Identification of Efficiency of Argan Shell Sawdust in the Adsorption of Thorium Solution

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Abstract

One of the most important problems currently is water pollution due to contamination by heavy metal wastes from industrial effluents. Traditionally, a lot of different methods have been used to address this problem and most recently, the sawdust of several trees have been used for adsorption of hevay metal ions from contaminated water samples. However, no studies have been reported testing the efficiency of Argan shell sawdust in adsorption of heavy metal ions.

As Argan shells are readily available in the southwestern region of Morocco, the efficiency of adsorption of Argan shell powder using standard thorium solution was tested. It was found that the adsorption efficiency was 98.07%, which is comparable to results obtained in other studies using sawdust of other trees. The initial results were found to be promising, but they need to be further characterized to identify optimum conditions of adsorption.

1. Introduction

The most important source of water pollution currently is the discharge of heavy metal wastes such as uranium and cadmium. This is mainly due to the rapid improvement in industrial development leading to widespread heavy metal pollution of air and water (Al-Masri *et al*., 2009). Traditionally, this major environmental problem and health hazard has been addressed through chemical treatment methods such as precipitation, filtration, membrane separation, ion exchange, and oxidation-reduction. However, when heavy metal wastes are present in tremendous quantities in water, these conventional methods become ineffective and expensive. Hence, there is a constant need to look for more effective ways to address this environmental problem (Kim *et al*., 2005).

In recent times, people have tried to move away from chemical methods and have explored biological methods to absorb heavy metal wastes from water. One of the approaches is biosorption, where microorganisms such as bacteria, fungi, and algae are used to absorb specific metals through biological interactions (Abd El Hameed *et al*., 2015). Although microbes have a very high adsorption capacity, they lack mechanical resistance and stability, and some strains are difficult to grow and maintain in the laboratory (Michalak *et al*., 2013). Natural materials such as poplar leaves and branches (Al-Masri *et al*., 2009), and brewery biomass (Kim *et al*., 2005) have also been used for the adsorption of heavy metals. Most recently, nanomaterials have also been used for removal of heavy metal wastes from water bodies due to their tremendous adsoprtion capacity (Yang *et al*., 2019). All these approaches have failed to reach large scale adoption for addressing the problem of heavy metal contamination either due to cost or impracticality in execution. Hence, there is still an important need for exploring better approaches for adsorption of heavy metals from the environment.

Another biosorbent material that has been extensively tested in various studies is the sawdust of different trees. Studies carried out for testing the feasibility of using sawdust for adsorption of specific metal ions have proven extremely promising. It has the added advantage of dealing with solid waste thereby bypassing the task of appropriate dissemination of the same (Lim *et al*., 2008). The sawdust of various species of trees has been tested for the adsorption of heavy metal ions. Demcak *et al* (2017) have proved the benefits of using poplar sawdust for removing copper, zinc, and ferrous ions from different samples and Cook (2017) has demonstrated column adsorption of copper ions using peanut hulls. However, no studies have been undertaken to demonstrate the usefulness of the sawdust of Argan tree as a biosorbent.

The Argan tree belongs to the Sapotaceae family and it is a tropical plant. Traditionally, the fruits of this tree have been used to prepare edible oils. Apart from that, it is also used for heating purposes, and for the preparation of moisturizing oils (Essabir *et al*., 2015). The Argan fruit that is used for oil production has a small fleshy pulp surrounded by a hard nut-like covering. This covering contributes to 25% of the weight of the fruit and is discarded during the oil production process. In regions where the Argan tree is grown and used for oil production locally, a considerable amount of fruit shells are generated as byproducts of the production process (Bouqbis *et al*., 2016). Hence, in this study we have attempted to analyze the feasibility of recycling these Argan fruit shells for the purpose of adsorbing heavy metal wastes from different samples.

Here, we have used Argan hull sawdust for adsorbing thorium from different dilutions of nitric acid. This was followed by an infrared analysis of thorium adsorption by Argan shell powder.

2. Materials and Methods

Sample preparation: Argan shells that were required for this experiment were obtained from southwestern Morocco, available as a byproduct of the Argan oil extraction process. These shells were finely ground in the mortar grinder, Retsch RM 200, and were seived to obtain two different particle sizes, 125 µm and 350 µm, to obtain homogeneity in the sample. These particles were not subjected to any further washing or drying process, but were used directly in their raw form. A small amount of unused sample was saved as control for infrared analysis.

Column preparation: The chromatography columns were prepared by passing 1g of Argan shell powder through a column of diameter 10 mm and length 250 mm. This was washed several times with pure water to ensure efficient and uniform packing.

Preparation of Thorium solution: The thorium solution was prepared as a standard concentrate of 10 ppm in a 10 ml solution of nitric acid. Further dilutions were prepared by diluting the stock solution in nitric acid.

Column chromatography: Once the column packed with Argan shell powder was ready, the thorium solution was passed through the column at a volume flow rate of 5 drops/s. The eluent used to move the thorium solution through the column was 10 ml of citric acid. The entire elution process was repeated five times, each time with 10 ml of citric acid. The isolate from the column was collected in batches of 10 ml each.

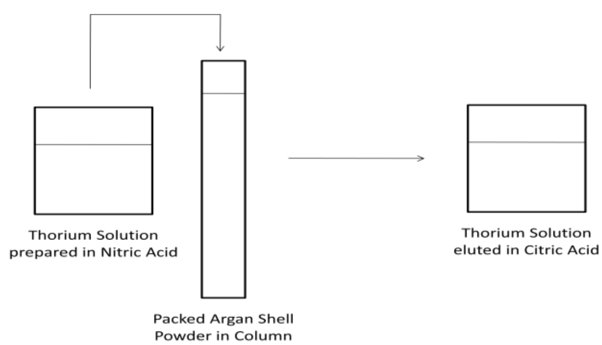


Fig: Graphic describing the passage and elution of thorium solution through a column packed with Argan shell powder.

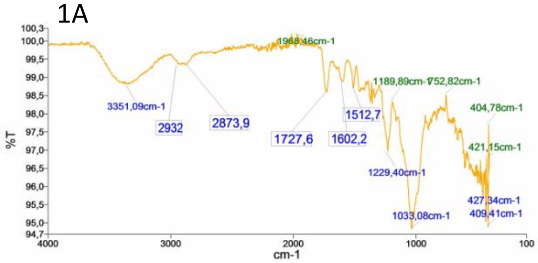
FTIR analysis of Argan shell samples: The Argan shell samples were subjected to FTIR analysis to detect the concentration of thorium in the samples. A sample of raw Argan shell powder that was not subjected to chromatography was used as control. The concentration of thorium was detected in three consecutive batches of elutions following the chromatographic process. The FTIR procedure was carried out using the instrument Spectrum Two NIOS2 Main 00.02.0064. The sample used for the analysis was prepared by mixing 1 mg of the sample with 99 mg of potassium bromide. The obtained infrared spectra were analyzed to identify the efficiency of adsorption of thorium by Argan shell powder.

3. Results

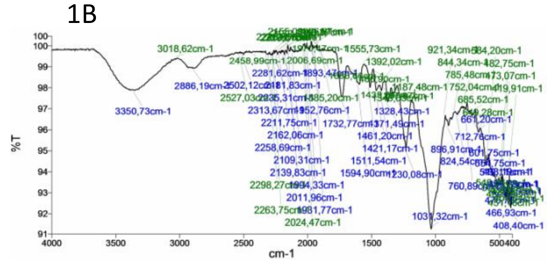
FTIR analysis of Argan shell samples was performed to detect the presence of functional groups corresponding to the adsorption of thorium in the sample. In order to perform a comparative study, infrared spectra of untreated and treated Argan shell powder samples were examined. A single spectrum of untreated sample and three spectra of samples following consecutive batches of elution are shown in Figure 1. Based on the differences between the infrared spectra of samples before and after elution, characteristic vibration bands were assigned to the peaks.

An analysis of the infrared spectra of Argan shell sawdust before and after chromatography reveals several differentiating features. There is a definite decrease in the intensity of absorption in all the spectra. This may be due to the formation of electrostatic bonds between the functional groups of Argan shell sawdust and thorium. There is a characteristic broad band around 3349 cm^{-1} which corresponds to the elongation vibrations of the O-H linkage, lignin group, and cellulose in the Argan shell sawdust. Another band appears between 2924 and 2852 cm^{-1} corresponding to the asymmetric elongation vibration of the C-H bond of cellulose.

1A



1B



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1D

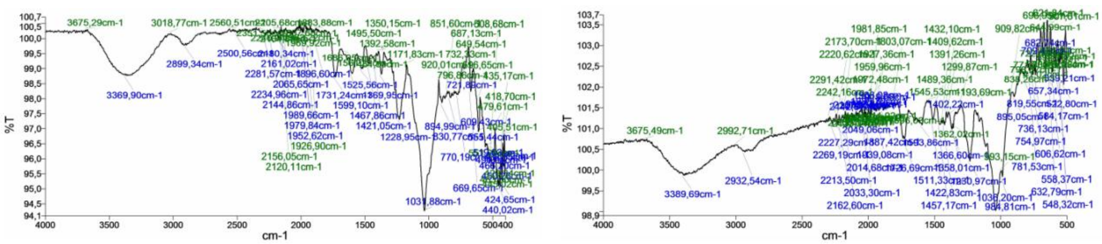

Fig 1: FTIR spectra of thorium concentrations before and after passing the concentrate through the column. 1A denotes the concentration of thorium in the eluent before passing the solution through the column. 1B, 1C, and 1D denote concentrations of thorium after first, second, and third elutions respectively.

The peak that appears around 1731 cm^{-1} corresponds to the valence vibration of the carbonyl group of carboxylic acids or esters present in lignins and hemicelluloses. This peak shows a change between the spectra of before and after chromatography, which is due to suppression of most of the hemicelluloses due to thorium adsorption. However, the bands observed at 1372 cm^{-1} and 1233 cm^{-1} due to the vibration of lignin methoxy groups do not show any difference between the two spectra. This could be due to the absence of lignin degradation indicating that the reduction of the carbonyl compounds is due to the partial elimination of hemicelluloses in Argan shell powder.

Hemicellulose is a heteropolymer that is present along with cellulose in plant cell walls. In contrast to cellulose, hemicelluloses have a random irregular structure with very little strength. Hence, it can easily be hydrolyzed by acids, bases, and enzymes. It is made up of different sugar monomers such as xylose, arabinose, mannose, and galactose in contrast to cellulose which is only made of glucose. Also, the sugar chains are shorter comprising of 500 to 3,000 sugar units whereas cellulose has larger sugar chains made of 7,000 to 15,000 sugar molecules.

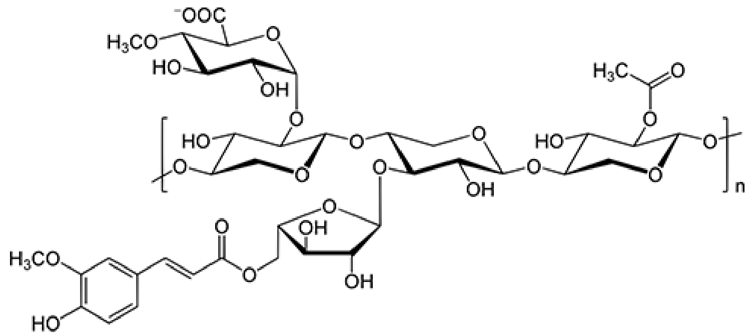

Fig: Chemical Structure of Hemicellulose

Another peak that is observed at 1032 cm^{-1} corresponds to the valence vibrations of the C-O and C-O-C bonds of cellulose. The peak observed at 849 cm^{-1} and bands appearing at frequency 720 to 400 cm^{-1} correspond to the C-H group of cellulose. Both these peaks are seen in spectra of Argan shell sawdust before and after chromatography.

4. Discussion

Although several studies have proved the efficiency of the sawdust of different species of trees in the adsorption of heavy metals, no study has been conducted to our knowledge regarding the efficiency of Argan shell sawdust in biosorption. The Argan tree is native to the southwestern region of Morocco and the Argan shells are readily available as a byproduct of Argan oil extraction from the Argan fruit. Hence, due to its widespread availability in the region and low cost, we decided to test the suitability of using Argan shell sawdust for the adsorption of heavy metals.

We performed column chromatography using Argan shell powder in the column and a standard thorium solution to test the adsorption efficiency. The initial concentration of thorium in our sample was 10.5 ppm, which drastically reduced to 0.202 ppm following chromatography. This gave us an adsorption rate of 98.07%. This is comparable to rates of adsorption of heavy metals by sawdust reported in other studies.

A study conducted by Witek-Krowiak *et al* (2013) using beech sawdust for the adsorption of copper and chromium ions showed considerable adsorption rates. Similarly, another study conducted by Raji *et al* (1997) proved that the adsorption rates of bicarbonate treated sawdust for lead, mercury, and cadmium ions was 98%, 97%, and 95% respectively. Bulut *et al* (2007) proved the efficiency of using walnut sawdust for the adsorption of lead, cadmium, and nickel ions. Holly sawdust has also been proven to adsorb nickel ions with great efficiency (Samarghandi *et al*., 2011).

Sawdust of *Acacia leucocephala* adsorbs copper, cadmium, and lead ions from contaminated aqueous solutions (Munagapati *et al*., 2010). A study by Lim *et al* (2008) showed that the sawdust of Pinus koraiensis could effectively adsorb lead, copper, and zinc ions. One of the highest adsorption rates has been demonstrated by Kapur and Mondal (2013), who used the sawdust of *Mangifera indica* to achieve an adsorption rate of 99.99% for chromium ions. This is considered to be one of the best adsorbents that have been discovered until now.

Characterization studies of sawdust for the purpose of adsorption have been extensively carried out for different heavy metals. A lot of studies have used varying conditions such as contact time, adsorbent concentration, adsorbent particle size, temperature, pH, and intial metal concentrations (Park *et al*., 2010). Kinetic, thermodynamic, and isotherm models have also been applied in several studies (Michalak *et al*., 2013; Shukla *et al*., 2002). The use of these models lets investigators calculate adsorption capacity, energy of adsorption, intensity of adsorption, and mechanisms by which heavy metals are adsorbed onto the sawdust sample.

Our study, too, requires several further tests and multiple experiments to prove the adsorption efficiency of Argan shell sawdust. The initial results do seem promising, but a lot of further work is required to establish the use of Argan shell sawdust for the adsorption of heavy metals. The percentage and identity of heavy metal wastes need to be identified in local water bodies and specific tests need to be carried out to see if our proposed sample can be used to deal with water contamination in our region.

5. Conclusion

In our study, we have attempted to test the efficiency of adsorption of heavy metal wastes from aqueous solutions using Argan shell sawdust. The reason we chose Argan shell powder was that it is easily available in southwestern Morocco and it can be sourced at a very low cost. Our initial studies using columns packed with Argan shell powder and standard thorium concentrate solutions have been very promising, showing an adsorption rate of 98.07%. This is comparable to results obtained from other studies where sawdust of other trees has been used for adsorption. However, these results need to be further analyzed to understand adsorption rates with other heavy metal ions in varying concentrations. Also, the optimum conditions for adsorption need to be standardized so that the adsorption efficiency can be increased to maximum.

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