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Article

Moringa oleifera Lam. Seeds as a Natural Solid Adsorbent for Removal of Ag^I in Aqueous Solutions

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Este trabalho descreve o potencial de sorção das sementes de *Moringa oleifera* para descontaminação de Ag^I em soluções aquosas. Espectroscopia de infravermelho foi usada para elucidação de possíveis grupos funcionais responsáveis pela adsorção de Ag^I. Estudos de adsorção foram feitos em batelada usando soluções padrão de Ag^I como função da massa do adsorvente, tempo de extração, tamanho da partícula e pH. A Ag^I foi quantificada antes e após os experimentos de remoção usando espectrometria de absorção atômica por chama. Adicionalmente, considerando-se os estudos de adsorção e isotermas de adsorção aplicadas ao modelo de Langmuir foi possível verificar que as sementes de *M. oleifera* apresentam alta capacidade de adsorção. As condições ótimas foram: 2,0g de adsorvente com tamanhos de partícula de 75-500 µm, 100 mL de solução 25,0 mg L^{-1} Ag^I, tempo de extração de 20 min e pH 6,5. Os resultados mostram que as sementes de *Moringa oleifera* podem ser usadas para remoção de Ag^I em soluções aquosas.

This work describes the sorption potential of *Moringa oleifera* seeds for the decontamination of Ag^I in aqueous solutions. Infrared spectroscopy was used for elucidating possible functional groups responsible for uptaking Ag^I. Sorption studies using Ag^I standard solutions were carried out in batch experiments as functions of adsorbent mass, extraction time, particle size and pH. The Ag^I was quantified before and after the removal experiments using flame atomic absorption spectrometry. Furthermore, based on adsorption studies and adsorption isotherms applied to the Langmuir model, it was possible to verify that *M. oleifera* seeds present a high adsorption capacity. The optimum conditions were: 2.0 g of adsorbent with particle size of 75-500 µm, 100 mL of 25.0 mg L^{-1} Ag^I, extraction time of 20 min and pH at 6.5. The results show that *Moringa oleifera* seeds can be used for removing Ag^I in aqueous solutions.

Keywords: removal, characterization, sorption, *Moringa oleifera*, silver

Introduction

Industrial processes have historically been an important factor of environmental degradation. The disposal of industrial wastes, mainly containing metal ions in water sources represents a problem of great concern not only in relation to biota in the receiving environment, but also to humans. Silver is included among the main pollutants because of its high toxicity.[1,2] Therefore methods to minimize pollution caused by this metal are attractive.

Conventional techniques used for removing metal ions include filtration, precipitation, flocculation, ion exchange resins and reverse osmosis.[3] However, these technologies have limitations such as high operating cost, incomplete removal of metal ions and generation of toxic sludge.[4-6] On the other hand, the biosorption process offers several advantages such as low cost of the biosorbent, high efficiency, minimization of chemical and/or biological sludge and regeneration of biosorbent.[7]

In this way, natural adsorbents constitute an excellent alternative for chemical remediation of heavy metals from aqueous solutions.[8-10]

Microorganisms such as algae, yeast, bacteria and fungi have been widely evaluated as biosorbents for removing metal ions from an aqueous solution.[11-13] However, biosorption of metal ions onto microorganisms is affected by several factors such as pH, metal concentration, biomass loading, temperature and other parameters.

Lignocellulosic materials such as cane bagasse, onion skins, peanut skins, rice husks, and so on, have been used

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for metal ions adsorption due to the characteristics of the functional groups present in these materials.[14]

Recently, natural adsorbents have been proposed for removing metal ions due to their good adsorption capacity.[1] In this context, the *Moringa oleifera* seeds present themselves as an alternative material for this propose.[15,16]

M. oleifera seeds have been used for treating turbid water due to their flocculating properties. A flocculating protein from *M. oleifera* Lam. seeds was isolated by Gassenschmidt *et al*. (1995).[17] The molecular protein mass was determined at about 6.5 kDa, the isoelectric point was above pH 10. Flocculation activity could be explained by the patch charge mechanism due to low molecular weight and high charge density.

The present work describes the sorption potential of *M. oleifera* seeds for decontamination of Ag^I in aqueous solutions. Variables such as particle size, pH, extraction time and sorbent mass were evaluated. The proposed adsorbent was applied to effluent samples.

Experimental

Sorbent preparation

The *M. oleifera* seeds were obtained from trees which were cultivated in the city of Uberlandia (Minas Gerais, Brazil) and collected from September-November 2007. The seeds were separated from the pods, crushed in a household blender (Black & Decker, São Paulo, Brazil) and strained through 500, 180 and 75 µm sieves.

The functional groups present in *M. oleifera* were characterized by Fourier transform infrared (FT-IR) spectrometer (Shimadzu, IRPrestige-21, Tokyo, Japan). The spectral range varied between 4000 to 500 cm^{-1}, with twenty eight scans in a resolution of 4 cm^{-1}.

Sorption studies

Removal studies using standard Ag^I solutions were carried out in triplicate. The seeds were shaken with 50 of 25 mg L^{-1} Ag^I for 20 min using a magnetic agitator and then the suspension was filtered using filter paper (Whatman 42,28 µm). Ag^I was quantified before and after the removal experiments.

In order to obtain the optimum condition for the percentage of Ag^I removal, the following variables were studied: particle size of the sorbent (500, 180 and 75 µm), pH (2.0, 4.0, 6.0 and 8.0), extraction time (5, 20, 35 and 50 min) and sorbent mass (0.1, 0.2, 0.3, 0.4, 1.0, 2.0, 3.0 and 4.0 g). The efficiency of the removal was evaluated from the Qe (uptake of metal per unit weight of sorbent) obtained by the equation 1:[16]

$$Qe = \frac{(Ci - Cf) \times V}{m} \qquad (1)$$

where Ci (mg L^{-1}) is the Ag^I initial concentration, Cf (mg L^{-1}) is the Ag^I final or equilibrium concentration, V (L) is the volume of the test solution and m (g) is the sorbent mass.

Isotherm adsorption

The experiments were carried out at a temperature range of between 25 and 28 °C, using 50.0 mg of non-shelled *M. oleifera* seeds (500 µm) and 50 mL of Ag^I solution in a concentration of 5 to 100 mg L^{-1}. The pH of the mixture was adjusted at 6.5 using 0.5 mol L^{-1} NaOH and extraction time was 20 min. The mixture was filtrated and the Ag^I was quantified using flame atomic absorption spectrometry.

Ag^I determination

Standard solutions of Ag^I were prepared from 1000 mg L^{-1} Ag^I (Carlo Erba, Val de Reuil, France). The Ag^I was quantified using an atomic absorption spectrometer (SpectrAA-220 Varian, Victoria, Australia). Instrumental conditions such as wavelength of 328.3 nm, slit of 0.1 nm, current lamp of 4.0 mA, air flow rate of 13.5 L min^{-1} and acetylene flow rate of 2.0 L min^{-1} were used.

Studies of interferent ions on the removal of Ag^I

The removal of Ag^I in the presence of Pb^{II}, Cu^{II}, Cd^{II} and Co^{II}, in various proportions, denominated by concomitant ions, was evaluated using non-shelled *M. oleifera* seeds. The experimental conditions were: particle size of 500 µm, extraction time of 20 min, sorbent mass of 2.0 g and pH of 6.5.

Application of the proposed method

The proposed sorbent was applied to residue obtained from chemistry classes, residue tested for chemical oxygen demand in this institution; film developing solution and residue from graphic material, obtained from local businesses. These effluents contained Ag^I, Pb^{II}, Cu^{II}, Cd^{II} and Co^{II} ions. Samples were filtered through filter paper and the pH adjusted at 6.5, using 0.5 mol L^{-1} NaOH. One hundred milliliters samples were shaken with 2.0 g of non-shelled

M. oleifera seeds for 20 min Ag^I was quantified using FAAS before and after removal experiments.

Results and Discussion

Biosorbent characterization

The main functional groups present in the *M. oleifera* seeds were characterized by infrared material analysis. The broadband centered at 3420 cm^{-1} can be attributed to O–H stretching of the connection in this protein, fatty acids, carbohydrates and the lignin units. Due to the seed high protein content there is also a relevant contribution to this region because of N–H stretching in the bondage of amides.[18] The peaks that appear in 2923 and 2852 cm^{-1} correspond respectively to the asymmetric and symmetric stretching of the connection of the C–H in CH_2 group. Due to the high intensity of these bands it is possible to assign them to the predominantly lipid component of the seed that is present in high proportion similar to the proportion of the protein.[19] In the 1800 to 1500 cm^{-1} region there are a number of overlapping bands between 1750 and 1630 cm^{-1}. This set can be attributed to the C=O connection stretching. Owing to the heterogeneous type of seed, the carbonyl group may be linked to different neighborhoods as part of the fatty acid portion of lipid and protein portion of the amides. The carbonyl that appears due to the lipid component in 1740 and 1715 cm^{-1}, which can be observed in the spectrum as a small peak or shoulder part of the main band at 1658 cm^{-1}, was assigned to the carbonyl amides in the protein portion. The peak at 1587 cm^{-1} can be attributed to the stretching of the C–N linkage and the deformation of the N–H linking proteins present in the seed jug. Literature reports that *M. oleifera* Lam. seeds present a protein mass composition of 29.36%. [20] Figure 1 presents the seeds infrared spectrum.

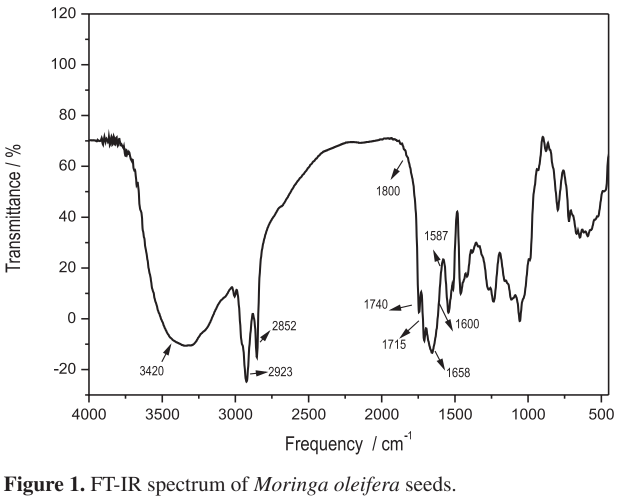

Figure 1. FT-IR spectrum of *Moringa oleifera* seeds.

Studies of sorption variables

Figure 2 shows Qe values in the function of sorbent mass for non-shelled and shelled seeds and husk using 5.0 mg L^{-1} Ag^I. It was observed that husks showed more efficiency for Ag^I removal than non-shelled and shelled seeds for quantities of 50 mg of sorbent or less. However, in quantities of sorbent above 50 mg, differences were not observed between non-shelled and shelled seeds and husk. Significant differences were not observed for the test-F with a 95% assurance. Therefore, non-shelled seeds were used for further studies.

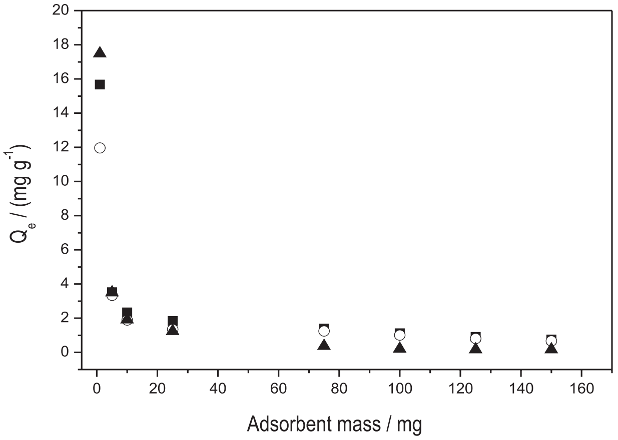

Figure 2. Capacity of sorption of the *Moringa oleifera* seeds in the Ag^I removal. Experimental conditions: Extraction time = 5 min; pH = 6.5; Volume of Ag^I = 25.0 mL; Concentration of Ag^I = 5.0 mg L^{-1}. ■ non-shelled seeds, ▲ husk, ○ shelled seeds.

The following variables were studied: particle size of sorbent, pH, time of extraction, sorbent mass, metal concentration and volume of Ag^I solution.

Qe values in function of the adsorbent particle size (500, 180 and 75 μm) were obtained (Figure 3). A decrease in particle size showed a favorable effect on metal sorption justified by an increase in the adsorbent surface area. However, particle sizes of 180 and 75 μm were not used because the filtration step was very slow. Moreover, Qe values were similar, *i.e.*, 0.289 and 0.301 mg g^{-1} for ≤ 500 μm and ≤ 75 μm, respectively.

The effect of pH range on Ag^I adsorption was studied from 2.0 to 8.0 (Figure 4). The conditions were: 500 μm particle size, 20 min extraction time, 4.0 g adsorbent mass and 50 mL of 25.0 mg L^{-1} Ag^I. Optimum values of Qe were obtained in pH > 4.0; above this Qe values were found constant.

Biosorbent materials primarily contain weak acidic and basic functional groups. This is in accordance to the acid-base equilibria theory, in the 2.5-5 pH range, the binding of heavy metal cations is primarily determined by the

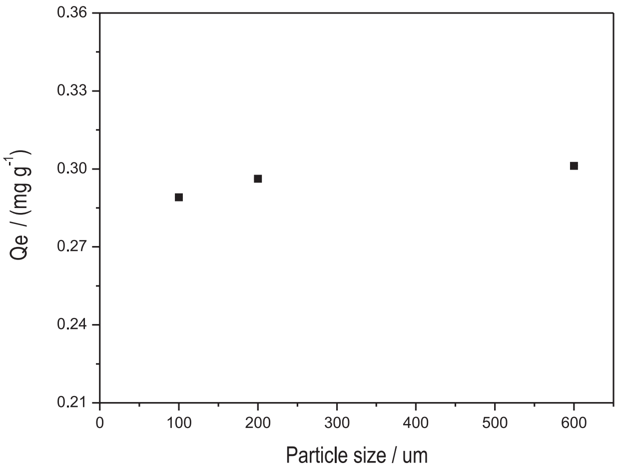

Figure 3. Ag^I removal in the function of the particle size. Experimental conditions: Extraction time = 20 min; *Moringa oleifera* mass = 4.0 g.; Volume of Ag^I = 50.0 mL; pH = 6.5; Concentration of Ag^I = 25.0 mgL^{-1}.

state of dissociation of the weak acidic groups. Carboxyl groups (–COOH) are the important groups for metal uptake by biological materials.[16] The ionic states of cell wall 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 a poor uptake. At higher pH values, 5-7, there is a lower number of competing hydrogen ions and more ligands are exposed with negative charges, resulting in greater sorption. Whereas at a pH > 7, it occurs the solution precipitation, leading to a reduction sorption capacity.[16] These results are in accordance with literature. Therefore, the 6.5 pH value was then chosen for further studies.

The effect of extraction time on Ag^I sorption was studied in the 5 to 50 min range. Figure 5 shows that the amount of silver ions retained by the adsorbent material increased considerably for up to 20 min and was constant after that. The time of 20 min was chosen due to the good results presented in the removal (Qe = 0.302 mg g^{-1}) and the shortest time for sorption process.

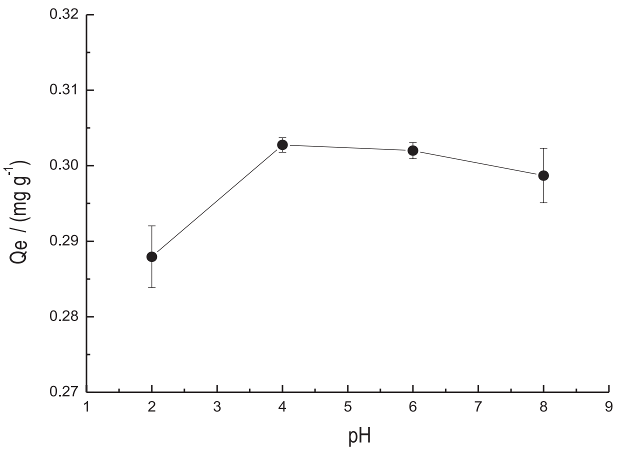

Figure 4. Ag^I removal in the function of the pH. Experimental conditions: particle size = 500 µm; Extraction time = 20 min; *Moringa oleifera* mass = 4.0 g.; Volume of Ag^I = 50.0 mL; Concentration of Ag^I = 25.0 mg L^{-1}.

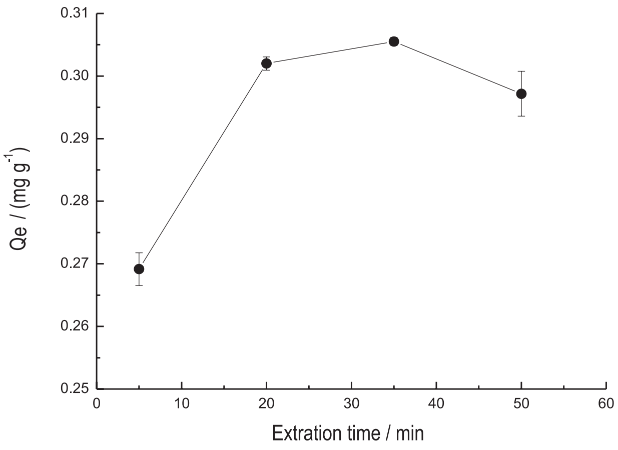

Figure 5. Capacity of sorption of the *Moringa oleifera* in the function of extraction time. Experimental conditions: particle size = 500 µm; *Moringa oleifera* mass = 4.0 g.; Volume of Ag^I = 50.0 mL; pH = 6.5; Concentration of Ag^I = 25.0 mg L^{-1}.

Figure 6 shows the removal studies made using 25 mg L^{-1} Ag^I and non-shelled *M. oleifera* seeds from 0.1 to 4.0 g. The results show that the uptake of quantity of adsorbed metal *per* unit weight of sorbent decreases suddenly until 1.0 g of *M. oleifera*, indicating an increase in the Ag^I removal. In the 1.0 to 4.0 g interval, the Qe values remained constant probably due to the equilibrium reached.

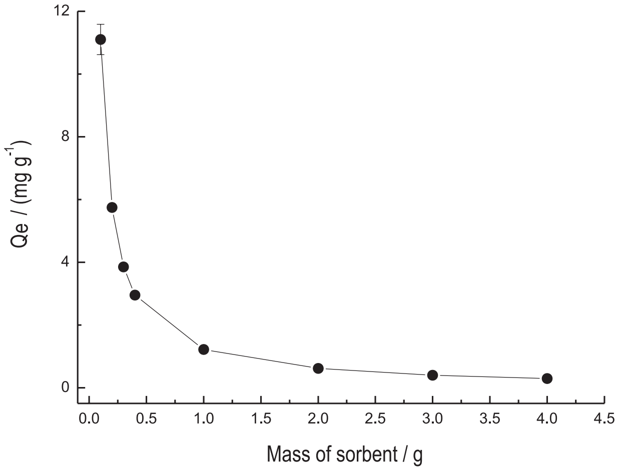

Figure 6. Effect of *Moringa oleifera* mass on sorption of Ag^I. Experimental conditions: particle size = 500 µm; pH = 6.5; Extraction time = 20 min; Concentration of Ag^I = 25.0 mg L^{-1}; Volume of Ag^I = 50.0 mL.

Isotherm adsorption

One of the important physicochemical aspects for the sorption process evaluation is the equilibrium of sorption.

Figure 7 shows the isotherm sorption of Ag^I on non-shelled *M. oleifera* seeds.

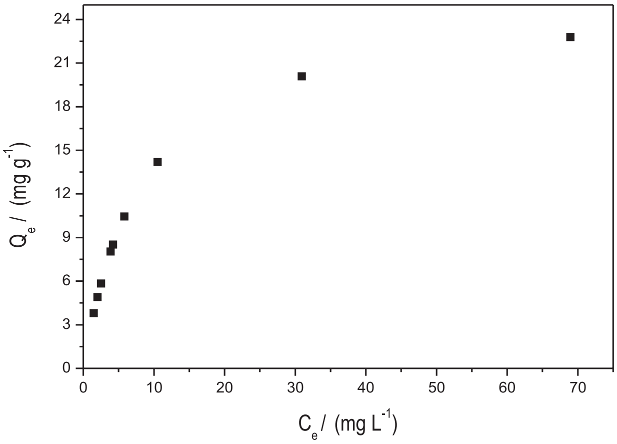

Figure 7. Adsorption isotherm for Ag^I by *Moringa oleifera* seeds. Experimental conditions: size of particle = 500 µm; pH = 6.5; Concentration of Ag^I = 5.0 at 100 mg L^{-1}; Extraction time = 20 min; *Moringa oleifera* mass = 50 mg. (A).

The isotherm curve obtained indicates favorable adsorption process and highlights the strong tendency of the process for monolayer formation. Therefore, the extent of sorption was adequate to 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 of 0.99352) in Langmuir isotherm linear equation from 5 to 100 mg L^{-1} Ag^I (Figure 7). The plot of Ce/Qe *versus* Ce gives a straight line of slope 1/Qmax and intercept 1/Qmaxb. The magnitude with Langmuir Qmax and b constants show adsorption capacity of 23.13 mg of Ag^I *per* gram of non- shelled *M. oleifera* seeds and adsorption energy of 0.1586 L mg^{-1}, respectively.

Comparison of the present study with other adsorbents

The present study showed that *Moringa oleifera* seeds demonstrated good removal capacities for Ag^I (23.13 mg g^{-1}) as compared to the reports with other adsorbents (Table 1).

Studies of interferent ions in the removing of Ag^I

Removing of Ag^I in the presence of Pb^{II}, Cu^{II}, Cd^{II} and Co^{II} ions was studied in the following conditions: 500 µm particle size, 20 min extraction time, 2.0 g adsorbent mass, 6.5 pH and 100 mL Ag^I volume. The results are shown in Table 2. The influence of interferents was verified by comparing the percentages of removal of a solution containing only Ag^I and a solution containing Ag^I ions and interferent ion. Removal percentage was calculated based on analytical signals obtained before and after the removal procedure and the tests performed in triplicate.

In this study, a specie is considered as interferent for the removal of Ag^I in the proposed procedure, when the difference between the values of removal of the solution containing only ions Ag^I and those containing the possible interfering ions is more than 10%.[25]

Thus, the interference factor, IF, is defined by equation 2:

$$IF = A'/ A \qquad (2)$$

where A′ is the value of the percentage of removal on the solution of Ag^I in the presence of possible interference, and A is the percentage of removal on the solution of Ag^I in the absence of possible interference.

In this case, IF = 1.00 means that there is no interference, while factors greater than 1.10 or smaller than 0.90 indicate an increase or a decrease of analytical signal due to interference.

Table 3 shows the results of removal of Ag^I in real samples. The values obtained satisfactory confirm the excellent potential for removal of ions Ag^I using *M. oleifera* Lam seeds. The methodology is simple, low cost and can therefore be used in remediation techniques.

Table 1. Comparison with other adsorbents

Absorbent	Maximum adsorption capacity (mg g^{-1})	Reference
Resin Amberlite XAD-16	4.66	21
Modified silica gel using 2,4,6-trimorpholino-1,3,5-triazin	0.384	22
Naphitalene modified with dithizone	0.029	23
Octadecil silica membrane disks modified by (CBT)	0.214	24
M. oleifera seeds	23.13	This work

CBT-1,3-bis (2- cyanobenzene) triazine.

Table 2. Effect of interferent ions on the removal of Ag^I. Experimental conditions: Particle size = 500 µm, extraction time = 20 min, mass of adsorbent = 2.0 g, pH 6.5

Proportion analyte: interferent	Removal % of Ag^I	Interference Factor (IF)
1 : 0	99.32	1.00
1 : 0.2	99.65	1.00
1 : 0.1	98.61	0.99
1 : 1	99.96	1.01
1 : 5	99.97	1.01
1 : 10	99.98	1.01

Table 3. Results of the removal of Ag^I ions in the samples

Samples	Initial conc. (mg L^{-1})	Final conc. (mg L^{-1})	Removal %
Residue of chemistry classes	339.0	27.1	92
Residue of chemical oxygen demand testing	4267.0	768.1	82
Solution of photographic film	5284.5	475.6	91
Residue of graphic material	ND*	-	-

* ND = no detected.

Conclusions

In this work non-shelled *M. oleifera* seeds were used as sorbent for removing Ag^I in aqueous solutions. The optimum conditions for removing Ag^I were: 2.0 g of adsorbent with 75-500 µm particle size, 20 min extraction time and 6.5 pH. The adsorption capacity was 23.13 mg of Ag^I *per* gram of *M. oleifera* seeds. The proposed method has advantages, such as, the low cost of sorbent, high efficiency and the minimization of chemical sludge. The sorbent is an alternative material for chemical remediation and is economical and environmental friendly.

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