

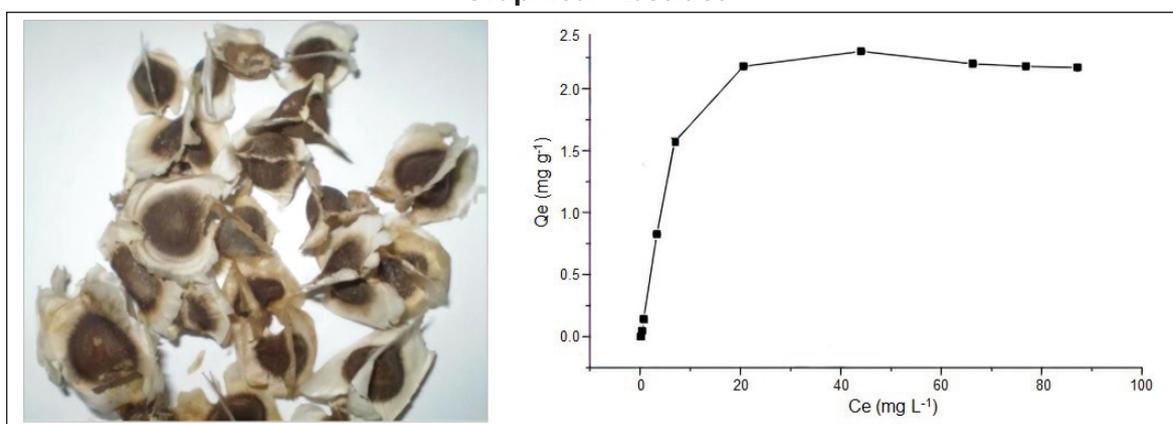
Selective Extraction of Manganese using *Moringa oleifera* Seeds as Bioadsorbent

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Graphical Abstract



Moringa oleifera seeds used for selective extraction of manganese in aqueous samples. Around 60% of the Mn(II) was removed at an initial pH of 3.0. The maximum adsorption capacity for Mn(II) was 10.35 mg g⁻¹.

The adsorption of manganese onto *Moringa oleifera* seeds was optimized as a function of pH, adsorbent mass, particle size and contact time in aqueous solutions in batch tests. The results show that the optimized conditions for manganese adsorption were: pH 3.0, particle size $\leq 180 \mu\text{m}$, adsorbent mass 1.0 g and contact time 15 min. Varying the pH allowed the separation of the manganese species, the seeds selectively retained Mn(II) while Mn(VII) remained free in solution. Around 60% of the Mn(II) was removed at an initial pH of 3.0 with a manganese concentration of 4 mg L⁻¹. The adsorption process was evaluated through adsorption isotherms and kinetics studies. The maximum adsorption capacity for Mn(II) was 10.35 mg g⁻¹. The isotherm followed the Langmuir model and the adsorption kinetics followed a pseudo-second-order kinetic model.

Keywords: manganese, selective extraction, *Moringa oleifera*.

INTRODUCTION

Manganese (Mn) is the tenth element in order of abundance in the earth's crust and it is mainly used in metallurgical processes, approximately 90% being used in the manufacture of steel, and as a component in metallic alloys. Other uses of Mn include the manufacture of ceramics, dry cell batteries and pigments. These activities constitute the major anthropogenic sources of this metal to the aquatic environment [1].

Manganese is an essential micronutrient in the human diet. It activates many enzymes used in metabolic processes and is also required for protein and fat metabolism. Mn helps to maintain

healthy nervous and immune systems and to regulate blood sugar levels [2-4]. However, high doses of manganese cause DNA mutations, neurological disorders (e.g., manganism), overflow of the liver, hallucinations, depression and excessive sleep [5,6]. Therefore, the study of trace elements is gaining importance, especially when these elements are present in the environment in different oxidation states [7]. There are 11 oxidation states of manganese, the most prevalent being Mn(II), Mn(IV) and Mn(VII), and their order of toxicity is Mn(II) > Mn(VII) > Mn(IV) [8]. In this context, it is essential to establish methods for the removal of this metal, especially Mn(II), which is the most toxic species in aqueous or solid effluents.

Precipitation as a hydroxide is one of the most commonly used techniques for metal removal, through its reaction with a base added to the effluent; however, this procedure is not appropriate for low concentrations.

The use of solid phase extraction (SPE) has been frequently proposed as a technique for metal removal and it is suitable for use in batch or flow experiments. The choice of the adsorption phase is dependent on the adsorption capacity associated with each species considered [9].

The use of natural adsorbents has been successfully employed in metal ion adsorption. The significant benefits of adsorption processes include effective and economical contaminant removal, recovery of the adsorbent metals from the adsorbent and its recycling, low sludge production, simple process procedures and high removal efficiencies. In this context, the *Moringa oleifera* seeds have been gaining attention. Moringa seeds have been most widely applied as a coagulant agent, but many studies have been performed in order to explore other potential applications of this material, especially in the removal of metals from aqueous systems. This material is of low cost and is easy to obtain, and it has good potential for application in procedures for the removal and selective extraction of metal ions [10].

The aim of this study was to describe the use of *M. oleifera* seeds for the extraction of Mn(II) from natural water samples, since the physiological and toxicological effects of manganese are dependent on its chemical form [11], the bivalent species being the most toxic.

MATERIALS AND METHODS

Adsorbent Preparation

The *Moringa oleifera* seeds were obtained from trees which were cultivated in the city of Uberlândia (Minas Gerais, Brazil). The seeds were separated from the pods, crushed in a household blender (Black & Decker, São Paulo, Brazil) and sieved at 500, 300 and 180 μm . They were then washed in deionized water and dried at ambient temperature. The functional groups present in the seeds were characterized using a Fourier transform infrared (FT-IR) spectrometer (Shimadzu, IR Prestige-21, Tokyo, Japan).

Manganese Determination

A Varian Model SpectrAA 220 (Victoria, Australia) flame atomic absorption spectrometer, with air-acetylene flame, was used for the manganese determination. A manganese hollow cathode lamp was run under the conditions recommended by the manufacturer. The wavelength used was 279.5 nm and conventional values were applied for the slit width and burner height.

Standard Solutions and Reagents

All solutions were prepared with analytical grade reagents and high purity deionized water produced by a Milli-Q[®] system (Millipore, Bedford, MA, USA). The glassware and containers for the storage of the solutions were immersed in 10% (v/v) nitric acid and rinsed with deionized water before use. The working solutions of Mn(II) were prepared through dilution of a 1000 mg L⁻¹ stock solution (Carlo Erba, Val de Ruil, France) in deionized water. Since a stock solution of Mn(VII) was not available, the 1000 mg L⁻¹ solution of this species was prepared by dissolving 0.034 g of KMnO₄ (Vetec, Rio de Janeiro) in 100 mL of deionized water. Solutions of 0.1 mol L⁻¹ HNO₃ and 0.1 mol L⁻¹ NaOH were used to adjust the pH.

Adsorption Studies

The solution pH is a critical variable that directly affects the ion adsorption. *Moringa oleifera* seeds can adsorb cations or anions depending on the pH solution. The effect of the pH solution on the Mn(II) and Mn(VII) separation was investigated by varying the pH from 1 to 8. In this procedure, 0.5 g of seeds were shaken for 40 minutes with 25 mL of a manganese solution containing one of the Mn species (4.0 mg L^{-1}). The suspension was then filtered, and the supernatant was directly analyzed by flame atomic absorption spectrophotometry (FAAS). The amount of manganese retained in the biosorbent was calculated by the difference between the initial and final manganese concentrations in the solution.

The pH 3.0 is the pH at which separation of the manganese species occurs and this value was used in order to obtain the optimum conditions for Mn(II) adsorption. The following variables were studied: particle size (180 to 500 μm), adsorbent mass (0.05 to 4.0 g) and stirring time (5 to 120 min).

Studies on Interference from Ions in Mn(II) Adsorption

The Mn(II) adsorption in the presence of Na^+ , Ca^{2+} , Mg^{2+} and Fe^{3+} , considered as concomitant ions, in various proportions, was evaluated. The experimental conditions were: pH 3.0, particle size 500 μm , adsorption mass 2 g and stirring time 15 min.

Isotherm Adsorption

The experiments for the isotherm tests were carried out at a temperature range of 25 to 28 $^{\circ}\text{C}$ using 50.0 mg of moringa seeds (500 μm) and 50 mL of Mn(II) solution in a concentration of 0.2 to 100 mg L^{-1} . The pH of the mixture was adjusted to 3.0 and the stirring time was 60 min. The mixture was filtered and the Mn(II) was quantified using flame atomic absorption spectrometry (FAAS).

Kinetic Studies

The kinetics of the Mn(II) adsorption onto moringa seeds in the batch tests was investigated. In this study, 0.05 g of moringa seeds were added to 50 mL of the solution containing manganese ions in the concentration of 4 mg L^{-1} in polyethylene jars. The mixtures were agitated at 180 rpm for intervals between 5 and 120 min. After agitation, the mixture was filtered and the manganese concentration determined by FAAS.

The adsorption capacity of the adsorbent q (mg g^{-1}) in relation to manganese ions was calculated by the Equation 1:

$$q = [(C_o - C_f)/m] * V_s \quad (1)$$

where C_o is the initial concentration in mg L^{-1} , C_f is the final concentration in mg L^{-1} , m (g) is the adsorbent mass and V_s (L) is the solution volume.

The kinetic parameters of the manganese adsorption process by moringa seeds were determined through linear regression of the graphs for pseudo-first-order, pseudo-second-order model and intraparticle diffusion using the respective equations given below [12,13].

$$\log_{10}(q_e - q) = \log_{10}(q_e - k) * t \quad (2)$$

where q_e and q are the amounts adsorbed from the solution (mg g^{-1}) at equilibrium and at time (t), respectively, and k is the adsorption rate constant (min^{-1}). The constant k is calculated from the slope of the line in the graph $\log(q_e - q) \times t$. This model considers that the sorption rate is dependent on the number of active sites available.

$$\frac{t}{q} = \left(\frac{1}{k_2} \times \frac{1}{q_e^2} \right) + \left(\frac{1}{q_e} \right) t \quad (3)$$

where k_2 is the pseudo-second-order constant ($\text{g mg}^{-1} \text{min}^{-1}$), t is the time (min) and q_e and q are the amounts of solute adsorbed (mg g^{-1}) at equilibrium and at time t , respectively. From the plot of $t/q \times t$, the values of the constants k_2 and q can be calculated. The k_2 constant is used to calculate the adsorption rate “ h ” ($\text{mg g}^{-1} \text{min}^{-1}$) for t_0 , as follows: $h = k_2 q_e^2$. For the intra-particle diffusion model this equation is:

$$q_t = k_{\text{dif}} t^{1/2} + C \quad (4)$$

where q_t is the amount of adsorbed solute (mg g^{-1}), t is the agitation time (min) and C (mg g^{-1}) is the constant related to the resistance to the diffusion. The k_{dif} ($\text{mg g}^{-1} \text{min}^{-0.5}$) can be obtained from the slope and the C value from the intersection of the curve for q_t versus $t^{0.5}$ [14].

According to this model, when the intraparticle diffusion is involved in the sorption process, the curve defined by this equation must be linear.

Accuracy Tests

To verify the selective adsorption of Mn(II), standard addition and recovery tests were carried out with samples containing Mn(II) and Mn(VII). The samples were: tap water, river water and mineral water. The river water samples were collected from Uberabinha River, which runs through an urban zone in the city of Uberlândia, and mineral water samples were acquired from a local store in the city of Uberlândia. Since the analyte concentration was below the detection limit, samples were spiked with the same concentrations of Mn(II) and Mn(VII) (4 and 50 mg L^{-1}). Also, samples of a drinking water certified reference material (APS 1075) was used in the accuracy tests.

RESULTS AND DISCUSSION

Optimization for the Selective Adsorption of Manganese

Metals in aqueous systems are dissolved in different forms, some are present as simple hydrated ions, or ion complexes bound to organic ligands such as amines, humic and fulvic acids and proteins. Thus, the adsorption of the metals can occur through ion exchange mechanisms and complexation, which can even occur simultaneously [15]. In this context, the pH is a critical variable since it directly affects the manganese adsorption.

Since the seeds can adsorb cation and anions depending on the electrical charge on the surface, the initial pH of the solution is the determining factor in the separation of inorganic manganese species. Thus, controlling the initial pH of the solution may be sufficient to ensure a significantly different percentage of the adsorption of the Mn(II) or Mn(VII) species, thus promoting their selective extraction. The influence of the pH on the adsorption of the Mn(II) and Mn(VII) species is shown in Figure 1.

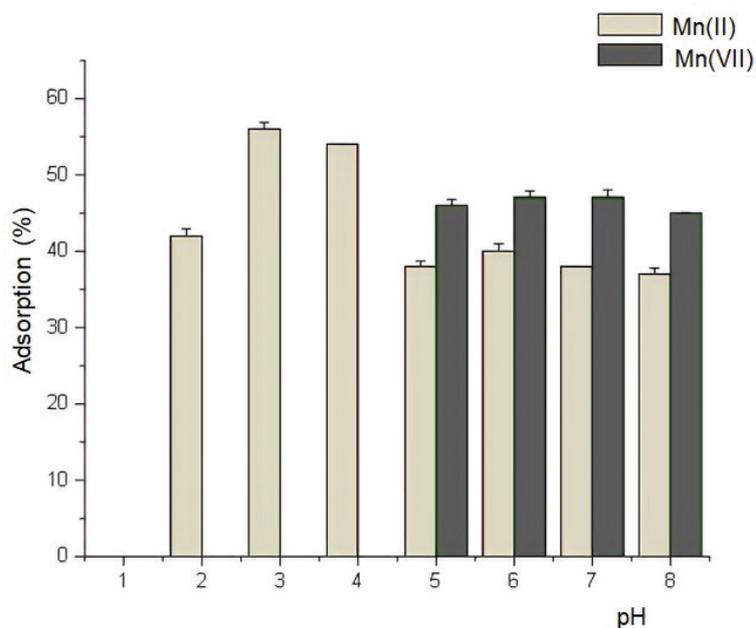


Figure 1. Evaluation of Mn species retention at different pH values. Experimental conditions: Adsorbent mass = 0.5 g, stirring time = 40 min.

The isoelectric point determined for *Moringa oleifera* seeds is between 5-6 and for pH values under 6.0 the surface of moringa seeds has a positive charge [10]. In Figure 1 it can be observed that at pH values under 4.0, only the Mn(II) species is adsorbed, the highest adsorption occurring at pH 3.0. Thus, at pH 3.0 it is assumed that the material is positively charged and can thus adsorb negative species, but, in acidic medium, Mn is predominantly in the Mn^{2+} form. The better adsorption observed can be attributed to the fact that the mechanism responsible for the metal retention by lignocellulosic adsorbents is based not only on ion exchange mechanisms but also complexation. So, at pH 3.0, the Mn(VII) species is predominantly in the uncharged form (MnO_4H) and cannot electrostatically interact with the adsorbent.

Another process that may be involved is the oxidation reactions of organic matter present in the seeds, promoted by the permanganate ion in alkaline medium ($pH > 6$). Permanganate ion is a strong oxidizing agent. So, can be a conversion of MnO_4^- to the insoluble MnO_2 , which cannot be quantified by F AAS in the supernatants [16]. Therefore, at pH 3.0, Mn(II) can be adsorbed with no adsorption of Mn(VII), allowing the selective separation of Mn(II) and Mn(VII) with pH control.

Optimization Strategy for Mn(II) Adsorption

Several variables can interfere with the adsorption process and in the next part of this study the variables evaluated were particle size, adsorbent mass and contact time.

The influence of varying the particle size of the *Moringa oleifera* seeds (≤ 500 , ≤ 300 and $\leq 180 \mu m$) on the Mn(II) adsorption was evaluated and the results are shown in Figure 2(a).

A decrease in the particle size had a favorable effect on the metal sorption, possibly due to the increased contact surface, suggesting an increase in the number of reactive sites, thus favoring ion adsorption by the adsorbent [17]. The experimental conditions for the study were: pH 3.0, adsorbent mass 0.5 g, contact time 40 min and Mn(II) solution concentration 4 mg L^{-1} .

The influence of the adsorbent mass on the Mn(II) adsorption was studied by varying the mass (0.05, 0.5, 1.0, 1.5, 2.0 and 4.0 g) of adsorbent. The percentage of manganese ions adsorbed increased with increasing mass up to 1.0 g of seeds, and then remained relatively constant (Figure 2(b)). This probably occurred because the system reaches saturation. Thus, a mass of 1.0 g is sufficient to ensure the

adsorption of Mn(II) ions.

The effect of the contact time on the adsorption of Mn(II) was studied in the range of 5 to 120 min (Figure 2(c)). The amount of Mn(II) retained by the adsorbent decreased as the contact time was increased to 60 min and after this time there was no significant variation in the percentage of metal adsorbed, possibly due to the system reaching equilibrium. Since 15 min was sufficient time to ensure good adsorption, this time was selected for the subsequent studies, in order to obtain a simple and fast methodology.

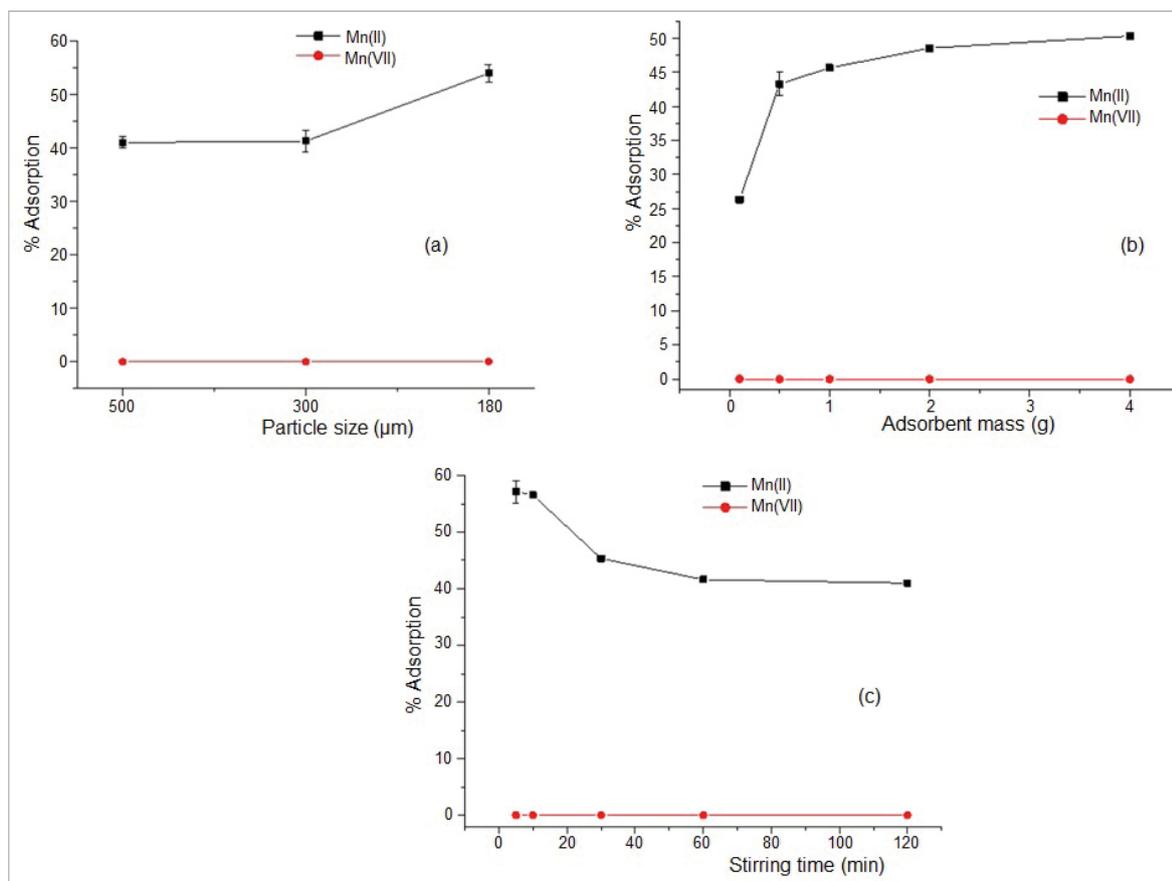


Figure 2. Percentage adsorption of Mn(II) onto *Moringa oleifera* seeds on varying the particle size (a), adsorbent mass (b) and contact time (c).

Adsorption Isotherm

The mechanisms associated with metal adsorption by biomass are still not clear; however, it is important to note that this process is not based on a single mechanism. Metal sequestration occurs through complex mechanisms, including ion-exchange and complexation, and it is quite possible that at least some of these mechanisms act simultaneously in various degrees depending on the biomass, the metal ion and the solution environment. The isotherm models can be used to describe this process.

Figure 3 shows the sorption isotherm for Mn(II) adsorption onto *Moringa oleifera* seeds.

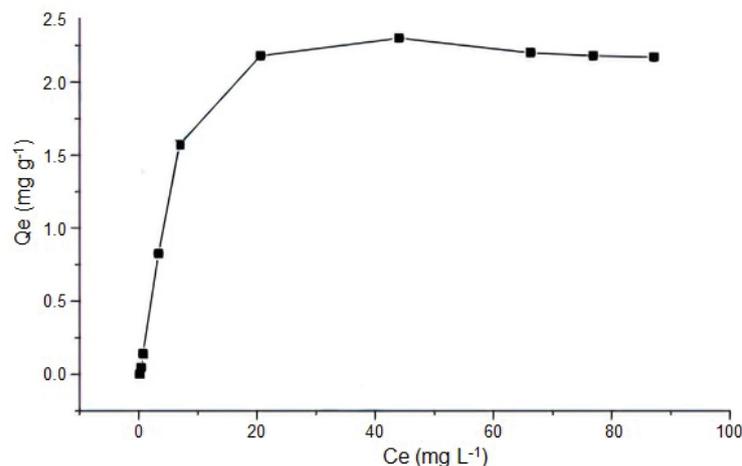


Figure 3. Adsorption isotherm for Mn(II) adsorbed onto *Moringa oleifera* seeds. Experimental conditions: pH = 3.0, adsorbent mass = 0.5 g, stirring time = 15 min.

Figure 3 demonstrates graphically the isotherm obtained, which can be compared with the class L proposed by Oscik [18]. The isotherms of this class are nonlinear and the slope is concave in relation to the abscissa. Since the sites on the adsorbent are all occupied, further adsorption of the adsorbate molecules is hindered. This behavior is expected in chemical adsorption and occurs for ion exchange or complexation [19].

The experimental data was analyzed using the Langmuir and Freundlich models, and the associated linearized equations are:

$$\text{Langmuir equation: } 1/q = 1/Q_{\max} Ce^b + 1/Q_{\max}$$

$$\text{Freundlich equation: } \log Q_e = \log(K_f) + 1/n \log C_e$$

where: Q_e is the amount of species adsorbed in the solid phase at equilibrium, C_e is the species concentration in the liquid phase at equilibrium, Q_{\max} is the Langmuir parameter related to the maximum adsorption capacity, b is the constant related to adsorbent/analyte interaction forces, K_f is the Freundlich constant and is indicative of the degree of adsorption and the constant n is indicative of the heterogeneity of the surface of the solution.

The relative values of Q_{\max} , K_f and n calculated from the Langmuir and Freundlich models for the Mn(II) in the adsorbent are listed in Table I.

Table I. Parameters of the adsorption isotherm models

| Langmuir | | | Freundlich | | |
|----------------------------------|-------|--------|-----------------------------|-----|--------|
| Q_{\max} (mg g ⁻¹) | R_L | R^2 | K_f (mg g ⁻¹) | n | R^2 |
| 10.35 | 0.24 | 0.9943 | 1.19 | 9.3 | 0.9651 |

As shown in Figure 4, when the Langmuir model was used to described the Mn(II) adsorption onto the adsorbent, the linear plot of C_e vs C_e/Q_e , with a coefficient of determination of $R^2 = 0.9943$, was obtained. When the Freundlich model was used, for the linear plot of $\log q$ vs $\log C_e$ the coefficient of determination was $R^2 = 0.9651$.

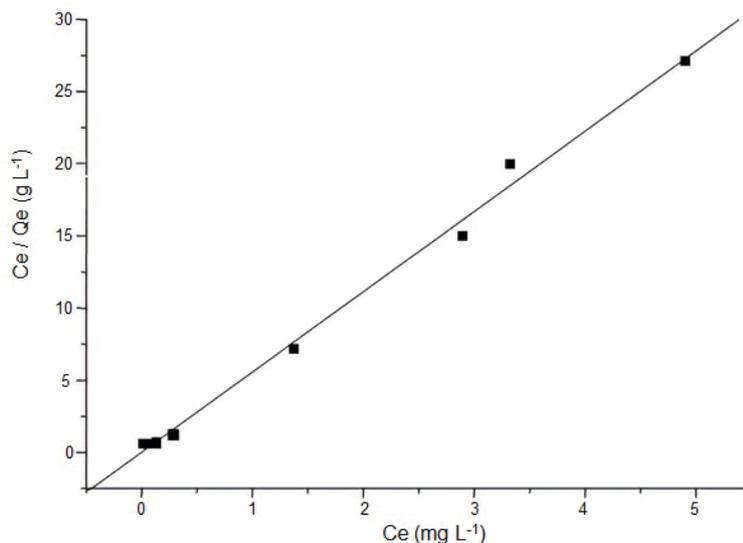


Figure 4. Plots of the Langmuir isotherm for the sorption of Mn(II) onto *Moringa oleifera* seeds. Experimental conditions: pH = 3.0, adsorbent mass = 0.5 g, stirring time = 15 min.

The results showed that the value for the coefficient of determination (R^2) of the Langmuir isotherm model was higher than that of the Freundlich model. Thus, the experimental data are well fitted to the linear Langmuir isotherm, agreeing with the finding when compared to the system proposed by Oscik [18]. In the Langmuir model it is assumed that the adsorption is limited to the monolayer and thus maximum adsorption indicates the saturation of this monolayer. The process probably occurs through chemical adsorption, basically by ion exchange and complexation, and the maximum adsorption capacity of the adsorbent for Mn(II) was calculated to be 10.35 mg g^{-1} . The R_L factor was calculated and its value indicates favorable adsorption ($R_L > 1$).

The good adsorption capacity of *Moringa oleifera* seeds for manganese is shown in Table II, where higher Q_{max} values can be observed when compared to results reported for the other natural adsorbents.

Table II. Comparison of methods for the manganese ion removal

| Adsorbent | Maximum Capacity (mg g^{-1}) | Reference |
|--------------------------------------------------|--------------------------------------------|------------|
| Chitin + associated protein | 5.44 | [17] |
| Black carrot (<i>Daucus carota</i>) | 3.87 | [20] |
| Activated carbon (AC) derived from coconut shell | 2.54 | [21] |
| Tannic acid immobilized on AC | 1.13 | [22] |
| <i>Moringa oleifera</i> seeds | 10.35 | This study |

Kinetic Studies

Based on an analysis of Figure 2(b), it can be observed that manganese adsorption increases with increased contact time, reaching equilibrium.

The main models used to evaluate the kinetic profile were the pseudo-first-order, pseudo-second-order, and intraparticle diffusion kinetic models. For the fitting of these models, two criteria must be satisfied. The first is that the linearity must be acceptably high (R^2). The second is that the calculated q_e

values must be close to the experimental q_e values.

Table III. Kinetic parameters for Mn(II) adsorption onto moringa seeds

| Pseudo-first-order model | | |
|---------------------------------------------|----------------------------------|----------------|
| K_1 (min ⁻¹) | q_e exp. (mg g ⁻¹) | R ² |
| 0.2218 | 1.075 | 0.637 |
| Pseudo-second-order model | | |
| K_2 (g mg ⁻¹ m ⁻¹) | q_e exp. (mg g ⁻¹) | R ² |
| 0.27 | 4.05 | 0.999 |
| Intraparticle diffusion model | | |
| C | K_{dif} | R ² |
| 2.58 | 0.073 | 0.994 |

The kinetic parameters for the adsorption of Mn(II) ions onto the *Moringa oleifera* seeds (Table III) were obtained by linear regression of the graphic models of pseudo-first-order, pseudo-second-order and intraparticle diffusion. The calculated q_e was 0.42 and the q values determined experimentally are included in the table for comparison.

It can be noted that the kinetics of the manganese ion adsorption onto the seeds could be fitted with a pseudo-second-order kinetic model because it fulfills the two criteria mentioned above.

The C value (2.58) being different from zero indicates that the plot of qt vs $t^{0.5}$ does not pass through the origin and therefore the intraparticle diffusion mechanism is not the rate determining step of the transfer process, and other bulk mechanisms must act simultaneously in the control of the adsorption process.

Accuracy Tests

The accuracy of the proposed method was evaluated by recovery tests applying the method of standard addition using water samples (tap water, mineral water and river water).

By placing the samples in contact with moringa seeds under shaking, Mn(II) ions will be selectively retained and Mn(VII) will be free in the supernatant allowing its determination by F AAS. The Mn total concentration can be determined by direct analysis of the samples with the adsorbent without agitation, and thus the Mn(II) concentration can be calculated as the difference between the total Mn concentration and Mn(VII).

Since the concentration of analyte was below the detection limit, samples were spiked with Mn(II) in concentrations of 4 and 50 mg L⁻¹ and the results for the recovery, shown in Table IV, are within the acceptable range of 80 to 120%.

Table IV. Determination of Mn(II) in water samples and experimental recovery in water samples spiked with 4.0 and 50.0 mg L⁻¹ Mn(II)

| Samples | Mn(II) spiked (mg L ⁻¹) | Mn(II) found (mg L ⁻¹) | Recovery (%) |
|---------------|-------------------------------------|------------------------------------|--------------|
| Mineral Water | -- | N.D. | -- |
| | 4.0 | 3.6 ± 0.2 | 90 |
| | 50.0 | 52.1 ± 0.5 | 104 |
| Tap water | -- | N.D. | -- |
| | 4.0 | 3.7 ± 0.1 | 92 |
| | 50.0 | 48.1 ± 0.3 | 96 |
| River water | -- | N.D. | -- |
| | 4.0 | 3.9 ± 0.2 | 98 |
| | 50.0 | 51.0 ± 0.2 | 102 |

N.D.: not detectable. N=3.

The accuracy of the method was further evaluated by analysis of the drinking water certified reference material APS 1075. Table V shows the results obtained. These results are consistent with the reference value, confirming the reliability of the method.

Table V. Determination of manganese in drinking water certified reference material

| Sample | Proposed method | Certified Value |
|----------|-------------------------------|-------------------------------|
| APS 1075 | 98.3 ± 1.0 mg L ⁻¹ | 99.4 ± 0.3 mg L ⁻¹ |

CONCLUSIONS

The central point of the method developed in this study is the variation in the percentage adsorption of the inorganic species of Mn according to the pH, since the pH changes the surface charge of the adsorbent, influencing its ability to adsorb cations and anions. It was observed that at pH 3.0 only Mn(II) is retained, confirming the possibility of an extraction method with high selectivity.

The good accuracy of the method was observed through recovery tests and analysis of reference material. It was verified that the method can be applied in the selective extraction of Mn(II) from water samples using *Moringa oleifera* seeds as a bioadsorbent.

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