
Moringa oleifera tree leaves	Pb(II)	50	5.0	313	40	0.04 a	209.540	Langmuir[b] Freundlich Dubinin-Radushkevich Temkin	Pseudo-first-order Pseudo-second-order[b] Weber and Morris model	[24]
Moringa oleifera husk	Cd(II)	60	6.0	293	5	0.40	13.023	Langmuir[b]	Pseudo-first-order	Present study
	Cu(II)						13.089	Freundlich	Pseudo-second-order[b]	

Note: N.A.: Non available.

[a] Volume of solution N.A.

[b] Model selected.

3.5. Comparison of operating conditions in previous biosorption studies using M. oleifera

After analyzing the results obtained for this biosorption study using *M. oleifera* seed husk as bioadsorbent, for removing Cd(II) and Cu(II) in synthetic water, Table 7 summarizes the optimal operational conditions obtained in present study and its comparison with previous studies for other biosorbents prepared from *Moringa*. The table also includes heavy metals type, isotherm and kinetic mathematical models, and maximum adsorption capacities are obtained.

Regarding operating conditions, it is observed that:

1. Most part of the works obtain its better result of adsorbent capacity ($q_{\max}$) for contact time similar to the one optimized in our study (1 h).
2. For pH, best results for $q_{\max}$ are obtained for pH values neutral or slightly acid.
3. For temperature, best results for $q_{\max}$ are obtained for room temperature (293–313 K).
4. For initial concentration of heavy metal, it is observed that values that maximize $q_{\max}$ are very different. Comparing results of this study with the ones performed with similar C_0 values [14,19], $q_{\max}$ in present study is between 5 and 75 times higher with adsorbent dosages much lower (between 25 and 60 times). This implies a higher efficiency of the bioadsorbent produced in this study.
5. For the dosage of bioadsorbent, it is observed that values that maximize $q_{\max}$ are also very different. Comparing results of this study with the ones performed with similar dosage values [22,23], it is observed that $q_{\max}$ obtained in this work shows an intermediate value but with initial concentration of metal 10 times lower. However, this results it is not conclusive since both metals and parts of the tree used as bioadsorbent are different in each study.

4. Conclusions

This work has studied the application of *M. oleifera* husk as biosorbent for the removal of cadmium and copper heavy metals from synthetic water.

The morphological observation of the husk of the *M. oleifera* seeds has shown that it has a spongy structure with a high number of pores, which makes it ideal to be used as natural biosorbent.

With regard to operational parameters of the sorption process of cadmium and copper, it has been determined the following optimal conditions:

1. The contact time between biosorbent and solution is about one hour for both heavy metals, since adsorption capacity keeps constant after this time.
2. The pH of the solution that produces better adsorption results is 6 units. At values of pH higher than six, metal removal is produced by hydroxide precipitation but not due to adsorption.
3. In the range of temperature studied, between 273 and 303 K, it was found that adsorption capacity was higher at a temperature value of 293 K.
4. Adsorption capacity is higher with the lowest husk dosages tested (values around 0.05 g), although percentages of removal increase when husk dosages are also increased, because the total amount of biosorbent added is higher. Future studies should determine the best way of adding the sorbent to reach similar removal percentage with low sorbent dosages, as it seems that lower husk dosage in different stages will perform more efficiently than a unique high initial dosage, thus reducing the amount of biosorbent needed.
5. Although adsorption capacity increases with the concentration of metals in water (due to higher concentration gradient), the highest percentages of metal removal have been obtained for metal concentrations in water below 5 mg/L.

In relation to isothermal and kinetic models, it has been shown that the process of biosorption with the husk of *M. oleifera* follows better the model based on Langmuir isothermal, and for both metals, the mathematical regression based on the pseudo-second-order fits better with the biosorption process. In addition, it has been found a higher affinity between the biosorbent used and the copper metal, but the values obtained for both studied heavy metals prove that the husk of *M. oleifera* is a suitable biosorbent for the treatment of water contaminated with these heavy metals.

The results of this research show that the husk of *M. oleifera* is a suitable biosorbent for the treatment of water contaminated with cadmium and copper, especially when these heavy metals are in low concentrations.

Future studies, should be performed with multicomponent synthetic solutions (in order to study the competitive and co-ion effect over the adsorption capacity) and also with real contaminated waters.

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Nomenclature

B — Langmuir constant representing adsorption intensity (L mg^{-1})
C_0 — initial concentration of metal ion in solution (mg L^{-1})
C_e — equilibrium concentration of metal ion in solution (mg L^{-1})
C_t — concentration of metal ion in solution at any time t (mg L^{-1})
EDX — energy dispersive X-ray spectroscopy
K_1 — pseudo-first-order rate constant (min^{-1})
K_2 — pseudo-second-order rate constant (g mg^{-1} min^{-1})
K_F — Freundlich constant representing multilayer adsorption capacity (mg g^{-1})
m — mass of adsorbent (g)
n — Freundlich constant affinity
N.A. — non available
q_e — adsorption capacity (mg g^{-1})
q_t — adsorption capacity at any time (mg g^{-1})
R^2 — correlation coefficient
SEM — scanning electron microscope
T — temperature (K)
t — contact time (min)
V — volume of adsorbate solution (L)
X_m — monomolecular adsorption capacity (mg g^{-1})

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