

Assessment of the Use of *Moringa oleifera* Seeds for Removal of Manganese Ions from Aqueous Systems

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Moringa oleifera seeds were investigated for the removal of manganese ions from aqueous solutions. The seeds utilized were obtained from plants grown in Uberlândia, Brazil. After being dried and pulverized, the seeds were treated with 0.1 mol L⁻¹ NaOH. Using the optimized methodology (50 mL of 4.0 mg L⁻¹ Mn(II), pH range of 4.0–6.0, contact time of 5 min, and biosorbent mass of 0.5 g) it was found that 100% of Mn(II) could be removed from water samples. In order to remove up to 95% of Mn ions in 50 mL of a laboratory residue produced during biochemical oxygen demand determinations with 112.0 mg L⁻¹ of manganese, the contact time and pH were maintained, but a mass of 3.0 g was used. The kinetic data were fitted to a pseudo-second-order kinetic model. The sorption data were fitted satisfactorily to the Langmuir and Freundlich isotherm models. Evaluation applying the Langmuir equation gave the monolayer sorption capacity as 5.61 mg/g. In this application the method was found to be efficient, fast, simple, and economical.

Keywords: *Moringa oleifera*; Manganese ions; Adsorption behavior

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INTRODUCTION

Manganese is a very abundant metal in the earth's crust, and its presence in groundwater originating from leaching process varies greatly depending on the type of rock. Furthermore, the extensive industrial use of manganese has led to this metal being present in many rivers and sediments around the world. Activities such as metallurgical processes, mining, and the manufacture of ceramics, dry cell batteries, pigments, and paints can all be sources of groundwater pollution (Mejía-Saavedra *et al.* 2005; Nassar 2007; Roccaro *et al.* 2007).

Manganese can be found in natural water in the most reduced and soluble form as Mn (II) and also in the oxidized and insoluble form as MnO₂. If manganese ions are not oxidized during the water treatment process and are present in the public potable water distribution system, they are gradually oxidized, forming insoluble MnO₂ and generating various water quality related issues, such as water color, metallic taste, odor, turbidity, corrosively, hardness, and discoloration of laundry and plumbing fixture (Roccaro *et al.* 2007).

In addition to damaging property, manganese is also toxic to human health and particularly affects the brain. This metal can become abnormally concentrated in the brain, particularly in the basal ganglia, resulting in neurological disorders related to

Parkinson's disease (Okoniewska *et al.* 2007). Thus, the World Health Organization defines the maximum acceptable concentration of manganese ions in drinking water as 0.1 mg L^{-1} (WHO 2011). The conventional treatments for the removal of manganese ions are primarily based on physicochemical processes, such as air and chloride oxidation, where initially an oxidation step occurs. This is followed by the precipitation of MnO_2 , and subsequently a clarification and/or filtration step. However, in general, these processes have disadvantages including the use of toxic reagents and generation of toxic pollutants. Moreover, these techniques are laborious, time consuming, and expensive (Roccaro *et al.* 2007; Xu *et al.* 2009).

Efforts are being made to develop improved and innovative methods of wastewater treatment. In the development of new methods, economically feasible and user-friendly concepts are given much importance. In this regard, considerable attention has been given to developing low-cost adsorbents for the removal of various heavy metal ions when the concentration is not very high (Anandkumar and Mandal 2009). In recent years, biosorption has been widely applied in the removal of heavy metal ions, due to its technical and economical feasibility. Recently, the removal of manganese ions from aqueous solution using several types of non-living biomass has been evaluated by different authors. Güzel *et al.* (2008), Nassar (2007), Okoniewska *et al.* (2007), Rajic *et al.* (2009), and Robinson-Lora and Brennan (2010) studied the sorption of manganese ions using black carrot, maize cobs, impregnated active carbon, natural zeolitic tuff, and chitin or chitin plus proteins, respectively.

Moringa oleifera seeds can be considered as a natural adsorbent material that presents some important characteristics in relation to its application in effluent treatment. These seeds have been used for the treatment of turbid water due to their flocculation properties (Gassenschmidt *et al.* 1995). Our research group has previously performed studies involving the treatment of aqueous solutions containing silver (Araújo *et al.* 2010) and nickel (Marques *et al.* 2012) ions using *M. oleifera* seeds, and in both cases, the percentage removals achieved were around 90%. However, there are no reports available on the use of *Moringa* seeds for the adsorption of manganese ions.

In this study, *M. oleifera* seeds were used as a new low-cost adsorbent to remove manganese ions from the public potable water supply, river water, and a laboratory residue generated from the determination of biochemical oxygen demand (BOD). Experiments were performed to optimize the parameters affecting the adsorption of the manganese ions, such as adsorbent dosage, agitation time, and pH. The fitting of the experimental data to several models was carried out to determine the most suitable kinetic model and isotherm to explain the results.

EXPERIMENTAL

Instrumentation

A Varian Model SpectrAA 220 (Australia) flame atomic absorption spectrometer, with air-acetylene flame, was used for the manganese determination. A hollow cathode lamp was run under the conditions recommended by the manufacture, and conventional values were used for the wavelength, slit width, and burner height. A pH meter (Gehaka, Brazil) was used to set the pH of the samples and working solutions. Magnetic stirrers (Hanna Instruments, USA) were used in the batch adsorption experiments.

Reagents and Solutions

All working solutions were prepared with ultra-pure water obtained from a Milli-Q (Gehaka, Brazil) water purification system. All reagents used were analytical grade. All laboratory glassware was previously washed with neutral detergent and then kept overnight in 10% (v/v) nitric acid solution and washed with deionized water. The working solutions used in this study were prepared through dilution of a 1000 mg L⁻¹ stock solution of manganese ions (Fluka Analytical, Germany) in deionized water. Solutions of 0.1 mol L⁻¹ HNO₃ and 0.1 mol L⁻¹ NaOH were used to adjust the pH.

Preparation of the Adsorbent

Moringa oleifera seeds were obtained from trees cultivated in the city of Uberlândia (Minas Gerais, Brazil). After drying, the pods were shelled and the seeds were ground in a commercial blender. The resulting powders were sorted using a sieve shaker, and the particle size range of 0.5 to 1.0 mm was retained for further experiments. The seed samples were mixed with 0.1 mol L⁻¹ NaOH. After this step, the material previously treated with NaOH was repeatedly washed with deionized water until obtaining a colorless supernatant of approximately pH 7. This treatment removes organic and inorganic matter from the surface of the adsorbent, as performed previously by our group to increase the affinity of the adsorbent for the metal ion, and verified through the physicochemical analysis reported in a previous paper (Marques *et al.* 2012).

Batch Adsorption Experiments

Removal studies using solutions of manganese ions were carried out in triplicate. The seeds were shaken for 15 min with 50 mL of manganese ions solution (4.0 mg L⁻¹) using a magnetic stirrer and then the suspension was filtered through filter paper (Whatman N°42). The metals were quantified before and after the removal experiments. In order to obtain the optimum conditions in terms of the percentage of metal removal, the following variables were studied: adsorbent mass (0.5 to 2.0 g), contact time (5 to 40 min), and pH (2.0 to 8.0).

The final residual manganese ion concentration after adsorption was directly measured by flame atomic absorption spectrophotometry (FAAS). To estimate the percentage removal of metal ions from the aqueous solution, the following equation was used,

$$\% \text{ Adsorption} = ((C_o - C_f)/C_o) * 100 \quad (1)$$

where C_o (mg L⁻¹) is the initial metal concentration and C_f (mg L⁻¹) is the final residual concentration of metal after the adsorption period, measured directly by FAAS.

Adsorption Kinetic Models and Isotherms

The experiments to investigate the adsorption kinetics were carried out at ambient temperature using 0.05 g of *M. oleifera* seeds, 25 mL of manganese ion solution (10.0 mg L⁻¹) at pH 4.0, and various contact times in the range of 2-120 min. In the experiments on the adsorption isotherms the same conditions were applied, except that the time was fixed at 90 min and concentration of manganese ions was varied within the range of 5-45 mg L⁻¹. In both experiments, these conditions were used to ensure that the equilibrium would be achieved; mixtures were then filtered and the metal ions quantified using FAAS.

Application of the Proposed Method

The studied adsorbent was applied in the adsorption of manganese ions from potable water (public supply), river water, and laboratorial residue generated from BOD experiments. The sample of potable water treated by a local sanitation company was collected from a residential property in the city of Catalão (Goiás, Brazil), and river samples were collected from three different locations along the Pirapitinga River, which runs through an urban zone in the city of Catalão. In these samples, manganese ions were not found. Thus, to assess the performance of the adsorbent material in these systems, the samples were spiked at a concentration of $4 \text{ mg L}^{-1} \text{ Mn(II)}$. The samples were filtered through filter paper and the pH was adjusted to within the range of 4.0 to 6.0 using $0.1 \text{ mol L}^{-1} \text{ HCl}$. The samples (50 mL) were then treated with 500 mg of adsorbent and using a contact time of 5 min. The manganese ions were quantified using FAAS before and after the removal experiments.

The proposed adsorbent was also evaluated in the treatment of a residue generated during BOD experiments (Winkler titration method). Initially, the pH of the residue was adjusted to 4.0 using a solution of $0.5 \text{ mol L}^{-1} \text{ NaOH}$, and the sample was then filtered. Subsequently, 50 mL this residue was agitated for 5 min with the addition of Moringa seeds.

The seed mass varied from 0.5 to 4.0 g, not only because the concentration of manganese ions in the residue is much greater than in the standard solutions utilized in the previous studies but also due to the presence of possible interfering ions. The mixture was filtered, and the metal ions were quantified using FAAS.

RESULTS AND DISCUSSION

Determination of Optimum Parameters and Adsorption Studies

The influence of the adsorbent dosage on the sorption of manganese ions was studied by varying the mass (0.5, 1.0, 1.5 and 2.0 g) of adsorbent. The adsorption percentage of manganese ions increased with increasing mass up to 1.0 g of *M. oleifera*, and then remained relatively constant. This occurred due to the increased number of particles of adsorbent and the adsorption sites available. With the use of 500 mg, more than 95% of the manganese ions in the solution are removed, and this mass was therefore chosen as the optimum value for the subsequent studies, in order to ensure a simple and economical methodology.

Subsequently, the adsorption time was studied (5, 10, 20, and 40 min), keeping all other parameters constant. The amount of manganese ions adsorbed increased in the first 40 min and then remained constant, but in the first 5 min the incremental removal was highest. Thus, 5 min was selected for the subsequent studies, in order to ensure a simple and fast methodology.

The effect of varying the pH (between 2.0 and 8.0) on the manganese ion adsorption was studied. The optimum values were obtained in the range of pH 4 to 6, and within this interval the removal was practically constant, although slightly higher values were obtained at pH 4.0 (Fig. 1).

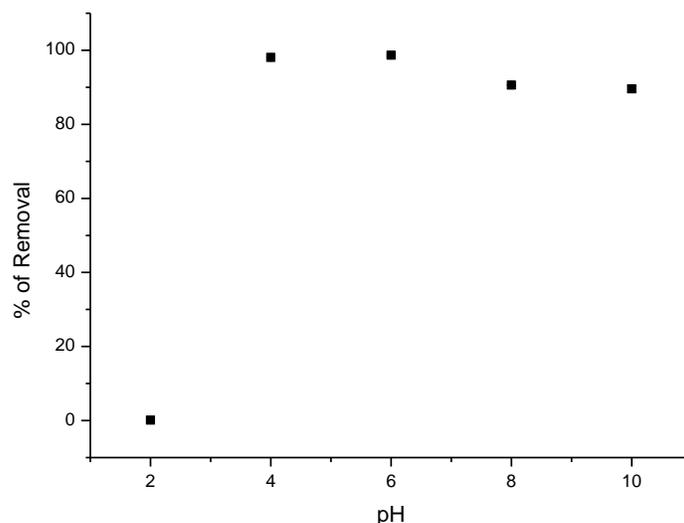


Fig. 1. Effect of pH on the manganese ion adsorption capacity of Moringa seeds. Initial conc.: 10.0 mg L^{-1} ; biosorbent mass: 0.050 g ; contact time: 5 min ; volume: 25 mL . Error bars represent $\pm \text{S.D.}$

Subsequently, there was a drop in the removal of manganese ions in solution when the pH was raised to 8.0. Low pH (2-4) conditions allow hydronium ions to compete with metal binding sites on the biomass, causing poor uptake, while at high pH values (≥ 8.0) precipitation occurs, leading to a reduced sorption capacity. Therefore, pH 4.0 was chosen for further studies. The pH is one of the most important parameters affecting any adsorption process. This dependence is closely related to the acid-base properties of various functional groups on the adsorbent surfaces (Pereira and Arruda 2003). The literature shows that an aqueous heterogeneous mixture of *M. oleifera* seeds presents various functional groups, mainly amino and acids groups. These groups have the ability to interact with metal ions, which is dependent on the pH. An increase in metal adsorption with increasing pH values can be explained on the basis of competition between the proton and metal ions for the same functional groups and a decrease in the positive surface charge, which results in a higher electrostatic attraction between the surface and the metal (Senthilkumar *et al.* 2000). With an increase of pH, the solubility of metal complexes decreases enough for precipitation to occur, defeating the biosorptive process. Therefore, it is recommended to study biosorption at pH values where precipitation does not occur. In this work it was noted that the precipitation of manganese was observable when the pH was greater than 8. Therefore, the pH of the samples was kept within the range studied (pH 4 to 6). The pH is not changed after the sorption processes.

The mechanism of biosorption of metals by biomass is still not clear. But it is important to note that biosorption of metals by biomass is not based solely on a single mechanism. Metal sequestration follows complex mechanisms including ion-exchange and complexation. It is quite possible that at least some of these mechanisms are acting simultaneously to varying degrees. *Moringa oleifera* seeds can be classified as lignocellulosic adsorbents, consisting mainly of cellulose, hemicellulose, and lignin. These natural polymers contain a variety of functional groups, so they have the ability to adsorb metal ions through ion exchange or complexation (Pagnanelli *et al.* 2003).

Kinetics

Figure 2 shows the effect of contact time on the manganese ion adsorption capacity of Moringa seeds.

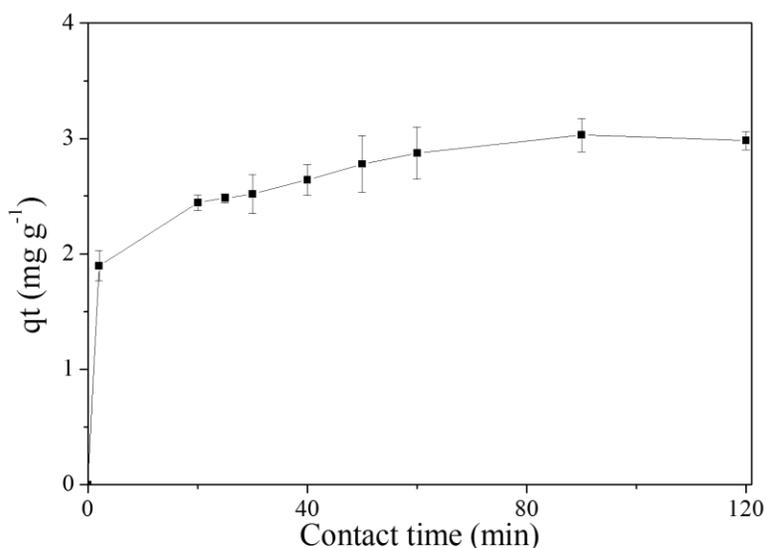


Fig. 2. Effect of contact time on the manganese ion adsorption capacity of Moringa seeds. Initial conc.: 10.0 mg L⁻¹; biosorbent mass: 0.050 g; pH: 4.0; volume: 25 mL. Error bars represent \pm S.D.

The main models used to evaluate the kinetic profile were the pseudo-first-order, pseudo-second-order, and Weber and Morris sorption kinetic models. The results obtained were evaluated by applying these three kinetic models (Nadeem *et al.* 2006; Zhao *et al.* 2011). For the fitting of these models, two criteria must be satisfied. The first is that the regression coefficient must be acceptably high (R^2). The second is that the calculated q_e values must approach the experimental q_e (Li *et al.* 2010).

The equation of pseudo-first-order, also known as the Lagergren equation, is expressed as follows (Barka *et al.* 2010; Bhaetti *et al.* 2007),

$$\log (q_e - q_t) = \log q_e - ((k_1/2.303) * t) \quad (2)$$

where q_t and q_e (mg g⁻¹) are the amounts of metal ions adsorbed per unit mass of the adsorbent at time t (min) and equilibrium, respectively, and k_1 (min⁻¹) is the pseudo-first-order rate constant of the sorption process (Barka *et al.* 2010). This kinetic model is based on the assumption that the rate of adsorption is proportional to the number of free sites available, adsorption occurring exclusively onto one site per ion (Lalhruaitluanga *et al.* 2010; Reddy *et al.* 2011). The graph plotted according to the Eq. 2 is shown in Fig. 3a, and the values calculated for k_1 , q_e , and R^2 are 0.03 min⁻¹, 1.34 mg g⁻¹, and 0.8297, respectively. It can be observed that the kinetics of the manganese ion adsorption onto Moringa seeds did not fit the pseudo-first-order kinetic model due to the low R^2 value (0.8297) and the lack of agreement between the calculated q_e (1.34 mg g⁻¹) and the experimental q_e (3.03 mg g⁻¹) values.

A pseudo-second-order kinetic model also can be derived based on an assumption that the sorption rate is controlled by a chemical sorption mechanism involving electron sharing or electron transfer between the adsorbent and the adsorbate (Ding *et al.* 2012). This can be expressed as,

$$t/q_t = 1/(k_2 * q_e^2) + t/q_e \quad (3)$$

where q_t and q_e (mg g^{-1}) are the amounts of metal ions adsorbed per unit mass of the adsorbent at time t (min) and equilibrium, respectively, and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the pseudo-second-order rate constant of the sorption process (Ding *et al.* 2012). The graph plotted according to Eq. 3 is depicted in Fig. 3b and the values for k_2 and for calculated q_e and R^2 are $0.27 \text{ g mg}^{-1} \text{min}^{-1}$, 4.05 mg g^{-1} , and 0.9946 , respectively. It can be noted that the kinetics of manganese ion adsorption onto the seeds could be fitted to a pseudo-second-order kinetic model because it fulfills the two criteria mentioned above.

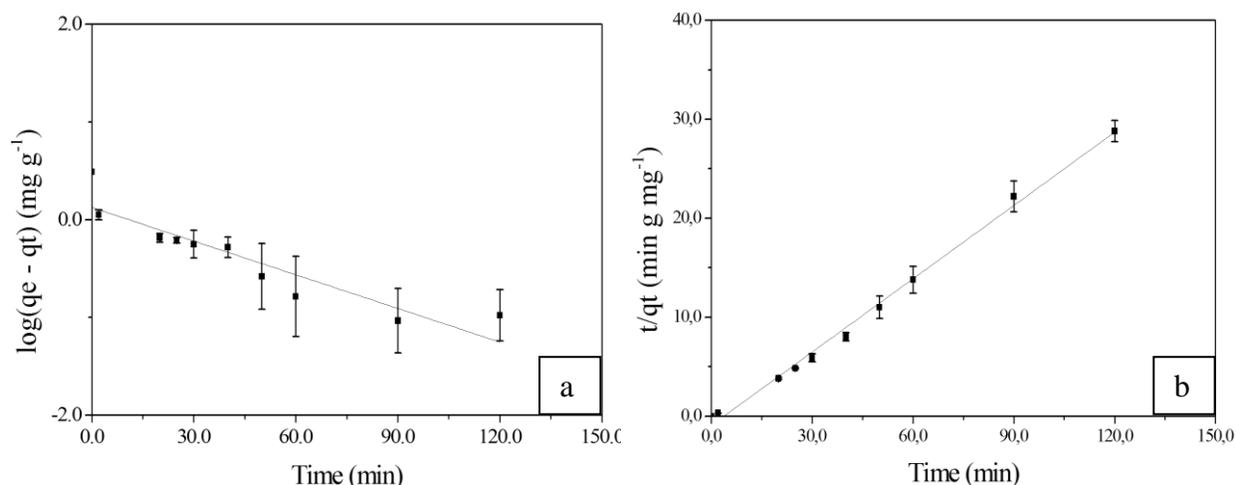


Fig. 3. Pseudo-first-order (a) and pseudo-second-order (b) kinetic plots for the sorption of manganese ions in Moringa seeds.

Considering that the application of neither the pseudo-first-order model nor the pseudo-second-order model led to a diffusion-limited mechanism being identified, another kinetic model was needed in order to study this process. For this end, the Weber and Morris sorption kinetic model (Reddy *et al.* 2010) was applied. This model also is known as the intra-particle diffusion model since this is a process that in many cases is the rate-limiting step. According to the model the adsorption may be determined using the following equation,

$$q_t = (k_{id} * t^{0.5}) + c \quad (4)$$

where q_t (mg g^{-1}) is the amount of metal ions adsorbed per unit mass of the adsorbent at time t (min), c (mg g^{-1}) is a constant, and k_{id} ($\text{mg g}^{-1} \text{min}^{-0.5}$) is the intra-particle diffusion rate constant (Baidas *et al.* 2011). According to this model, if the plot of q_t versus $t^{0.5}$ gives a straight line, then the sorption process is controlled by intra-particle diffusion, while if the data exhibit multi-linear plots, then two or more steps influence the adsorption process (Bilgili 2006). The graph was plotted according to Eq. 4 and is shown in Fig. 4, while the values of k_2 , calculated q_e and R^2 are 0.10 , 3.09 mg g^{-1} and 0.9358 , respectively. According to Fig. 4, the kinetics presented a multi-linear profile, and the model's R^2 value of 0.9358 was not good. This indicated that intra-particle diffusion was not the only rate-controlling step (Reddy *et al.* 2010).

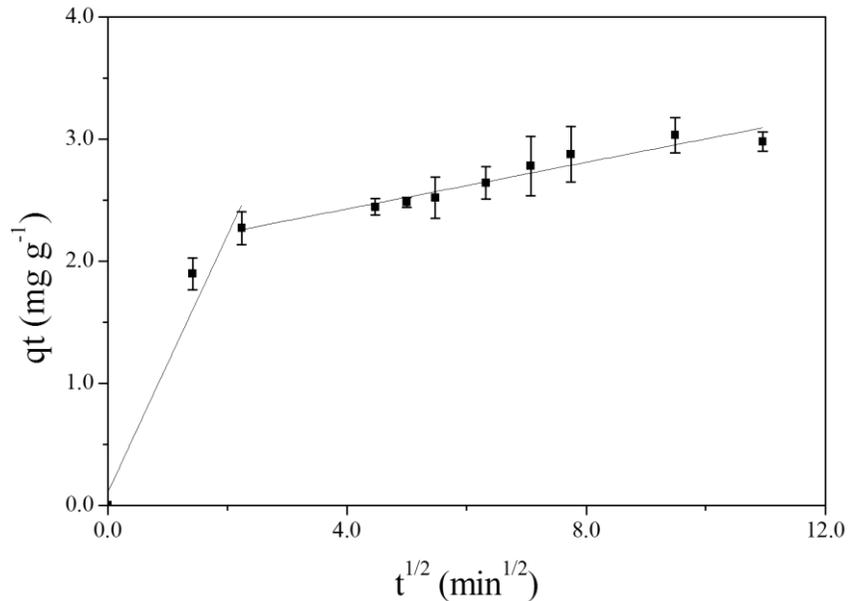


Fig. 4. Weber and Morris kinetic plots for the sorption of manganese ions onto *Moringa* seeds

Isotherm

Figure 5 shows the sorption isotherm for manganese ion adsorption onto *Moringa oleifera* seeds. Error bars show standard deviations that were low at the 95% confidence level. Among the isotherm models found in the literature, the primary ones are the Langmuir and Freundlich (Nadeem *et al.* 2006).

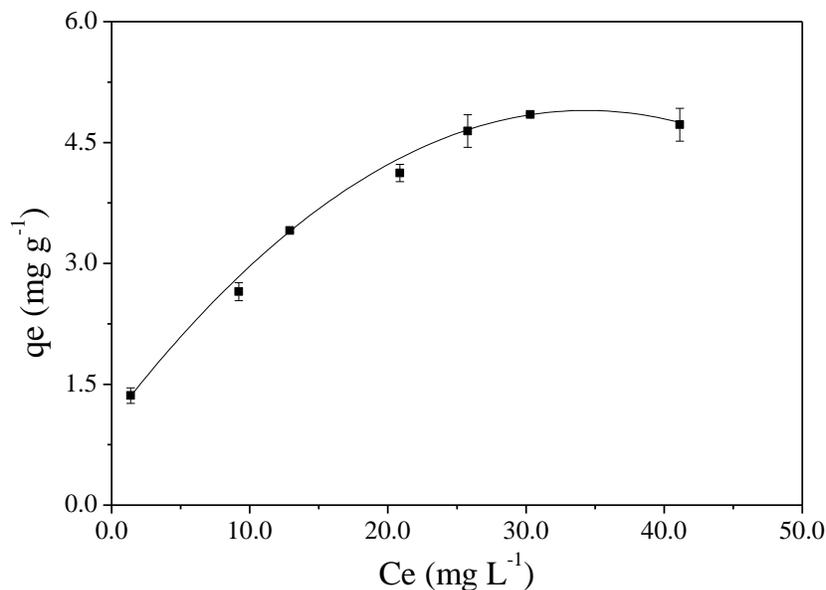


Fig. 5. Adsorption isotherm for manganese ions adsorbed onto *Moringa oleifera* seeds. Contact time: 90.0 min; biosorbent mass: 0.050 g; pH: 4.0; volume: 25 mL. Error bars represent \pm S.D.

The Langmuir model assumes that adsorption is limited to the monolayer; a maximum adsorption indicates the saturation of this monolayer. The fitting of the experimental data to the Langmuir linear equation (Sari *et al.* 2007) can be expressed by the following equation:

$$C_e/q_e = C_e/q_{max} + 1/(K_L * q_{max}) \quad (5)$$

where C_e (mg L^{-1}) is the equilibrium concentration of the metal, q_e (mg g^{-1}) is the amount of metal ions adsorbed per unit mass of the adsorbent at equilibrium, and q_{max} (mg g^{-1}) and K_L (L g^{-1}) are the Langmuir constant related to the adsorption capacity and the energy of adsorption, respectively. Figure 6a was plotted according to Eq. 5, and the values of q_{max} , K_L , and R^2 are 5.61 mg g^{-1} , 0.15 L mg^{-1} , and 0.9823 , respectively. The coefficient of determination obtained was 0.9823 , and the calculated q_{max} found was 5.61 mg g^{-1} , which is very close the experimental q_{max} (4.85 mg g^{-1}) value, thus showing that the data fit the Langmuir model as observed in Fig. 5a.

The Freundlich isotherm is an empirical expression that takes into account the heterogeneity of the surface and multilayer adsorption onto the binding sites located on the surface of the sorbent (Witek-Krowiak *et al.* 2011). The Freundlich model can be expressed as follows,

$$\log q_e = (1/n) * \log C_e + \log K \quad (6)$$

where C_e (mg L^{-1}) is the equilibrium concentration of the metal, q_e (mg g^{-1}) is the amount of metal ions adsorbed per unit mass of the adsorbent at equilibrium, and n and K (mg g^{-1}) are the Freundlich constants related to the biosorption intensity and adsorption equilibrium constant, respectively (Bhaetti *et al.* 2007; Witek-Krowiak *et al.* 2011). Figure 6b was plotted according to Eq. 6, and the values of n , K , and R^2 were 2.46 , 1.20 mg g^{-1} , and 0.9905 , respectively. The determination coefficient obtained was 0.9905 , thus showing that the experimental data provide a good fit with the Freundlich model, as observed in Fig. 6b. The value of n was between 0 and 10 , suggesting relatively strong adsorption of these ions onto the surface of Moringa seeds (Witek-Krowiak *et al.* 2011).

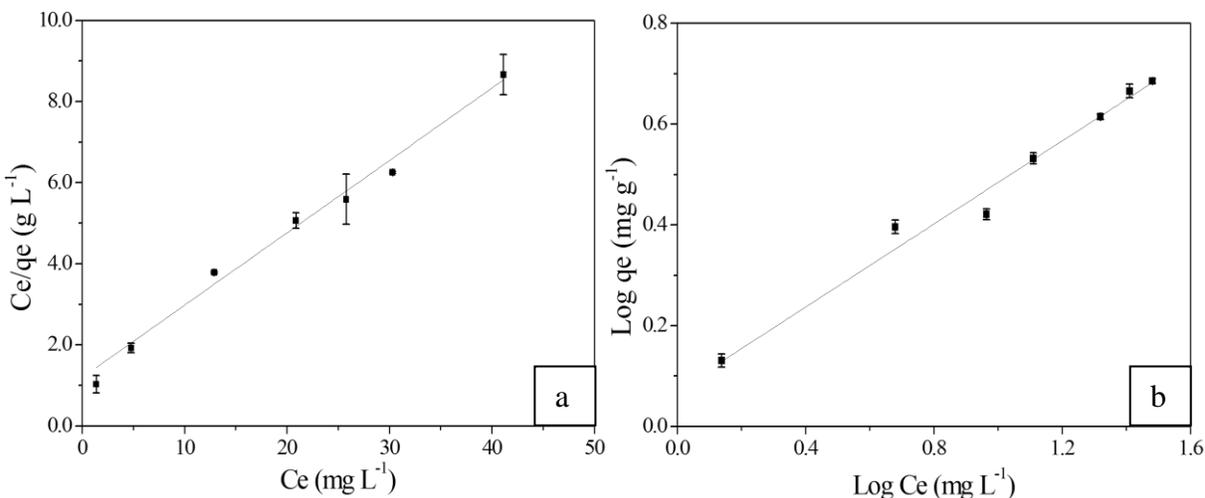


Fig. 6. Langmuir (a) and Freundlich (b) isotherm plots for the sorption of manganese ions onto Moringa seeds

It can be observed that in the isotherm study, the experimental data for the adsorption of manganese ions onto Moringa seeds provided good fits to the two isotherm models, despite the fact that the value for the linear correlation (R^2) of the Freundlich

model was slightly higher than that of the Langmuir model. It is reasonable to assume that manganese adsorption behavior on biosorbent may take place in multilayers on the surface of the adsorbent. However, based on satisfactory correlation coefficients, the data also are consistent with a model in which the monolayer adsorption takes place on the adsorbent materials. Though the sorption data were fitted by the Langmuir and Freundlich adsorption models, it is not possible to say exactly what should be the adsorption process. This result is somewhat expected, bearing in mind the complexity of the structure and composition of the biosorbent.

Comparison of the Material Used in this Study with Other Adsorbents

The capacity of Moringa seeds to remove manganese ions was compared with other natural adsorbents described in the literature. The results of this study showed that *Moringa oleifera* seeds demonstrate good removal capacities for manganese ions (5.61 mg g^{-1}) when compared to results reported for other adsorbents (Table 1). Although some materials exhibit capacity close to or better than that of Moringa seeds, this material yielded the development of a rapid and simple methodology. Combined with their low cost and ease of purchase, and considering the satisfactory experimental results, Moringa seeds can be considered as an effective adsorbent for manganese ion removal from aqueous solution.

Table 1. Comparison of the Manganese Ion Removal Capacity of *M. oleifera* Seeds with That of Other Natural Adsorbents

Adsorbent	Maximum Adsorbent Capacity (mg g^{-1})	Reference
Natural Zeolitic Tuff	10.0	Rajic <i>et al.</i> 2009
Chitin	0.98	Robinson-Lora and Brennan 2010
Chitin + Associated Protein	5.44	Robinson-Lora and Brennan 2010
Black Carrot (<i>Daucus carota</i> L.)	3.87	Güzel <i>et al.</i> 2008
Activated Carbon (AC) – Coconut Shell	2.54	Jusoh <i>et al.</i> 2005
Rice Husk	7.7	Krishnani <i>et al.</i> 2008
Tannic Acid immobilized AC	1.13	Üçer <i>et al.</i> 2006
<i>M. oleifera</i> seeds	5.61	This study

Application

The proposed method was applied in the treatment of potable water (public supply) and river water. In these samples manganese ions were not found, and thus, they were spiked with manganese ions at a concentration of 4.0 mg L^{-1} . The samples were subsequently treated with the adsorbent material to determine the percentage removal of the analyte, and the results obtained are shown in Table 2. The results showed that *Moringa oleifera* seeds are effective in removing manganese ions from water samples. Also, this was found to be a rapid and simple method which was easy to apply. In addition, this type of sample did not require pH adjustment, because the pH values were within the optimal range obtained for the method.

Table 2. Use of *Moringa oleifera* Seeds in the Removal of Manganese Ions from Aqueous Samples

Sample	Initial Concentration (mg.L ⁻¹)	Removal (%)
A	3.8	100.8(±0.8)
B	4.0	100.0(±1.0)
C	3.9	100.7(±0.3)
D	4.0	102.9(±0.3)
E	112.0	95.7(±0.2)

A, B, and C: Samples taken from three different locations along the Pirapitinga River which runs through an urban zone in the city of Catalão, Goiás State, Brazil. D: Sample of potable water treated by a sanitation company. E: Laboratory residue generated from biochemical oxygen demand (BOD) determination by the Winkler titration method.

According to the results obtained in this study, it was evident that *Moringa* seeds were very efficient in the removal of manganese ions from samples of potable water (public supply) and river water. Metal removal efficiencies were greater than 95% under the experimental conditions used, that is, 50 mL of 4.0 mg L⁻¹ manganese ions, pH range 4.0-6.0, contact time 5 min and 500 mg of *Moringa oleifera* seeds treated with 0.1 mol L⁻¹ NaOH for the potable water and river water samples.

The methodology was also applied in the treatment of a residue produced in BOD experiments. After preliminary treatment of this residue, the initial concentration of manganese ions was determined as 112.0 mg L⁻¹. Using the methodology optimized with 500 mg of treated seeds, it was possible to remove 34.84% of the metal in solution. This removal was low because the concentration of manganese ions present in the sample is 28 times greater than that used in the optimization step and also due to the presence of interfering ions, such as Cr(III), which are used in the Winkler titration method, and other metals that may be present in high concentrations in the laboratory residue sample. Thus, it was necessary to carry out experiments in order to determine the optimal mass for the treatment of this waste. It was found that it was possible to remove 95.7% of the manganese ions of the residue with 3.0 g of seeds and 50 mL of residue, a mass six times greater than that obtained for the optimized methodology.

CONCLUSIONS

1. Based on the results obtained in this study, it is evident that *M. oleifera* seeds are very efficient in the removal of manganese ion removal from potable water supplies that have levels of this metal above the legal limits.
2. The metal removal efficiencies were greater than 95% from water samples and laboratory residue under the optimum experimental conditions.
3. The satisfactory maximum adsorption capacity obtained and negligible cost of biosorbent means that *Moringa* seeds can be considered as a reliable natural material for the removal of manganese ions from aqueous effluents.

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REFERENCES CITED

- Anandkumar, J., and Mandal, B. (2009). "Removal of Cr(VI) from aqueous solution using Bael fruit (*Aegle marmelos correa*) shell as an adsorbent," *J. Hazard. Mater.* 168(2-3), 633-640.
- Araújo, C. S. T., Melo, E. I., Alves, V. N., and Coelho, N. M. M. (2010). "Moringa oleifera Lam. seeds as a natural solid adsorbent for removal of Ag¹ in aqueous solutions" *J. Braz. Chem. Soc.* 21(9), 1727-1732.
- Baidas, S., Gao, B., and Meng, X. (2011). "Perchlorate removal by quaternary amine modified reed" *J. Hazard. Mater.* 189(1-2), 54-61.
- Barka, N., Abdennouri, M., Boussaoud, A., and Makhfouk, M. (2010). "Biosorption characteristics of cadmium(II) onto *Scolymus hispanicus* L. as low-cost natural biosorbent," *Desalination* 258(1-3), 66-71.
- Bhaetti, H. N., Mumtaz, B., Hanif, M. A., and Nadeem, R. (2007). "Removal of Zn(II) ions from aqueous solution using *Moringa oleifera* Lam. (horseradish tree) biomass," *Process Biochem.* 42(4), 547-553.
- Bilgili, M. S. (2006). "Adsorption of 4-chlorophenol from aqueous solutions by XAD-4 resin: Isotherm, kinetic, and thermodynamic analysis," *J. Hazard. Mater.* 137(1), 157-164.
- Ding, Y., Jing, D., Gong, H., Zhou, L., and Yang, X. (2012). "Biosorption of aquatic cadmium(II) by unmodified rice straw," *Bioresour. Technol.* 114, 20-25.
- Gassenschmidt, U., Jany, K. D., Tauscher, B., and Niebergall, H. (1995). "Isolation and characterization of a flocculating protein from *Moringa oleifera* Lam.," *Biochim. Biophys. Acta* 1243(3), 477-482.
- Güzel, F., Yakut, H., and Topal, G. (2008). "Determination of kinetic and equilibrium parameters of the batch adsorption of Mn(II), Co(II), Ni(II) and Cu(II) from aqueous solution by black carrot (*Daucus carota* L.) residues," *J. Hazard. Mater.* 153(3), 1275-1287.
- Jusoh, A. B., Cheng, W. H., Low, W. M., Nora'aini, A., and Noor, M. J. M. M. (2005). "Study on the removal of iron and manganese in groundwater by granular activated carbon," *Desalination* 182(1-3), 347-353.
- Krishnani, K. K., Meng, X., Christodoulatos, C., and Boddu, V. M. (2008). "Biosorption mechanism of nine different heavy metals onto biomatrix from rice husk," *J. Hazard. Mater.* 153(3), 1222-1234.
- Lalhruaitluanga, H., Jayaram, K., Prasad, M. N. V., and Kumar, K. K. (2010). "Lead(II) adsorption from aqueous solutions by raw and activated charcoals of *Melocanna baccifera* Roxburgh (bamboo) – A comparative study," *J. Hazard. Mater.* 175(1-3), 311-318.

- Li, X. M., Zheng, W., Wang, D. B., Yang, Q., Cao, J. B., Yue, X., Shen, T. T., and Zeng, G. M. (2010). "Removal of Pb (II) from aqueous solutions by adsorption onto modified areca waste: Kinetic and thermodynamic studies," *Desalination* 258(1-3), 148-153.
- Marques, T. L., Alves, V. N., Coelho, L. M., and Coelho, N. M. M. (2012). "Removal of Ni(II) from aqueous solution using *Moringa oleifera* seeds as a bioadsorbent," *Water Sci. Technol.* 65(8), 1435-1440.
- Mejía-Saavedra, J., Sánchez-Armass, S., Santos-Medrano, G. E., González-Amaro, R., Razo-Soto, I., Rico-Martínez, R., and Díaz-Barriga, F. (2005). "Effect of coexposure to DDT and manganese on freshwater invertebrates: pore water from contaminated rivers and laboratory studies," *Environ. Toxicol. Chem.* 24(8), 2037-2044.
- Nadeem, M., Mahmood, A., Shahid, S. A., Shah, S. S., Khalid, A. M., and McKay, G. (2006). "Sorption of lead from aqueous solution by chemically modified carbon adsorbents," *J. Hazard. Mater.* 138(3), 604-613.
- Nassar, M. M. (2007). "Adsorption of Fe^{+3} and Mn^{+2} from ground water onto maize cobs using batch adsorber and fixed bed column," *Sep. Sci. and Technol.* 41(5), 943-959.
- Okoniewska, E., Lach, J., Kacprzak, M., and Neczaj, E. (2007). "The removal of manganese, iron and ammonium nitrogen on impregnated activated carbon," *Desalination* 206(1-3), 251-258.
- Pagnanelli, F., Mainelli, S., Veglio, F., and Toro, L. (2003). "Heavy metal removal by olive pomace: Biosorbent characterization and equilibrium modeling," *Chem. Engineering Sci.* 58, 4709-4717.
- Pereira, G. M., and Arruda M.A.Z. (2003). "Trends in preconcentration procedures for metal determination using atomic spectrometry techniques," *Microchim. Acta* 141, 115-121.
- Rajic, N., Stojakovic, D., Jevtic, S., Zabukovec Logar, N., Kovac, J., and Kaucic, V. (2009). "Removal of aqueous manganese using the natural zeolitic tuff from the Vranjska Banja deposit in Serbia," *J. Hazard. Mater.* 172, 1450-1457.
- Reddy, D. H. K., Ramana, D. K. V., Seshaiyah, K., and Reddy, A. V. R. (2011). "Biosorption of Ni(II) from aqueous phase by *Moringa oleifera* bark, a low cost biosorbent," *Desalination* 268(1-3), 150-157.
- Reddy, D. H. K., Harinath, Y., Seshaiyah, K., and Reddy, A. V. R. (2010). "Biosorption of Pb(II) from aqueous solutions using chemically modified *Moringa oleifera* tree leaves," *Chem. Eng. J.* 162(2), 626-634.
- Robinson-Lora, M. A., and Brennan, R. A. (2010). "Biosorption of manganese onto chitin and associated proteins during the treatment of mine impacted water," *Chem. Eng. J.* 162(2), 565-572.
- Roccaro, P., Barone, C., Mancini, G., and Vagliasindi, F. G. A. (2007). "Removal of manganese from water supplies intended for human consumption: A case study," *Desalination* 210(1-3), 205-214.
- Sari, A., Tuzen, M., and Soylak, M. (2007). "Adsorption of Pb(II) and Cr(III) from aqueous solution on Celtek clay," *J. Hazard. Mater.* 144(1-2), 41-46.
- Senthilkumar, S., Bharathi, S., Nithyanandhi, D., and Subburam, V. (2000). "Biosorption of toxic heavy metals from aqueous solutions," *Bioresource Technol.* 75, 163-175.
- Üçer, A., Uyanik, A., and Aygün, Ş. F. (2006). "Adsorption of Cu(II), Cd(II), Zn(II), Mn(II) and Fe(III) ions by tannic acid immobilised activated carbon," *Sep. Purif. Technol.* 47(3), 113-118.

- WHO, 2011. *Guidelines for Drinking Water Quality*, Fourth Ed. WHO Press, Switzerland.
- Witek-Krowiak, A., Szafran, R. G., and Modelski, S. (2011). "Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent," *Desalination* 265(1-3), 126-134.
- Xu, J. C., Chen, G., Huang, X. F., Li, G. M., Liu, J., Yang, N., and Gao, S. N. (2009). "Iron and manganese removal by using manganese ore constructed wetlands in the reclamation of steel wastewater," *J. Hazard. Mater.* 169(1-3), 309-317.
- Zhao, G., Wu, X., Tan X., and Wang, X. (2011). "Sorption of heavy metal Ions from aqueous solutions: A review," *Open Colloid Sci. J.* 4, 19-31.

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