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Biossorção de Mn(II) por vagem de *Moringa oleífera* a partir de águas contaminadas

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Dissertação apresentada ao programa de Pós Graduação em Ciência de Alimentos da Universidade Estadual de Maringá, como parte dos requisitos para obtenção do título de Mestre em Ciência de Alimentos.

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Orientadora

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BIOGRAFIA

Laura Adriane de Moraes Pinto nasceu em 18 de novembro de 1987 na cidade de Pilar do Sul- SP. Possui graduação em Engenharia de Alimentos pela Universidade Estadual de Maringá. Trabalha na área de tratamento de água atuando na área de métodos alternativos para o tratamento de água.

Dedico

Aos meus amados pais, Ana e José Carlos (*in memoriam*), minha irmã Mariana, meus avôs Rosária e José de Moraes (*in memoriam*) e minhas queridas tias Elvira e Cida, pela felicidade de ter uma família muito especial.

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APRESENTAÇÃO

Esta dissertação de mestrado está apresentada na forma de um artigo científico

Laura Adriane de Moraes Pinto, Fernanda de Oliveira Tavares, Marcelo Fernandes Vieira, Rosangela Bergamasco, Angélica Marquetotti Salcedo Vieira**, Mn (II) biosorption from contaminated water using Moringa oleifera pods**, Bioresource Technology, 2016.

RESUMO GERAL

A crescente poluição das águas de superfície, fez com que as águas subterrâneas fossem mais exploradas se tornando uma nova fonte de abastecimento em todo o mundo. O manganês está naturalmente presente em águas subterrâneas e mesmo em baixas concentrações pode ocasionar uma série de problemas na qualidade da água, tornando sua remoção essencial. A presença de manganês na água é uma preocupação tanto para a população como para a indústria, água de qualidade é um pré-requisito de grande importância para a produção de qualquer gênero alimentício seguro. A incidência de manganês na água está diretamente ligada a oxidação e corrosão de tubulações, além de ser a principal responsável por conferir, odor, sabor metálico e coloração enegrecida para água em sistemas de distribuição e abastecimento. O manganês (Mn) é um importante microelemento essencial, está envolvido na mineralização dos ossos e cartilagens, especialmente nas crianças em fase de crescimento. Contudo, altas concentrações são toxicas para os seres humanos e animais, podendo causar efeitos neurotóxicos, sendo assim, essencial sua remoção antes do consumo. Neste contexto, o objetivo deste trabalho foi encontrar métodos alternativos para a remoção de manganês de água destinada ao consumo e produção de alimentos. Inicialmente, as vagens de moringa foram coletadas na cidade de Aracajú- SE . Em seguida, foram lavadas para remoção de sujidades e secas em estuda a 60ºC por 24 horas. Após a secagem, o material foi submetido a padronização granulométrica de 0,32 mm e este material então recebeu o nome de vagens sem tratamento (VAI). Foram avaliados os agentes de tratamentos NaOH 0,1mmol (Synth, 97% de pureza) como agente básico e HCl 0,1 mmol L^{-1} (Nuclear 36,5% de pureza) como agente ácido, por sua capacidade em melhorar a sorção de Mn pela biomassa. O pré-tratamento foi realizado seguindo a metodologia descrita por Kumar e Gaur (2011), onde 50 mg do biossorvente sem tratamento foi adicionado em 50 mL de agente de tratamento e agitado a 80 rpm durante 30 min a 25 °C. Posteriormente a biomassa foi centrifugada (300 rpm, 15 min), o sobrenadante descartado e o pellet lavado com água Milli-Q até a neutralização do pH, em seguida, a biomassa tratada foi seca em estufa a 60 °C até peso constante. Após a secagem o material foi submetido ao processo de padronização granulométrica, a fim de se obter partículas com um tamanho de 0,32 mm. A vagem pré-tratada ácida recebeu o nome de vagem de VTA, a vagem pré-tratada básica recebeu o nome de VTB, onde todos foram avaliados quanto a sua capacidade para remoção de manganês da água testada. Os biossorventes foram caracterizados por EDS, MEV e FTIR. Os dados experimentais foram analisados cineticamente e descobriu-se que a biossorção pelos nove diferentes adsorventes seguiu a cinética de pseudo-segunda ordem, com tempo de contato de 30 min para todas as vagens. Os dados de equilíbrio foram analisados usando os modelos isotérmicos de Langmuir e Freundlich, onde o modelo foi mais adequado para todos os adsorventes foi o de Freundlich, confirmando a natureza heterogênea dos biossorventes. As propriedades termodinâmicas também foram avaliadas e confirmaram a natureza espontânea da reação assim como a viabilidade do processo de biossorção a partir das vagens. O presente estudo relevou que o tratamento básico promoveu uma melhora na capacidade de remoção de Mn (II) para todos os adsorventes. As melhores remoções foram obtidas utilizando-se pH 6,0, 0,50 g de adsorvente e em tempo de contato de 60 minutos. O biossorvente mais eficiente para a remoção de manganês foi a vagem tratada básica com 94% de remoção, seguida da vagem integral (VAI) com 82% e por fim da vagem ácida (VTA) com remoção de 61%. A utilização da *Moringa oleifera* como adsorvente é uma opção atraente para o tratamento de águas contaminadas com Mn, já que além de ser um produto natural de fácil obtenção ela é um material renovável e biodegradável. A biossorção pode ser ser adotada como um pré-tratamento das águas subterrâneas destinadas a indústria, colaborando não apenas com a

manutenção da saúde dos consumidores, mas também com o aumento da vida útil dos equipamentos.

Palavras-chave: Biossorção, Manganês, *Moringa oleifera*, pré-tratamento.

GENERAL ABSTRACT

The increasing pollution of surface waters, caused groundwater to be further explored becoming a new source of supply worldwide. Manganese is naturally present in groundwater and even at low concentrations can cause a number of problems in water quality, making its removal essential. The presence of manganese in water is a concern for both population and industry, quality water is a prerequisite of great importance for any safe food production. The incidence of manganese in water is directly linked to oxidation and corrosion of pipes, as well as being primarily responsible for adding odor, metallic taste and blackened coloring to water in distribution and supply systems. Manganese (Mn) is an essential microelement, involved in bones and cartilage mineralization, particularly in children in the growth phase. However, high concentrations are toxic to humans and animals, may cause neurotoxic effects, thus, its removal before consumption is essential. In this context, this work objective was to find alternative methods for removing manganese of consumption and food production water. Initially, the moringa pods were collected in the city of Aracajú- SE. They were then washed for removing dirt, and dried in an oven at 60ºC for 24 hours. After drying, the material was subjected to particle size patterning of 0,32 mm and this material then received the name of non-treated pods (VAI). The agent treatment NaOH 0,1mmol (Synth, 97% purity) was evaluated as a basic agent and HCl 0,1 mmol L-1 (Nuclear 36,5% purity) as an acid agent for its ability to improve the Mn sorption by biomass. The pretreatment was carried out following the methodology described by Kumar and Gaur (2011), where 50 mg of untreated biosorbent was added to 50 mL of treating agent and stirred at 80 rpm for 30 min at 25°C. Subsequently the biomass was centrifuged (300 rpm, 15 min), the supernatant discarded and the pellet washed with Milli-Q water until neutral pH, then treated biomass was dried in an oven at 60 °C to constant weight. After drying the material was subjected to particle size standardization process, to obtain particles with a size of 0,32 mm. The pretreated acid pod was named VTA pod, the basic pre-treated pod was named VTB, all were evaluated for their manganese removal ability from tested water. The biosorbents were characterized by EDS, SEM and FTIR. The experimental data was kinetically analyzed and it was found that the biosorption by nine different adsorbents followed pseudo-second order kinetics, with a residence time of 30 min for all the pods. The equilibrium data was analyzed using the Langmuir and Freundlich isotherm model, and the more appropriate model for all adsorbents was Freundlich, confirming the heterogeneous nature of the biosorbents. The thermodynamic properties were also evaluated and confirmed the spontaneous nature of reaction, as the biosorption process by pods viability. This study revealed that the basic treatment promoted an improvement in Mn (II) removal capacity for all the adsorbents. The best removal results were obtained using a pH 6,0, 0,50 g of adsorbent in a contact time of 60 minutes. The most efficient biosorbent for the manganese removal was the basic treated pod, obtaining 94% removal, followed by the integral pod (VAI) with 82% and last, the acid pod (VTA) with 61% of removal. The usage of Moringa oleífera as adsorbent is an attractive option for the treatment of Mn polluted water, since beyond being a natural product of easy obtainment it is a renewable and biodegradable material. The biosorption can be adopted as a pre-treatment for groundwater with industrial purpose, helping not only with health maintenance but also with the improvement of equipment lifespan.

Keywords: Biosorption, Manganease, *Moringa oleifera*; pretreatment

ARTICLE
Mn (II) biosorption from contaminated water using *Moringa oleifera* pods

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Abstract

This research aims the removal of manganese from water with excess of this ion, were used as biosorbent the pods of *Moringa oleifera*. The biosorbents were prepared from *Moringa oleifera* raw pods and chemically modified by NaOH e HCl, showing capacity to remove Mn (II) from the tested water. The biosorbents were chacacterized by EDS, SEM and FTIR. The experimental data was kinetically analyzed and it was found that the biosorption of three different adsorbents followed pseudo-second order kinetics and equilibrium time of 30 min. The equilibrium data was analyzed using the Langmuir and Freundlich isotherm models, being Freundlich the most appropriate model. The thermodynamic properties were also evaluated and confirmed the spontaneous nature of the reaction and the feasibility of bioremediation process from the pods. The most efficient biosorbent for the manganese removal was the basic treated pod with 94% of removal.

Keywords: Biosorption; Manganese; Chemical modification; Moringa oleifera Lam.

1. Introduction

The increasing pollution of surface waters, caused groundwater to be further explored becoming an important source of supply worldwide (Moyosore and Coker, 2014). Manganese is naturally present in groundwater and even at low concentrations can cause several problems in water quality, making its removal essential (Taffarel and Rubio, 2010). Consumption of food and water contaminated by havy metals is a main reason of human contamination by metals, accounting for 90% of cases. In this regard, the risks associated with metal contamination in foodstuffs has aroused great concern worldwide (Islam et al., 2015; Khan et al., 2013). Although the Mn, as well as certain micronutrients are essential for plants growth and / or human nutrition, in high concentrations they become toxic to the body, since they are not biodegradable and can cause serious adverse effects on human health (Rahman et al., 2012).

Manganese (Mn (II)) is responsible for a number of diseases such as Parkinson's disease, and also cause damage to the brain, liver, kidneys and nervous system; in pregnant women affect fetal development and induces abortion, as well as being neurotoxic for children (Rahman et al., 2015; Usepa, 2004).

Presence of manganese in water is a concern for both the population and the industry (Longe and Balogun, 2010). Quality water is a prerequisite of great importance for the production of any safe foodstuff (Lu et al., 2015). In food industry water is used in all

operations, since direct incorporation into product as an ingredient or a vehicle for incorporation of ingredients for formulations and also indirectly in processes such as fluid for heat transfer, cleaning and sanitizing equipment and process areas (Kasaai, 2014). The incidence of manganese in water is directly linked to oxidation and corrosion of pipes, as well as being primarily responsible for conferring odor, metallic taste and blackened coloring to water distribution and supply systems (Peng et al., 2010). The fouling and corrosion in pipes, equipment and cooling systems increases maintenance costs, reduces operational efficiency and is a major source of contamination by manganese (Alvarez-Bastida et al., 2013; Hoyland et al., 2014).

The US Environmental Protection Agency sets a maximum level of manganese in drinking water of 0.05 $mg.L^{-1}$. Similarly the World Health Organization has established a 0.1 mg. L^{-1}, as well as the WHO, in Brazil, according to the law CONAMA2914/2011, the allowed level is $0.1mg.L^{-1}$ in water consumption.

Many physicochemical methods are available for the removal of heavy metals from aqueous solution. Among the various water treatment techniques exist adsorption, coagulation, advanced oxidation, membrane separation, chemical precipitation, solvent extraction, reverse osmosis, filtration and electrochemical treatment. Adsorption is preferred for removing heavy metal ions due to minimizing the use of chemicals, easy handling, variety and availability of different types of adsorbents, being a technique considered "ecofriendly" (Anastopoulos and Kyzas, 2015; Tounsadi et al., 2015a).

Currently, several alternative processes have been studied in order to find economic techniques and low-cost biomaterials for removing heavy metals from water. The biosorption process has some advantages over conventional processes of water purification, such as the replacement of synthetic compounds for natural compounds in the water treatment, low cost, low sludge production, good biodegradability and is not aggressive to the environment, since most materials used are organic residues (Abdeen et al., 2015; Alfarra et al., 2014; Reddy et al., 2012). The *Moringa oleifera* Lam has emerged as an important natural coagulant and presents interesting features for its use as a promising biosorbent, since it has the ability to anchor metals, renewability and low cost, making its use attractive in biosorption processes (Meneghel et al., 2013). Along the natural biosorbents, the biomass chemical modification has shown an alternative currently studied for improvement in the efficiency of metals biosorption (Varga et al., 2013).

Thus, the present study aimed the evaluation of *Moringa oleifera* Lam. pods (Moringa) modified by chemical treatments in Mn (II) biosorption and its removal from aqueous solutions. We studied the influence of parameters such as pH, the adsorbent dose and the adsorption contact time. Kinetic and equilibrium data and thermodynamic parameters were obtained.

2. Materials and methods

All chemical products / reagents used in this study were of analytical grade. A Mn (II) solution (1000 mg. L^{-1}) was prepared and all other solutions were prepared by diluting this stock solution. A pH meter (ThermoScientific® Orion Versa Star Model) was used to measure pH. The pH was calibrated with standard buffer solutions of pH 4.0, 7.0 and 9.2. The concentration of Mn (II) metal in the samples was determined after filtering in cellulosic membrane of 0.45 mm and quantified in an atomic absorption spectrophotometer (AAS, Varian® AA spectra, 55Australia). The absorbance was measured at a wavelength of 279.5 nm and a spectral bandwidth of 0.2 nm.

2.1 Biosorbents characterization

The in-natura pod (VAI) and the pretreated pods (VTA and VTB) were characterized before and after the biosorption process by infrared spectroscopy (FTIR) and scanning electron (SEM). The Scanning electron microscopy with EDS microprobe (SS 550 Superscan Model, Shimadzu®) was used to study the surface morphology of biosorbents and its composition. The FTIR spectrometry analyzes were performed using KBr pellets, prepared in a ratio of 1/100 m / m.

The zero charge point (ZCP) was determined for all biosorbents in order to check from which pH the adsorbent surface changes. The methodology used for the determination was proposed by (Wang et al., 2008), where 0.1 g of adsorbent was added to 50 ml of distilled water at different initial pH conditions, ranging from 1-12. The flasks were shaken for 24 hours at 25°C and a rotation of 200 rpm. After this period, the samples had their final pH measured and graphically confronted with the initial pH values. The acid solutions were adjusted from 0.1 mol.L^{-1} of HCl and the basics with 0.1 mol.L^{-1} of NaOH.

2.2 Biomass modification

Initially the pods were separated from the moringa seeds, crushed, washed with distilled water and dried in a circulating oven at 60ºC until a constant weight, being called in-natura pods (VAI)

The pods modification was performed following the methodology described by (Kumar and Gaur, 2011), where the evaluated treatment agents were: NaOH 0.1 mmol.L^{-1} (Synth®, 97% purity) and HCl 0.1 mmol.L^{-1} (Synth®, 36,5% purity). These agents were chosen due to its known adsorption improvement capacity (Zafar et al., 2015).

For the basic treatment VAI was added to the NaOH 0.1 mmol.L^{-1} solution treatment in a 3:1 proportion (NaOH volume/ moringa mass) agitated at 80 rpm during 30 minutes at 25 °C. Next the biomass was centrifuged (300 rpm, 15 min), the supernatant discarded and the pellet formed was washed with Milli-Q water to ensure removal of excess base. The treated pod was dried in an oven at 60 °C to constant weight. After drying, the material was subjected to particle size patterning of 0.1-0.32 mm and its manganese removal ability by adsorption evaluated. This material received the name of basic treated pod (VTB). The same procedure was repeated for the treatment agent HCl 0.1 mmol.L^{-1}, giving origin to the material named acid treated pod (VTA)

2.3 Biosorption experiments

The biosorption experiments were developed in batch using sealed plastic flask containing 50 mL of manganese ion solution at a 4 mg.L^{-1} concentration using stirring speed of 200 rpm in thermostatic bath. The parameters evaluated during adsorption tests were: contact time, pH, temperature, and adsorbent mass, where each parameter was varied one at a time.

The effect of the contact time was evaluated by varying the time from 2 to 150 min. Flask containing Mn (II) ions solution (4 mg. L^{-1}) and 0.5 g of biosorbent were stirred at 200 rpm in a thermostated bath at 25 ° C for different periods of time at a starting pH of 6 (solution natural pH). Finally the material was filtered through 0.45µm cellulose membrane

and aliquots were collected for metal concentration quantification, a time of 60 min was established as the optimum time for use in subsequent experiments.

The influence of pH was studied by balancing the initial solution (Mn (II), 4 mg.L^{-1}) with NaOH (0.1 mmol. L^{-1}) and HCl solution (0.1 mol.L^{-1}) for different pH (1.0, 3.0, 5.0, 6.0, 7.0 and 8.0), setting a fixed agitation speed of 200 rpm, adsorbent mass of 0.5 g, a temperature of 25 ° C and 60 min.

The effect of adsorbent mass was investigated by varying the mass in 0.5, 0.7, 1.0 and 1.3 grams. The experiment was conducted setting the Mn (II) concentration in 4 mg.L^{-1}, stirrer speed of 200 rpm, 60 min contact time, temperature of 25 ° C and optimum pH found.

To evaluate the temperature effect, the parameters, metal concentration and rotation were maintained,for the mass was used 0.5g of adsorbent, optimal pH found and varied temperature in 15, 25, 35 and 45 °C with contact time of 60 min.

After stablishing contact time, metal concentration was measured using AAS. The percentage removal of metal ions was calculated using Eq. (1):

$$Removal \% = ((Co - Cf) / Co) . 100 \tag{1}$$

The quantity of metal adsorbed by biomass in equilibrium was calculated using Eq. (2).

$$q = (Co - Ce).V/m \tag{2}$$

Where Co is the solute concentration in the initial solution (mg.L^{-1}); Cf is the final residual metal concentration after the absorption period in mg/L; Ce is the final solute concentration in equilibrium (mg.L^{-1}); V is the solution volume (L) and m is the adsorbent mass (g).

For the study of Mn (II) adsorption isotherms by biosorbents the optimal conditions were applied to each of the adsorbents, ensuring balance of the system. The concentration of manganese ions was varied from 5-50 mg.L^{-1}; the solutions after adsorption were then filtered through a cellulose membrane of 0,45μm and metal ions quantified using an atomic absorption spectrophotometer. In this study, we applied two widely used isotherms, Langmuir and Freundlich; Eqs. (3) and (4) indicate these models respectively.

The Langmuir model (Langmuir, 1916) used to evaluate the adsorption nature is expressed as:

$$qe = \frac{qmax.KL.Ce}{1+KL.Ce} \tag{3}$$

Where Eq.(3) Ce (mg.L^{-1}) refers to the equilibrium metal concentration, qe (mg.g^{-1}) is the quantity of metallic ions adsorbed by mass unit of adsorbent in equilibrium state, $qmax$ (mg.g^{-1}) is the maximum capacity of adsorption and KL (L.mg^{-1}) the Langmuir constant.

The Freundlich equation can be described as:

$$qe = K_f.Ce^{1/n} \tag{4}$$

Where K_f and n are Freundlich constants related to the adsorption capacity by several layers and adsorption intensity. If the n values were hold within 1-10, indicate that the

biosorption process is favourable, for *n* values lower than 1, the adsorption is unfavorable, the *n* values same as 1, indicate that the adsorption was linear. However, values lower than *n* indicate that the adsorption was favorable by chemical interactions; values greater than *n* characterize the favor of adsorption via physical processes (Lalhruaitluanga et al., 2010).

To evaluate the kinetic of Mn (II) ions removal, pseudo-first and pseudo-second order kinetic models were used with the purpose of understand the biosorption dynamics of adsorbents VAI, VTA and VTB.

The pseudo-first order kinetic model (Lagergren, 1898) is shown below (Eq.5).

$$Q_t = Q_e(1 - e^{1k_1t}) \tag{5}$$

Where, Qt (mg.g^{-1}) is the quantity of metallic ions adsorbed in moment t and K_1 (min^{-1}) is constant in the adsorption process of pseudo-first order.

The pseudo-second order kinetic equation (Blanchard et al., 1984) is expressed in Eq.6.

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \tag{6}$$

Where, Q_e represents the equilibrium adsorption capacity (mg.g^{-1}) and K_2 (g.mg^{-1}.min^{-1}) is the pseudo-second order adsorption velocity constant.

3. Results discussion

3.1. Biosorbents characterization

The biosorbent surface and structure characterization are important for understanding the mechanism of interaction between the biomass and the metal (Araújo et al., 2013). For characterization and composition of surfaces were used the techniques of scanning electron microscopy (SEM) with microprobe EDS (Energy Dispersive Spectroscopy) and FTIR analysis.

EDS (Table 1) analysis of the adsorbents (VAI VTA and VTB) after Mn (II) adsorption shows the manganese incorporation of the samples, as initially none of the adsorbents had Mn (II) in their composition. The presence of Mn (II) in the samples after the adsorption process confirms the pods capacity to adsorb metals. Reddy et al (2011) working with moringa shells, report that compounds present in moringa, such as cellulosic structures and proteins favor the bonding with metals, once the metal ion is associated with functional groups on the biosorbents surface, favoring the biosorption process present in moringa.

Fig.1 shows the images obtained by SEM of the superficial morphology of adsorbents VAI, VTA e VTB.

By analyzing Fig. 1 can be seen that the adsorbents have surface with fibrous and heterogeneous aspect, irregular pores of varied dimensions, relatively open and asymmetrical. Such features can benefit e the process of metals biosorption (Meneghel et al., 2013).

FTIR analysis is an effective way to obtain information about the functional groups present on the materials surface. Fig. 2 shows the FTIR spectra of VAI, VTA and VTB pods.

Using FTIR technique, the main functional groups present in the samples were identified. Fig. 2 shows a broadband of 3360 cm^{-1} assigned to O-H stretching. The peak present at 2923 cm^{-1} is attributed to the symmetric and asymmetric stretch of CH_2, this functional group is present in fatty acids, proteins, cellulose, hemicellulose and lignin (Marques et al., 2012). The peaks in the region of 1740 to 1630 cm^{-1}, show a change in the intensities of these peaks indicating potential changes occurring in the C=O bonds during the proposed treatments. Possibly the basic and acid treatments can cause hydrolysis reactions resulting in new carboxylic groups (-COO) and hydroxyls (-OH) in the biomass, that can favor the metals biosorption (Lalhruaitluanga et al., 2010; Zafar et al., 2015). The spectral region of 1224 to 1248 cm^{-1} confirms the presence of carboxylic acids and is associated with the C-O bond stretching with phenols (Meneghel et al., 2013). The peak present at 1054 cm^{-1} is attributed to connections C-O type, confirming the presence of lignin structure, which has functional groups such as hydroxyl and carbonyl with capacity to form interactions with metals and remove them. The peak at 893 cm^{-1} is attributed to C-O bonds, characteristic of cellulosic structures presence such as hemicellulose and cellulose (Alves and Coelho, 2013; Esfandiar et al., 2014; Reddy et al., 2012, 2011)

The pretreatment favor the presence of active functional groups such as hydroxyl (-OH) groups and carboxylic groups (-COOH) which are known to favor metals adsorption (Reddy et al., 2010a).

Fig.3 shows the spectra of FTIR in the biomass in-natura, before and after Mn (II) biosorption. The spectra show an intense band at 3360 cm^{-1} indicating the presence of hydroxyl groups. The presence of peak at 2917cm^{-1} can be attributed to symmetric and asymmetric stretching of C-H bond. The alteration of the wavenumber of the carbonyl band from 1743 cm^{-1} to 1734 cm^{-1} after the adsorption process, indicates the possible connection of metal groups to carboxylic groups. Reddy et al. (2012) working with biomass of *Moringa oleífera* modified leaves as adsorbents for Cd(II), Ni(II) e Cu(II) removal, reported a similar behavior for their adsorbent, where they claim that such modification is related to the interactions occurred between the carboxylic and hydroxyl groups and the metals in solution. From these results, it is assumed that the Mn (II) is preferably adsorbed by hydroxyl groups (OH) and carboxyl groups (COOH). The subtle shift in the spectra before and after the adsorption process can be associated with the fact that the metal ions concentration is relatively low compared to adsorbent mass in the adsorption process, which ultimately appropriates the non-appearance of new peaks and spectrum distortion, characterizing a mild physical adsorption process (Reddy et al., 2010a; Zafar et al., 2015). The pre-treated adsorbents (VTA and VTB) had a similar behavior to the in-natura pod after adsorption in their FTIR spectra, showing alteration in the carbonyl band of 1743cm^{-1} that possibly indicates the connection of metal groups.

3.1.1 Point of zero charge

The determination of the biosorbent point of zero charge (PCZ) is important to elucidate the biosorption mechanism. Fig.4 shows the PCZ analysis of the studied biosorbents.

In figure 4, it is possible to elucidate the effect of pH on Mn (II) adsorption for studied adsorbents. The PCZ values were in the range of 6.2-7.2 for VAI, de 3.9- 4.2 for VTA and 6.3-8.7, for VTB, this indicates that the biosorbents acquire positive charge below the ZCP range and above this value, they acquire negative charge. On zero charge point the electrostatic forces between the dissolved Mn (II) ions and the surfaces of the adsorbent are

balanced, so that their charges are canceled. As pH < PCZ, the biosorbent assumes positive surface charge, resulting in an electrostatic repulsion of Mn (II), reducing the adsorption capacity. When pH > PCZ, the superficial changes of the biosorbent became negative, thus attracting Mn (II) ions in solution to the surface, favoring adsorption. Reddy et al., (2012) reported that the metal adsorption is related to both the pH and the nature of the biosorbent, since each biomass has its own optimum pH for the adsorption of metal ions. Thus, different behaviors provide a preliminary indication of the adsorbent behavior related to different pH.

3.2 Contact time effect

The effect of contact time in removal capacity of Mn (II) ions by VAT, VTA and VTB was investigated and is shown in Fig. 5.

Analyzing Fig. 5, it can be noticed that the adsorption percentage increases with contact time until equilibrium is reached. The contact time study for the three adsorbents (VAI VTA and VTB) for the Mn (II) ions in solution removal process revealed that they tend to have similar adsorptive behavior, most of the metal ions were removed within the range of 2-30min. As observed, the removal percentage increases considerably in the initial phase (0-20 minutes) reaching equilibrium in about 30 min. The equilibrium state between the solution and the adsorbent was reached at 30 min for three adsorbents studied. However, a longer time was chosen to obtain the adsorption isotherm (60 min), ensuring the system equilibrium. The maximum biosorption was 81% for VAI, 60% for VTA and 93% for VTB, showing residual manganese in solution of 0.73 mg.L^{-1} for the in-natura pod, 1.56 mg.L^{-1} for the acid treated pod and 0.25 mg.L^{-1} for the basic pod. After the treatment, the biomass goes through a series of changes such as surface impurities removal, membrane rupture and new functional groups exposure, such as hydroxyls and carboxylic groups, which may favor or not the biosorption process (Zafar et al., 2015).

3.3 pH influence in adsorption process

The pH effect on the manganese adsorption by the adsorbents VAI, VTA and VTB varying the pH in 1, 3, 5, 6, 7 and 8 is shown in table 2.

In the adsorption process the pH of the solution is an important variable, since they directly affect the metals adsorption due to protonation / deprotonation of functional groups of the adsorbent (Anastopoulos and Kyzas, 2015).

It may be noted that removal capacity for acid treated pods (VTA), in-natura pods (VAI) and basic treated pod (VTB) initially increased with the increase of pH, and then from pH 6 remained practiacally unchanged. The maximum removal was observed in the pH 6-8 range for the three adsorbents studied, thus the pH chosen for further studies was 6 once this value showed good removal for all adsorbents and is the natural pH of the solution. At pH above 8.0 Mn (II) precipitates in the form of Mn(OH)$_2$, becaming it unavailable for adsorption, in addition metal precipitation causes turbidity (Meneghel et al., 2013). The VTA adsorbent performance in the removal of Mn (II) ions in solution confirms the data obtained in CZP analysis, where the manganese adsorption is favored at higher pH values. As for VAI and VTB removal was favored in the zero load range. Variations on metals sorption at different pH can be related to the ionic strength (Kumar and Gaur, 2011). Furthermore, the alkaline treatment can contribute to the exposure of certain chemical groups, reinforcing the connection between the cation and the metal adsorbent (Zafar et al., 2015). Another factor to correlate is that on the CZP the adsorbents superficial charge tend to be neutral and

electrostatic forces between metal ions and the adsorbent surface equilibrated, even in equilibrium certain carboxylic, and hydroxyl groups present in the sorbent molecule further are available for connecting with metals (Helen Kalavathy and Miranda, 2010).

3.4 Biosorbent dose effect

The Mn (II) biosorption by studied adsorbents (VAI, VTA e VTB) was evaluated varying the adsorbent amount from 0.5 to 1.5 g in solution, with initial concentration of 4 mg.L^{-1}, pH 6 and contact time of 60 min. The removal percentage varied from 66% to 83% with the in-natura pod, from 47% to 65% with the treated pod by acid, and from 87% to 95% with a treated pod by basic. Obtaining residual manganese in solution of 0.68 mg.L^{-1}, 1.4 mg.L^{-1} e 0.2 mg.L^{-1}, respectively for the VTI, VTA and VTB pods. As the adsorbent dose was raised, the adsorbents efficiency also raised, however, remained constant starting from the 0.5 g dose, which justified the use of 0.5g biosorbent mass for further studies. This result can be explained by the fact that increasing the amount of biomass, the surface area and number of active sites available for new connections increase, improving the bioremediation capacity (Abdeen et al., 2015). Furthermore, Lalhruaitluanga et al., (2010) reported that the alkali biomass pretreatments improve the capacity related of adsorption to the biomass without treatment, once it may contribute to the availability of certain functional groups present responsible for anchoring metals, improving the biomass adsorption capacity.

3.5 Temperature effect in biosorption

With a contact time of 60 min, pH 6 and fixed adsorbent dose of 0.5g, the effect of temperature on the Mn ions adsorption per VAI, VTA and VTB was studied at temperatures ranging from 15-45 ° C. The removal ranged from 79% to 85% for VAI, 61% to 62% for VTA and 92% to 94% for VTB; resulting in a residual manganese solution of 0.6 mg.L^{-1} for the in-natura pods, 1.52 mg.L^{-1} for the pod treated by acid and 0.24 mg.L^{-1} for the basic treated pod by basic.

The obtained results show the biosorption of the three adsorbents that is enhanced with increasing temperature. This fact is accordance with the endothermic nature of adsorption process, whereas the temperature rises adsorption tends to increase (Khobragade and Pal, 2014). However, the variation in temperature showed no significant difference in manganese biosorption capacity from 25°C, being this (25 °C) the temperature chosen for further studies. Tounsadi et al., (2015) when working with *Diplotaxisharra* and *Glebioniscoronaria L.* biomass for Cd (II) and Co (II) adsorption observed that the temperature did not influence on their adsorptive process, this fact would be associated with morphological nature of the biosorbent, which had no defined pores that don't the favor adsorption process.

3.6 Kinetic study

The kinetic parameters of the studied adsorbents are showed in Table 3.

As can be seen in Table 3, both models fit the kinetic data. However, the pseudo-second-order model is which best describes the biosorption of Mn (II) by moringa pods, presenting the biggest R^2 coefficient values (0.9960-0.9990) and the values closer to Q_{eexp} and Q_{tcal}, reinforcing the applicability of this model. The second order kinetic model indicates that the limitative rate stage was the adsorption, indicating that the adsorption

process is dependent of the amount of adsorbed metal on the surface of the adsorbent and the amount of adsorbed at equilibrium (Helen Kalavathy and Miranda, 2010).

3.7 Equilibrium isotherms

The experimental data was fitted to the Langmuir and Freundlich experimental models and are shown in Fig 6.

The adsorption isotherm expresses the relation between the biosorbent amount per gram of adsorbed metal ions, in addition to providing information about the adsorption behavior (Abdeen et al., 2015). Several isothermal models have been widely used to determine a model for the equilibrium of a system adsorption. The most widely used models are the Langmuir and Freundlich where the Langmuir adsorption model assumes that it occurs over a homogeneous monolayer surface without any interaction between the adsorbed ions.

On the other hand, the Freundlich equation is an empirical model based on adsorption onto a heterogeneous surface, which implies that the adsorption occurs multilayer, which suggests that the energy diminishes exponentially with the surface covering (Reddy et al., 2010b). The parameters obtained for each model are given in Table 4.

It can be seen in Table 4, the experimental data of VAI, VTA and VTB biosorbents were well-fitted by Langmuir and Freundlich. However, the Freundlich model was the one that best described the experimental data, with higher values of R^2, which that the calculated biosorption capacity used in the model is close to experimental values obtained. The Freundlich isotherm confirms the heterogeneity sites on the adsorbent surface, once the values of n are between 1 and 10, indicating that the Mn (II) ions biosorption foe the studied adsorbents was favorable. It was also observed that the maximum adsorption capacity (q_{max}) was 7.64 mg.g^{-1} for VTB, 6.00 mg.g^{-1} for VAI and 3.60 mg.g^{-1} for VTA.

The biosorption capacities of various biosorbents on manganese removal reported in the literature are shown in Table 5. Comparing the q_{max} values experimentally obtained to the other adsorbents reported in the literature it can be observed that the adsorbents studied VAI, VTA and VTB have Mn (II) removal capabilities close to those found in previous studies. The results of this study showed that treated moringa pods demonstrate good removal proprieties of Mn (II). Furthermore, pods offer a series of advantages in their use, such as low cost because it is a byproduct, renewability and biodegradability, simplicity in the treatment for obtaining the biosorbent

The basic treatment was the most efficient for the manganese removal, resulting with a residual value of 0.32 to 0.24 mg/L. These values are still above the admitted by the Brazilian legislation for drinking water. However, the high capacity of manganese removal indicates that moringa pod witch basic treatment is promising biosorbent for metal removal.

3.8 Biosorption thermodynamic

The temperature effect on the Mn (II) ions adsorption by the adsorbent was studied at 15, 25, 35 and 45°C in a constant concentration of 4 mg. L^{-1}, pH 6 and contact time of 60 min. The dependence of the equilibrium constant (Kc) for the Mn (II) ions adsorption was calculated for all temperatures using Eq. (7):

$$Kc = \frac{Fe}{1-Fe} \tag{7}$$

Where, Fe is the percentage sorption fraction in equilibrium. The thermodynamic parameters, Gibbs free energy ($\Delta G°$), enthalpy variation ($\Delta H°$) and entropy variation ($\Delta S°$) (Akhtar et al., 2007) were calculated using equations (8) and (9):

$$ln\ Kc = -\frac{\Delta H}{R.T} + \frac{\Delta S}{R} \tag{8}$$

$$\Delta G° = -R.T.\ln Kc \tag{9}$$

Where, R is the universal gas constant (8.314 J.(mol K)$^{-1}$) and T the absolute temperature (K). The values of $\Delta H°$ and $\Delta S°$ can be calculated from the intersection of ln Kc vs 1 / T rect. The thermodynamic parameters for the adsorption process of the different biosorbents are shown in Table 6.

The negative values found for $\Delta G °$ in the different temperatures for all adsorbents confirm the spontaneous nature of the reaction as well as the viability of the biosorption process. For $\Delta H°$ values found for all samples were positive, wich confirms the endothermic nature of the process. The positive entropy value shows the favoring system randomness system during the adsorption process (Abdeen et al., 2015).

4. Conclusion

This study revealed that the basic treatment showed maximum biosorption capacity of 6.0 mg.g^{-1}. In the best adsorption condition was reached a residual manganese content of 0.24 mg.L^{-1} in the treated water. Furthermore, the kinect datas were better described by the pseudo-second order model. The isotherm modeling indicated that the Mn (II) biosorption can occur in multilayer and the process in controlled by physisorption. These data demonstrate that the pods are an attractive option for the treatment of contaminated water with Mn (II); additionally these biosorbents are renewable and biodegradable.

5. Acknowledgements

6. References

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Figure Captions

Figure 1: SEM micrographs of adsorbents (A) In-natura pod (VAI), (B) Acid treated pod (VTA) and (C) Basic treated pod (VTB).

Figure 2: FTIR spectrum of (a) In-natura pod and (b) FTIR spectrum of in-natura pod after manganese adsorption.

Figure 3**:** FTIR pods spectrum (A) VTB; (B) VAI and (C) VTA.

Figure 4: PCZ analysis for the VAI, VTA and VTB biosorbents.

Figure 5: Contact time effect on manganese biosorption of VAI, VTA and VTB (biosorbent dose: 0.50 g, pH: 6).

Figure 6: Langmuir and Freundlich isotherms adjust of manganese adsorption experimental data at 10 to 50 $mg.L^{-1}$, 50 mL volume, 0.5 g of adsorbent at 25°C, pH 6 and time of 60min for VAI (a), VTA (b) e VTB (c) adsorbents.

Figures

Figure 1
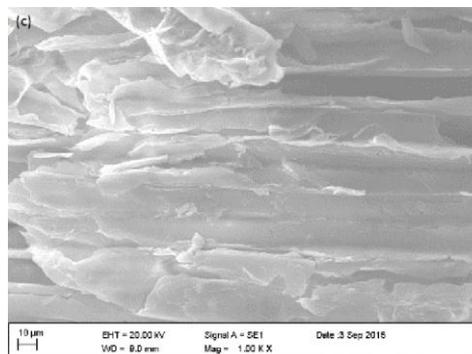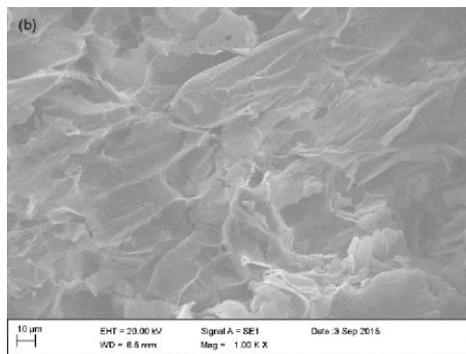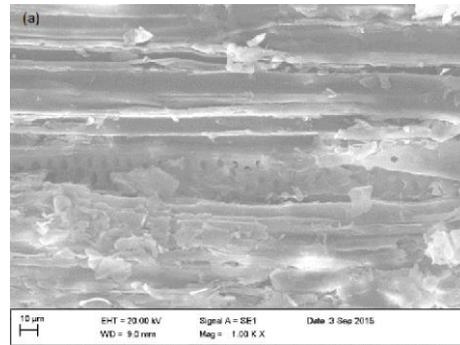
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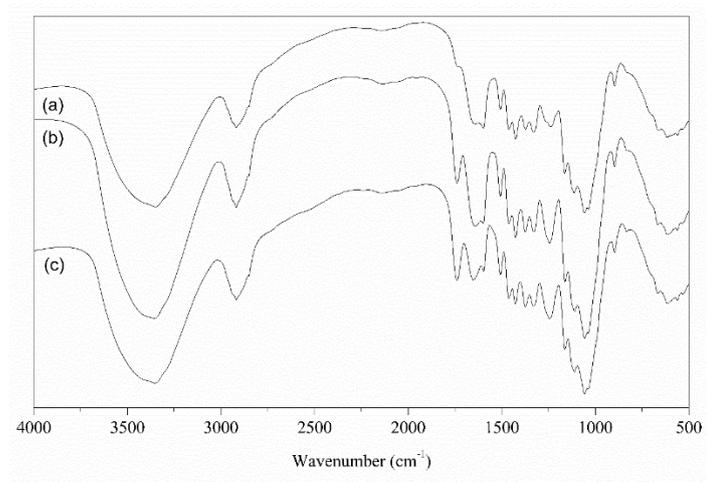
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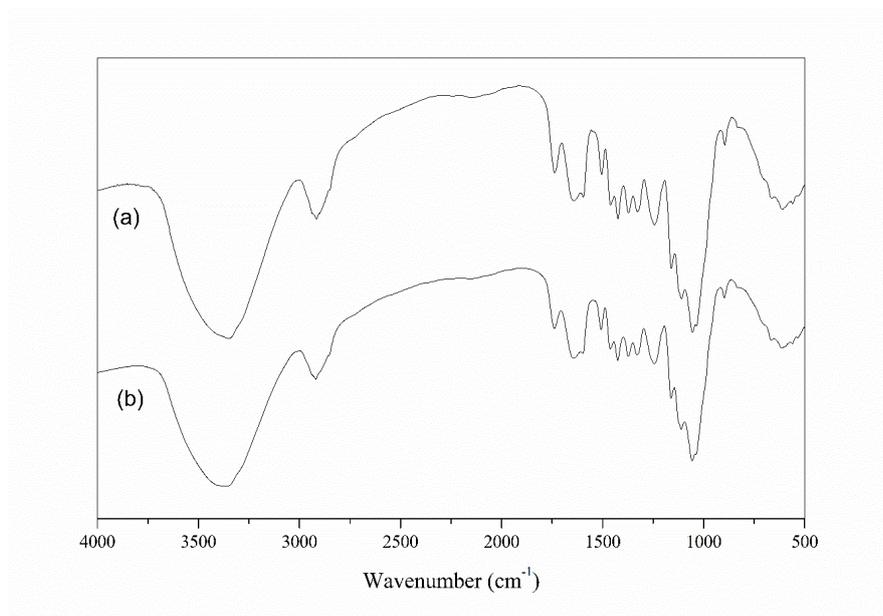
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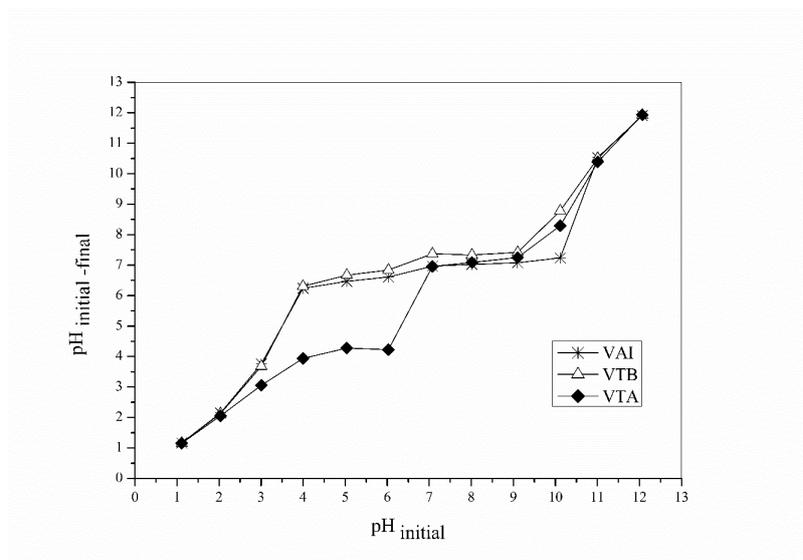
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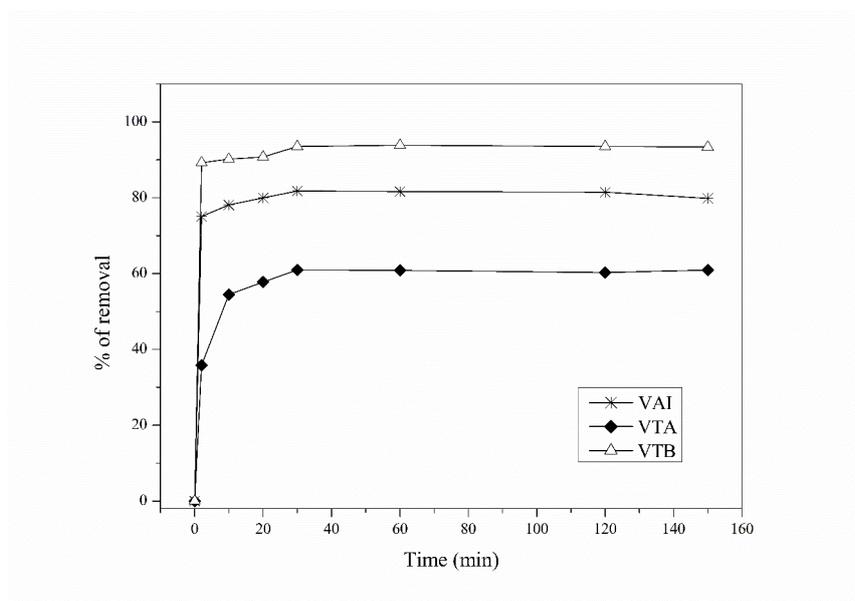
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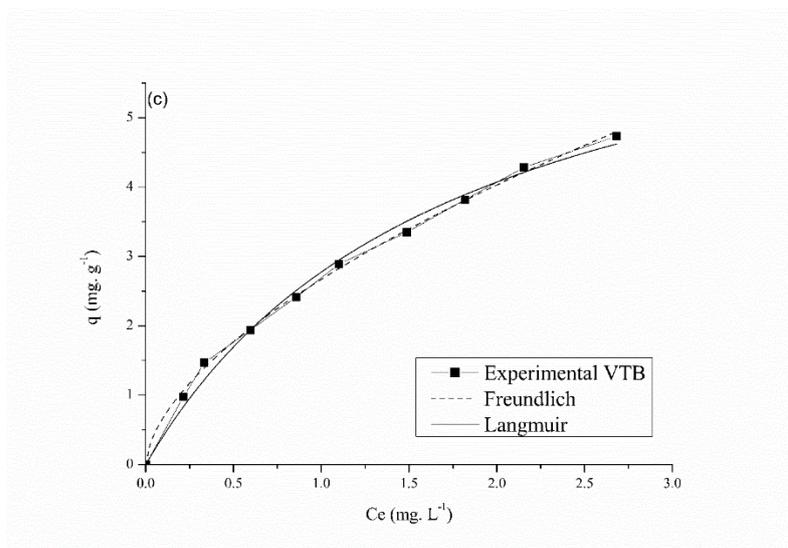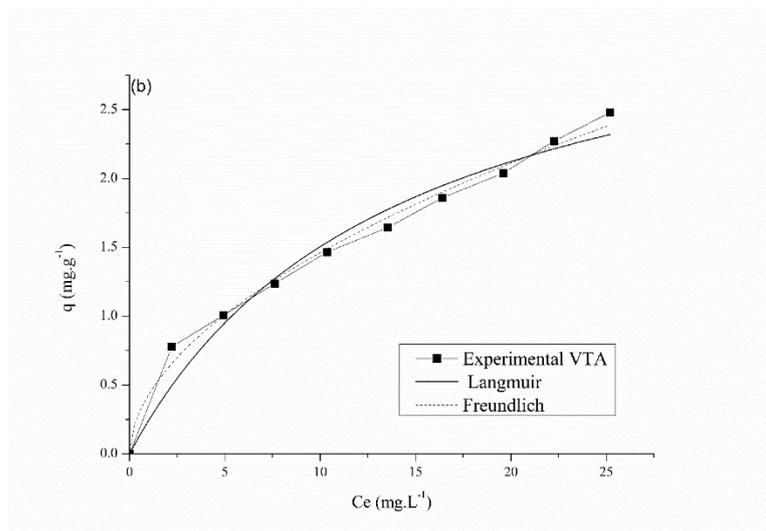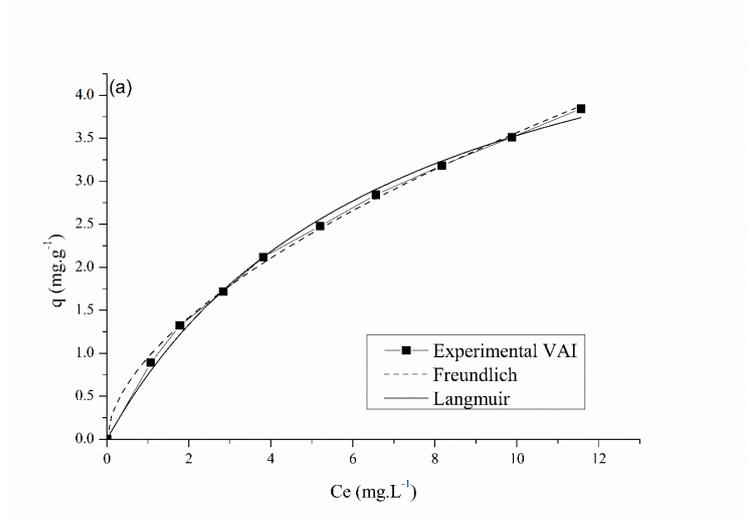
Tables

Table 1. Chemical composition of biosorbents obtained for EDS after adsoption

Biosorbents	Element (%)					
	C	O	Mg	Al	Ca	Mn
VAI	53.79	45.51	0.14	0.11	0.26	0.19
VTA	53.93	45.11	-	0.12	0.29	0.55
VTB	52.00	47.39	0.13	0.12	0.18	0.18

Table 2. Removal capacity of Mn (II) ions by VAT, VTA and VTB by the adsorbents VAI, VTA and VTB varying the pH.

Biosorbent	pH	% of removal					
		1	3	5	6	7	8
VAI		13.90	22.85	76.07	81.87	81.73	80.30
VTA		21.78	28.94	43.78	61.13	61.07	57.44
VTB		22.49	38.33	93.06	94.01	94.11	94.98

Table 3. Kinetic parameters of biosorbents VAI, VTA e VTB onto Mn (II) adsorption process

Biosorbents	Experimental			Pseudo-first order			Pseudo- second order		
	C_o (mg.L^{-1})	T (°C)	Q_{eexp} (mg.g^{-1})	$Q_{t\ cal}$ (mg. g^{-1})	K_1 (min^{-1})	R^2	$Q_{t\ cal}$ (mg. g^{-1})	K_2 (g.mg^{-1}min^{-1})	R^2
VAI	4	25	0.327	0.319±0,0012	1.403±0,0932	0.998	0.323±0,0004	19.561±1,0971	0.999
VTA	4	25	0.243	0.237±0,0048	0.366±0,0422	0.979	0.253±0,0029	2.329±0,1968	0.996
VTB	4	25	0.374	0.371±0,0005	1.753±0,0762	0.999	0.373±0,0001	36.449±1,2500	0.999

Table 4. Isotherm parameters for Mn (II)

Biosorbents	Langmuir			Freundlich		
	q_{max} (mg.g^{-1})	KL (L.mg $^{-1}$)	R^2	Kf (mg.g^{-1})	n(g. L^{-1})	R^2
VAI	6.001±0.248	0.143±0.012	0.996	0.950±0.023	1.741±0.036	0.998
VTA	3.601±0.422	0.071±0.017	0.971	0.429±0.321	1.877±0.941	0.993
VTB	7.644±0.503	0.570±0.071	0.993	1.684±0.035	2.671±0.023	0.998

Table 5. Adsorbents used for the manganese removal

Adsorbents	Mn removal capacity (mg.g^{-1})	References
Moringa pod in natura (VAI)	6.001	This work
Acid treated moringa pod (VTA)	3.601	This work
Basic treated moringa pod (VTB)	7.644	This work
Manganese oxide coated zeolite	1.123	(Taffarel and Rubio, 2010)
Polyvinyl alcohol/chitosan (PVA/CS) binary dry blend	10.51	(Abdeen et al., 2015)
Clinoptolite (natural zeótila)	7.69	(Doula, 2006)
Acid treated corncob	6.54	(Abideen Idowu Adeogun, Andrew E. Ofudje, Mopelola Idowu, 2011)

Table 6. Thermodynamic parameters used in Mn (II) adsorption for the different adsorbents used

Biosorbent	$-\Delta G°$(KJ. mol^{-1})				R^2	$\Delta H°$ (KJ.mol^{-1})	$\Delta S°$ (J. mol^{-1}.K^{-1})
	288K	298K	308K	318K			
VAI	9.34	12.18	14.85	15.71	0.902	11.88	52.10
VTA	1.08	1.18	1.25	1.30	0.907	1.08	7.49
VTB	6.12	6.64	6.95	7.67	0.936	8.937	51.61

Highlights

- The biosorbents were prepared from *Moringa oleifera* pods

- Pretreatments were used to enhance biosorbents

- The biosorbtion process was evaluated

- Application of low-cost biosorbents was evaluated to removel Mn (II).

Acid

Basic

In natura

Moringa oleifera pods

Treatments

Characterization of biosorbents

Batch studies

Biosorption kinetic and isotherm models