Cadmium Sorption by *Moringa oleifera* Lam.

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Authors’ contributions

This work was carried out in collaboration between both authors. Author PMAS performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Author ASM designed the study, managed the study analyses and literature searches. Both authors read and approved the final manuscript.

ABSTRACT

Inadequate disposition of industrial waste containing potentially toxic metals in water sources represents a major problem, concerning not only the biota but also to humans. The goal of this paper was to assess the adsorptive capacity of ground *Moringa oleifera* seeds as an alternate material to remove the cadmium ion of Capibaribe river waters in Recife, Pernambuco, Brazil, which were adjusted by a CCD experimental design. Measurements of pH and cadmium levels were performed before and after the experimental treatments in compliance with the official methodology. Obtained data from the treatments were statistically analyzed by Statistic program – version 10, using Box Plots technique. Graphics were employed to locate and assess the oscillations of a variable from different data groups. The results pointed the best efficacy of the alternate method employing moringa in removing cadmium in water treatments were: slightly alkaline pH (7.11); contact time between water and moringa of six hours; 01 grams of moringa per water litre. In these conditions there was a reduction in cadmium concentration of 70.28%, proving...
this alternate methodology not only to be cheap but also easily employed and contributes to diminishing the severe impacts on human health and environment that this metal could cause.

Keywords: Alternate biosorbent; heavy metals; adsorptive capacity; urban rivers.

1. INTRODUCTION

Soil and water pollution by metallic compounds affect environmental quality and presents a risk to human health [1]. Pollution caused by heavy metals results from a wide range of economic activities, most of which industrial, although agriculture and domestic waste also play a role in discarding heavy metals in the environment [2]. Metallurgic, ink, chloride, battery, plastic, and many other industries employ in their production lines many kinds of metals, part of which is released in waterbeds. Other sources of contamination are the incinerators of urban and industrial waste which cause volatilization of heavy metals forming ashes rich in cadmium, lead and mercury [3].

Control of waste emission-based in regimentation, Law enactment and Decrees results from worldwide concern over the poisonous effects of inconsiderate use of toxic chemicals and their disposal in the environment. Industrial effluent of mineral and metal-mechanic branches, particularly those generated by galvanoplasty industries, contains high densities of dissolved metals. According to World Health Organization [4], cadmium, aluminum, chromium, manganese, iron, cobalt, nickel, copper, mercury, and led are the most concerning metals [5], since their disposal as industrial waste could contaminate soil, water bodies and through such contamination reach distant places and oceanic waters [6].

Cadmium is toxic to humans when ingest or inhaled, depositing itself in several tissues of the human body, causing kidney dysfunction, hypertension and arteriosclerosis. Such metal is also widely employed in some industrial processes, being a common pollutant in residue waters and sediments [7].

In the past years, several alternate sorbent materials have been studied aiming to remove heavy metals. Some of the biologic origin, such as biosorbents, microorganisms (bacteria, microalgae and fungi) and macroscopic vegetables (algae, grass-plots, aquatic plants) present the capacity to accumulate heavy metals [8]. To improve environmental quality some of these materials have been investigated as possible solutions to remove metallic ions of diluted solutions and recovery of chemical compounds which possess economic value [9].

Among the existing methods to remove metals in the aqueous medium, the adsorption process has risen prominent, in which low-cost adsorbents with good removal properties can be employed. Natural adsorbents constitute an excellent alternative in chemical remediation due to their high adsorption capacity, low cost and high availability [10].

Based on the performed observations, the present study is founded on the study of new alternate natural materials which can be employed as potentially toxic metallic ions extraction systems, particularly cadmium. The natural adsorbent studied was Moringa oleifera Lam.

2. MATERIALS AND METHODS

2.1 Water Collection

The crude water employed in the experiment was collected from Capibaribe River, at the Teacher Lima de Castilho Bridge, located in Abdias de Carvalho Av., close to the Chico Science tunnel, in the city of Recife, Pernambuco, Brazil.

2.2 Collection and Preparation of Moringa oleifera Lam. Seeds

According to the recommendation of [11], moringa seeds were collected and dried in an oven at 70°C for 30 minutes. After drying the seeds were dusted and sieved at 14 mesh (modified from 11). The dust was stored in a sealed plastic recipient to avoid exposure to humidity.

2.3 Employed Treatments

The treatments (5 repetitions x 5 doses x 5 contact times = 125 experimental unities) were performed with 5 repetitions with doses
equivalents to zero, 250, 500, 1000 and 1500 mg of moringa seed dust to 1.000.0 ml of water, with a contact time/sedimentation of 1, 2, 4 and 6 hours. The pH was adjusted to 5, with standard solutions of NaOH and HNO₃, both of 0.5 mmol/l, so that cadmium stayed available in its ionic form as Cd⁺².

The correlation between moringa (mg/l) and sedimentation time (h) was adjusted according to a rotational central composite design (CCD) and its values combined in an experimental matrix.

After the calculations, the moringa powder was weighed in an analytical scale and then mixed to 1.000.0 ml of the water of the Capibaribe River, according to the combination between concentration and sedimentation time.

2.4 Chemical Determination

After the contact time of each sample, the supernatant was filtered and pH was determined using the ASTM 1293-12 test (Standard Test Methods for the pH of Water) and Cadmium by atomic absorption spectrophotometry with an air – acetylene flame atomization system.

2.5 Statistical Analysis

The data obtained from the different treatments were analyzed in the program Statistic - version 10, using the Box Plots techniques, graphics to locate and analyze the oscillation of a variable between different data groups.

The efficacy of the sorption process was expressed in percentage of sorption, which shows the percentage of metallic ions removed from the solution, calculated through Equation 1:

\[
\text{Sorption (\%)} = \left( \frac{C_s - C_e}{C_s} \right) \times 100
\]

Where: \(C_s\) (mg/l) is the starting concentration of cadmium in the solution; \(C_e\) is the remaining cadmium when the solution has reached equilibrium.

3. RESULTS AND DISCUSSION

The pH is the most important parameter to be assessed in metallic ion sorption, for it is a parameter that directly affects active sites of the sorbent (protonation and dissociation reactions) and the speciation of ions in solution, since hydrolysis, complex formation with organic and inorganic binders, redox and precipitation reactions are all phenomena highly influenced by pH and which affect availability of ions to sorption.

According to the majority of authors who performed sorption studies of metallic ions in biomass, negative charges favour the sorption of metallic cations due to the electrostatic interactions. As such, sorption would be completely determined by the acid-basic behaviour of the functional groups present in the sorbent material [12]. The real behaviour, in fact, is much more complex and goes beyond electrostatic attraction alone, since ionic trade and coordination of metallic ions with binding groups present in the soil can also occur [13].

Cadmium sorption in moringa, therefore, is higher in slightly alkaline pH, probably due to the electrostatic attraction between protonated and negatively charged sites and the Cd⁺² ions. The highest values of cadmium sorption are reached from two hours of contact time forward (Fig. 1).

It can be concluded, looking at the results presented in Fig. 1, that at a pH of 7.11, the contact time of six hours between moringa (1.000g) and water (1L) presented the highest efficacy in cadmium sorption (47.08%), in which the concentration was reduced to 154.53 mg/l, which equals to 70.28% of the starting concentration.

Such variation of time in function of the acid basic character of the medium can be related with biosorbent structural alterations (deprotonation in a pH above the pKa) since the change in pH value also alters the speed of ion diffusion (adsorbate) to the matrix, that is, the higher is the pH the higher is ion diffusion. According to [14] with increased pH, the negative load density on the surface of the composite increases due to surface deprotonation and thus the adsorption of cations is favoured. The value of pH cannot be too alkaline because the increase in OH⁻ ions in the medium could contribute to precipitate cadmium ions as the insoluble base, reducing, in turn, the process of organic matrix adsorption.

The highest efficacy with the increase in moringa dose is due to more biosorbent active sites with electrostatic affinity interactions with the adsorbate (Cd⁺²).

Fig. 2 represents the electron scanning micrographics of moringa’s seed in natura (left)
and treated (right). It can be perceived that the biosorbent material presents a complex matrix with a somewhat porous heterogeneous distribution. Regarding the electron scanning micrograph, it has been perceived that the treatment of moringa seed increases the porosity of the material, making moringa’s pulp more exposed to adsorption [15]. The morphologic change of the treated moringa surface is also a result of the superficial removal of some structural components such as carbohydrates, proteins, and lignin and in smaller proportion, fatty acids. These observations corroborate the hypothesis the treatment can improve the adsorption traits of the moringa associated with the adsorptive characteristics of this biomaterial.

Obtained results agree with what has been found by [16], who identified that the higher the dose of coconut straw the higher the percentage of UO$_2^{2+}$ ion removal. It has also been seen that from a certain point increases in organic matter mass reflects little change in ion adsorption, showing a trend to remain constant, reaching its state of equilibrium.

According to data found by [17], the use of dried green coconut husk, with sample pre-treatment, removed 98.5% of Cd$^{2+}$ ions, while in the proposed methodology, employing moringa, 70.28% of Cd$^{2+}$ ions were removed. The employed method presented less efficacy than the coconut fibre, although in our methodology no pre-treatment was applied which leads to less operational difficulty, lowering costs.

In literature, [18] of the application of Moringa in the removal of salts from the desalinator reject, report different data on the influence of pH in biosorption; pH alters biosorption of metallic ions depending on the kind of adsorbent (biomass) and adsorbate (metallic ion).

Taha et al. [19] investigated the influence of pH on the adsorption of Pb (II), Cd (II) and Zn (IV) using potato peels and concluded that removal efficiency increased when pH increased from 2 to 6 and in pH above 6 efficiencies decreased. [20] when evaluating the percentage of removal of Pb (II), Cd (II) and Ni (II) by modified orange peels concluded that the increase in pH from 2 to 5.5 increased the percentage of removal. By varying the pH from 1 to 6, [21] evaluating the removal of Cu$^{2+}$, Cd$^{2+}$ and Pb$^{2+}$ using sugarcane bagasse as adsorbent concluded that removal is highly dependent on pH, where pH increase from 1 to 6 promotes increased removal capacity from 19 to 213 mg/g for copper, 1 to 232 mg/g for cd and from 36 to 246 mg/g for lead.

**Fig. 1. Sorption of Cd (%) and pH according to the treatments employed**
Fig. 2. Electron scanning photomicrographs of *Moringa oleifera* Lam. “in natura” (left) and treated (right)

4. CONCLUSION

From the obtained data it is possible to state that the process is efficient and can be employed in water treatment processes. Based on the essays it was observed that the analyzed parameters with the highest efficacy of the toxic metal cadmium were: slightly basic pH, the contact
time of 6 hours using 1,000 mg of moringa per litre of water.

The process represents a sustainable alternative, for it can propitiate an adequate destination to organic material which are usually thrown into the environment, increasing waste volume. Furthermore, the adsorbed metal can be recovered by desorption processes in acid medium, allowing for new applications and significantly reducing the number of toxic metals released in waterbeds.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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