Removal of Ni(II) from aqueous solution using *Moringa oleifera* seeds as a bioadsorbent

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ABSTRACT

Metal contaminants are generally removed from effluents by chemical and physical processes which are often associated with disadvantages such as the use of toxic reagents, generation of toxic waste and high costs. Hence, new techniques have been developed, among them the study of natural adsorbents, for instance, the use of *Moringa oleifera* seeds. The potential of *M. oleifera* seeds for nickel removal in aqueous systems was investigated. 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 NaOH. Fourier transform infrared spectroscopy, scanning electron microscopy and thermogravimetric analyses were used for the characterization of the material. Using the optimized methodology (50 mL of 4.0 mg/L Ni(II), pH range of 4.0–6.0, agitation time of 5 min and adsorption mass of 2.0 g) more than 90% of Ni(II) could be removed from water samples. The sorption data were fitted satisfactorily by the Langmuir adsorption model. Evaluation applying the Langmuir equation gave the monolayer sorption capacity as 29.6 mg/g. The results indicate that this material could be employed in the extraction of nickel, considering its ease of use, low cost and environmental viability, which make it highly attractive for application in developing countries.

Key words | adsorption, *Moringa oleifera*, nickel

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INTRODUCTION

In recent years, the contamination of water bodies by toxic heavy metals through the discharge of industrial waste-waters is a world-wide environmental problem. Heavy metals such as lead, cadmium and nickel are among the most common pollutants found in industrial effluents. Even at low concentrations, these metals can be toxic to organisms, including humans.

Nickel has several applications including its use in the metallurgical industry. The extensive use of nickel in several activities means that a considerable amount finds its way into aquatic environments or biological wastewater treat-ment plants (Yang *et al.* 2011). Consequently, there is a need to remove this toxic metal from wastewater effluents. The US EPA has set specific nickel limits for wastewater effluent, which are 2.0 mg/L for short-term effluent reuse and 0.2 mg/L for long-term effluent reuse (US EPA 2004).

Many studies on the removal of heavy metals from water and effluents, including chemical precipitation, solvents

extraction and adsorption, have been reported in the litera-ture (Parab *et al.* 2006; Conrad & Hansen 2007; Sari *et al.* 2007a, b; Uluozlu *et al.* 2008; Vieira *et al.* 2010). Studies have demonstrated that selectivity and efficiency in the removal of pollution agents, such as heavy metals from effluents through an adsorption process, are highly depen-dent on the physical properties and chemical composition of the adsorbent (Vieira *et al.* 2010).

Moringa oleifera seeds can be considered as a natural adsorbent material which presents some important charac-teristics in relation to its application in effluent treatment. The seeds have been used for the treatment of turbid water due to their flocculation properties. A flocculation protein from the seeds of *M. oleifera* Lam. was isolated by Gassenschmidt *et al.* (1995) and its molecular mass found to be around 6.5 kDa and the isoelectric point above 10. However, the mechanism of coagulation by polypeptides is still unknown.

The use of *M. oleifera* seeds as a preconcentrator material in a flow system for Cd(II) determination in alcohol fuel is reported in the literature (Alves *et al.* 2010). Also, our research group has previously performed studies involving the treatment of aqueous solutions containing silver ions and percentage removals of around 98% were achieved (Araújo *et al.* 2010).

In this study, *M. oleifera* seeds were used as a new low-cost adsorbent to remove Ni(II) from aqueous solution. The operating parameters that affect the adsorption process, such as pH, agitation time and adsorbent dosage, were investigated.

EXPERIMENTAL

Instrumentation

A Varian Model SpectrAA-220 (Melbourne, Victoria, Australia) flame atomic absorption spectrometer, with air-acetylene flame, was used for the nickel determination. A hollow cathode lamp was run under the conditions recommended by the manufacturer and conventional values were used for the wavelength, slit width and burner height. A Gehaka Model PG1800 pH meter (São Paulo, SP, Brazil) was used to set the pH of the samples and working solutions. Magnetic stirrers (Tecnal TE141, Piracicaba, SP, Brazil) were used in the batch adsorption experiments.

Reagents and solutions

All working solutions were prepared with ultra-pure water obtained from a Milli-Q (Bedford, MA, USA) water purification system. Reagents 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 were prepared through dilution of a 1,000 mg/L stock solution of nickel (Carlo Erba, Milano, Italy) in deionized water. Solutions (Vetec, São Paulo, SP, Brazil) of 0.1 mol/L HNO_3 and 0.1 mol/L NaOH were used to adjust the pH.

Preparation for bioadsorbent and adsorbent characterization

The *M. oleifera* seeds were obtained from trees cultivated in the city of Uberlândia (Minas Gerais, Brazil). After drying, the unshelled seeds were ground in a commercial blender and then classified through a sieve shaker and separated into two particle sizes (0.5 and 1.0 mm). The seeds were treated with 0.1 mol/L NaOH to remove organic and inorganic matter from the sorbent surface.

The *M. oleifera* seeds were characterized using several techniques. Qualitative analysis of the main functional groups involved in metal adsorption was performed using a Fourier transform infrared spectrometer (Perkin-Elmer FTIR 1605, Rodgau, Germany). The experiment was carried out using KBr discs to prepare the seed samples and the spectral range varied from 4,000 to 500 cm^{-1}. Thermal analysis of the seeds was performed using a thermogravimetric analyzer (TA Instruments TGA 2950, New Castle, PA, USA). Approximately 10 mg of seeds were heated to 950 °C in an oxidizing atmosphere at a rate of 20 °C/min. A JEOL JMT-300 (Tokyo, Japan) scanning electron microscope was used to examine the morphological characteristics of the seeds and to evaluate the profile of the material in terms of retaining metal ions.

Batch adsorption experiments

Removal studies using standard Ni(II) solutions were carried out in triplicate. The seeds were shaken with 50 mL of 4 mg/L Ni(II) for 5 min using a magnetic stirrer and then the suspension was filtered using filter paper (Whatman no. 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 (0.5–2.0 g), extraction time (5–40 min) and pH (2–12).

Metal analysis

Final residual nickel concentration after adsorption was directly measured by flame atomic absorption spectrophotometry (FAAS). To estimate the percentage removal of metal ions from aqueous solution the following equation was used:

$$\% \text{ Adsorption} = \frac{C_o - C_f}{C_o} \times 100 \tag{1}$$

where C_o is the initial metal concentration (mg/L) and C_f is the final residual concentration of metal after the adsorption time.

Adsorption isotherm

The experiments were carried out in the temperature range of 25–28 °C, using 0.5 g seeds (500 μm) and 50 mL of a Ni (II) solution at a concentration of 5–100 mg/L. The pH of the mixture was adjusted to between 4 and 6 using 0.5 mol/L NaOH and the extraction time was 20 min. The mixture was filtrated and the metal ions were quantified using FAAS.

Studies on potentially interfering ions

The removal of Ni(II) in the simultaneous presence of Mn (II), Co(II), Cu(II), Cd(II) and Cr(III) in various proportions, represented by the interfering ions, was evaluated using unshelled seeds treated with NaOH. Ni(II):interfering ions ratios were 1:1, 1:2 and 1:4. The experimental conditions were: particle size of 500 μm, extraction time of 5 min, sorbent mass of 2.0 g and pH between 4 and 6.

Application of the proposed method

The proposed sorbent was applied to samples obtained from aqueous systems. These samples were collected from the following: three different locations along the Pirapitinga creek which runs through an urban zone in the city of Catalão (Goiás, Brazil) and a sample of drinking water treated by a sanitation company and collected from a residential property. In these samples the concentration of Ni(II) was low and therefore, to assess the performance of the adsorbent material in real systems, these samples were spiked with a 4 mg/L Ni(II) solution. Samples were filtered through filter paper and the pH adjusted to within the range of between 4 and 6 using 0.5 mol/L NaOH. 50 mL samples were shaken for 5 min with 2.0 g of unshelled seeds treated with NaOH and nickel ions were quantified using FAAS before and after the removal experiments.

RESULTS AND DISCUSSION

Characterization of the adsorbent material

The FT-IR technique was used to study the main functional groups present in moringa seeds. This technique allows some important functional groups which are capable of adsorbing metal ions to be identified. The spectra obtained for the material *in natura* and treated with NaOH are shown in Figure 1.
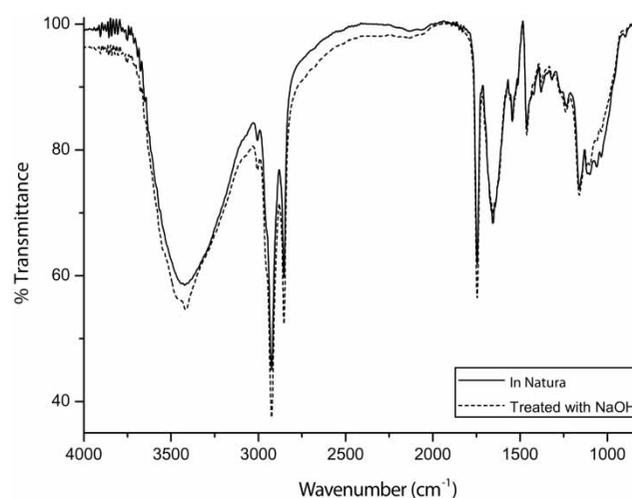

Figure 1 | FT-IR spectrum of *Moringa oleifera* seeds *in natura* and treated with NaOH.

The spectra for the material *in natura* and modified with NaOH present almost the same profile, with peaks characteristic of lignocellulosic materials. The broad band in the region of 3,750–3,000 cm^{-1} is associated with stretching of the O–H and N–H groups present in proteins, fatty acids, carbohydrates (cellulose and hemicellulose) and lignin (Gardea-Hernández *et al.* 2008). Both have intense peaks in the region of 1,745 cm^{-1}, characterized by C=O stretching of the acetyl ester and carbonyl groups of hemicellulose and lignin aldehydes, respectively. The intense broad band present at 1,654 cm^{-1} band is associated with water absorbed in the material. The peaks at 1,099, 1,062 and 1,033 cm^{-1} are due to the C–O stretching, and are characteristic bands of cellulose and hemicellulose from lignocellulosic materials. The main differences between the two spectra are the increase in the bands at around 3,400 and 1,745 cm^{-1} due to an increased amount of hydroxyl groups and lignin content in the material modified with NaOH. The decrease in the peaks at 1,099, 1,062 and 1,033 cm^{-1} is due to hydrolysis of some of the cellulose and hemicellulose present in the material modified with NaOH.

Thermogravimetric analysis was used to characterize the decomposition stages and thermal stability of the material. With respect to the thermogravimetric experiments, the global mass loss of the seeds *in natura* and treated with NaOH, the occurrence of five stages of thermal decomposition were observed for both materials as follows: 30–110 °C, 110–220 °C, 220–420 °C, 420–620 °C and 620–900 °C. For the material *in natura* the mass loss of around 9.2% which occurs at between 30 and 110 °C is associated with the loss of humidity. The second event, observed at between 110 and 220 °C, represents a stationary stage

where there is no decomposition of the material. In the temperature range of 220–420 °C there was a 60.2% loss in the mass of moringa *in natura* due to the decomposition of proteins, hemicellulose, cellulose, fatty acids and lignin, this being the sequence of increasing thermal stability of these constituents. In the temperature range of 420–620 °C a mass loss of 27.6% was observed, corresponding to the combustion of residual lignin, as well as the mineralization of the material. The thermogram obtained for the seeds treated with 0.1 mol/L NaOH showed characteristics similar to those described above, but the loss of humidity at 30–110 °C was only 6.1%. In the third stage the percentage of mass loss was higher (63.3%) and was shifted to higher temperatures. It was also observed that, in the fourth stage, there was a decrease in the percentage of residual lignin to 24.5%. This finding demonstrates that the treatment led to increased thermal stability of the material.

Figure 2 shows the scanning electron micrographs of the seeds. It appears that the treatment with NaOH increased the porosity of the material (Figure 2(b)), making it more exposed to the adsorption of metal species. This change in the morphology of the material also results from the removal of some superficial structural components such as carbohydrates, proteins and lignin.

Determination of optimum parameters and adsorption studies

The influence of the adsorbent dosage on nickel sorption was studied by varying the amount of adsorbent from 0.5 to 2.0 g. The percentage adsorption of nickel increased with an increase in the adsorbent mass for up to 2.0 g. This trend is to be expected because as the adsorbent dose increases the number of adsorbent particles also increases and there is greater availability of sites for adsorption. Thus, the mass of 2.0 g of bioadsorbent was chosen for further studies.

The nickel adsorption after different contact periods was studied keeping all other parameters constant. The amount of nickel ions retained by the adsorbent material increased for up to 20 min and remained constant thereafter. A period of 5 min was chosen due to the good results obtained applying the shortest time studied in the sorption process.

The effect of pH on the Ni(II) adsorption was studied from pH 2.0–12.0. Optimum values of Q_e were obtained at pH > 4.0 and above this pH value the percentage removal remained constant. In adsorption processes the pH is one of the most important parameters to be evaluated and the ionic states of functional groups can be used to explain the pH dependence of biosorption. Low pH conditions allow hydrogen and hydronium ions to compete with metal binding sites on the biomass, causing poor uptake. Biosorbent materials primarily contain weak acidic and basic functional groups. It follows from the theory of acid–base equilibrium that, in the pH range of 2.5–5, the binding of heavy metal cations is determined primarily by the dissociation state of the weak acidic groups. Carboxyl groups (–COOH) are important groups for metal uptake by biological materials. At higher solution pH values precipitation occurs, leading to a reduced sorption capacity. Therefore, the pH range of 4.0–6.0 was chosen for further studies. According to Srivastava *et al*. (2009), in this pH range there is only the form of Ni^{2+}. The pH_{pcz} (pH of point of zero charge) for *M. oleifera* seeds is between 6.0 and 7.0 (Alves *et al*. 2010). According to Abollino *et al*. (2003), the affinity between metal ions depends not only on pH but also on presence of ligands in solution. Thus, in our study, the pH was not buffered in order to reduce interferences in adsorptive process.

Adsorption isotherm

An important physicochemical aspect in terms of the evaluation of sorption process is the sorption equilibrium.
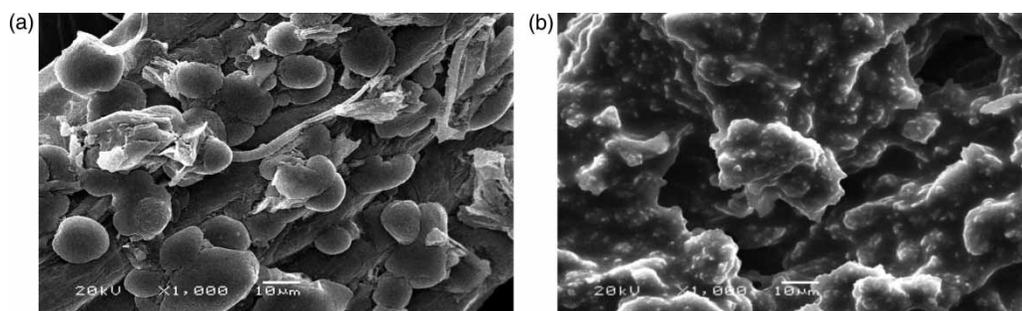

Figure 2 | Scanning electron micrograph of *Moringa oleifera*. *In natura* (a) and treated with NaOH (b).

Figure 3(a) shows the sorption isotherm for Ni(II) adsorption onto unshelled seeds.

The experimental data fitted to Langmuir linear equation expressed as the following equation:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m}$$

where C_e is equilibrium concentration of the metal (mg/L) and Q_e is the amount of the metal adsorbed (mg) per unit of adsorbent (g). Q_m and K_L are Langmuir constants related to adsorption capacity (mg/g) and the energy of adsorption (L/g), respectively.

The isotherm curve obtained indicates favourable adsorption and the formation of a monolayer. Therefore, the extent of sorption was appropriate for the application of the Langmuir model. The Langmuir equation assumes that adsorption is limited to the monolayer and a maximum adsorption indicates saturation of this monolayer. The experimental results obtained were plotted (correlation coefficient 0.99127) using the Langmuir isotherm linear equation from 5 to 100 mg/L for metal ions (Figure 3(b)). The plot of C_e/Q_e versus C_e gives a straight line of slope $1/Q_{max}$ and intercept $1/(b.Q_{max})$. The magnitude of Langmuir Q_{max} showed an adsorption capacity of 29.6 mg of Ni(II) per gram of *M. oleifera* seeds.

Studies on interfering ions in Ni removal

The influence of Mn(II), Co(II), Cu(II), Cd(II) and Cr(III) in various proportions was verified by comparing the percentage removal from a solution containing only Ni(II) and a solution also containing potentially interfering ions. The removal percentage was calculated based on the analytical signals obtained before and after the removal procedure. A species is considered as interferent when the difference between the values is more than 10% (Araújo *et al.* 2010). In the present method, there are interferences of Mn(II), Co(II), Cu(II), Cd(II) and Cr(III) for ratio greater than 1:4. The values obtained verified the excellent potential for the removal of Ni(II) ions using *M. oleifera* seeds. The methodology is simple, low cost and can therefore be used in remediation systems.

Comparison of the material used in the present study with other adsorbents

The results of this study showed that *M. oleifera* seeds demonstrate good removal capacities for Ni(II) (29.6 mg/g) when compared with results reported for other adsorbents (15.95 mg/g for coir pith, 7.9 mg/g for *Cladonia furcata* and 1.12 mg/g for bagasse fly ash). A low cost, easy purchase and the satisfactory experimental results indicated that seed is an effective adsorbent for Ni(II) removal from aqueous solution and has the advantage of the fact that it does not need to be previously subjected to chemical or thermal treatment.

Application

The proposed method was applied in the treatment of water samples. In these samples the concentration of the Ni(II) ions was low and thus they were spiked with Ni(II) at a concentration of 4.0 mg/L. The pH of samples was
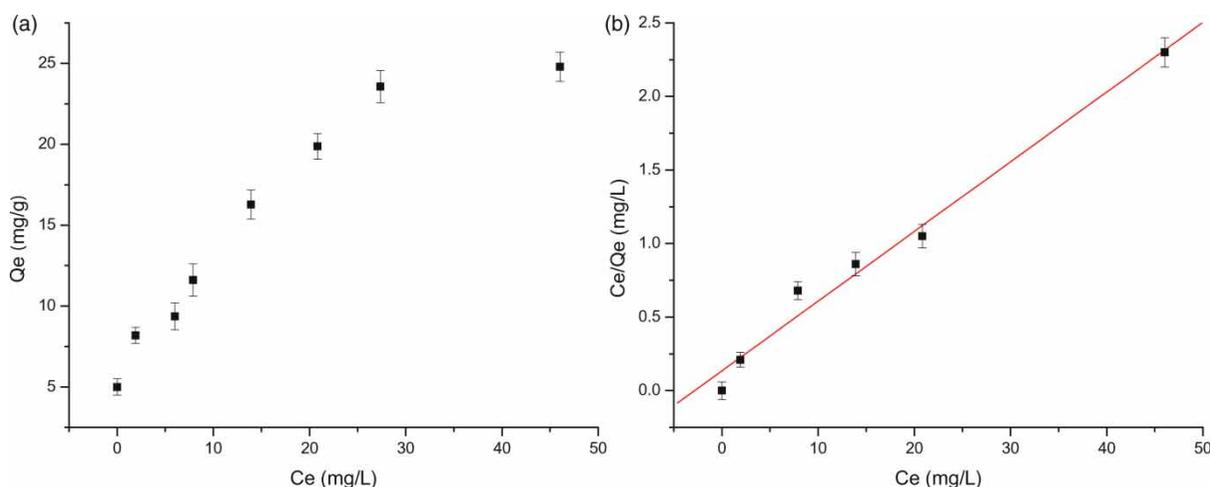

Figure 3 │ Adsorption isotherm for Ni(II) by *Moringa oleifera* seeds (a) and Langmuir linearized isotherm (b).

Table 1 | Use of *Moringa oleifera* seeds treated with NaOH in Ni(II) removal in aqueous samples

Sample	Ni(II) added (mg/L)	Ni(II) found (mg/L)	Removal (%)
A	0	0.36	108 ($\pm$10)
	4.0	4.36	
B	0	0.31	106 ($\pm$4)
	4.0	4.31	
C	0	0.33	109 ($\pm$9)
	4.0	4.33	
D	0	0.35	105 ($\pm$4)
	4.0	4.35	

A, B and C: samples of three different locations along the Pirapitinga creek which runs through an urban zone in the city of Catalão (Goiás, Brazil). D: sample of drinking water treated by a sanitation company.

within the range studied (pH 4 to 6). According to literature (US EPA 2004), the typical pH of waste treatment waters is 6, so the proposed method is as expected. 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 1.

CONCLUSIONS

According to the results obtained in this study, it is evident that moringa seeds are very efficient in the removal of nickel, even from real samples. The metal removal efficiencies were greater than 90% under the experimental conditions used, that are, 50.0 mL of 4.0 mg/L Ni(II), pH range 4–6, shaking time 5 min and 2.0 g seeds treated with 0.1 mol/L NaOH. The results obtained show that moringa seeds can be used for Ni(II) removal from public water supplies that have levels of this metal above the legal limits.

ACKNOWLEDGEMENTS

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