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Biosorption of mercury from aqueous solutions by powdered leaves of castor tree (*Ricinus communis* L.)

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Abstract

A new biosorbent produced from castor leaves powder [*Ricinus communis* L.] was used to remove mercury(II) from aqueous solutions. The initial mercury concentrations, contact time and initial pH were evaluated. The ability of castor leaves to remove mercury at various pH (2–8) was studied. The maximum capacity (Q_{max}) of biomass was found to be 37.2 mg Hg(II)/g at pH 5.5. Biosorption equilibrium was established in approximately 1 h. The equilibrium data were described well by Langmuir and Freundlich models. The adsorbed mercury on biomass was desorbed using 10 ml of 4 M HCl solution. The biomass could be reused for other biosorption assays. The ability of biomass to adsorb mercury(II) in a column was investigated. These studies consider the possibility of using leaves of castor tree as an inexpensive adsorbent for the removal of Hg(II) from contaminated chemical and mining industry wastewaters. It is also suggested that the dried biomass might be simply kept and used in a very low cost metal ion removal system.

Keywords: Biosorption; Mercury; Biomass; Desorption; *Ricinus communis* L.

1. Introduction

The accumulation of mercury in environment, which comes from municipal wastes and manufacturing of organo-mercurial compounds, causes potential risk to human health due to the uptaking of these amounts of mercury by plants and their introduction into the food chain, including marine organisms (algae, seaweed, fish, etc.) [1]. The toxic and carcinogenic effects of mercury on living beings are quite well known. According to the Environment Protection Agency (EPA), mercury is considered as a highly dangerous element because of its accumulation in the environment and in organisms [2].

Some workers indicated that precipitation is a suitable method for metal removal from wastewaters containing high concentrations of heavy metals [3]. In some cases, ion exchange and activated carbon adsorption have been used [4,5]. Electrochemical treatment, membrane process and biological methods are also used. However, these methods become non-economical when dealing with very small concentrations of metals due to the need to use expensive monitoring systems. Biosorption is considered to be one of the most economical and effective methods for removal of mercury from wastewaters. Some studies suggested the use of microorganisms [6,7], others used living [8] and non-living biosorbents such as dried plant leaves, roots [9–11], wheat shell [12], tea leaves [13] and algae [14]. A number of sorbents such as coal-fly ash [15] and coffee grounds [16] were used to remove mercury from aqueous solutions. Others used *Ulva lactuca* biomass [17] and marine macroalga (*Cystoseira baccata*) [18]. These materials are potentially inexpensive adsorbents.

Recently Karunasagar et al. [19] have reported that the coriander plant (Chinese parsley) can remove mercury(II) and methyl mercury from aqueous media as an excellent biosorbent.

The aim of the present work was to investigate the ability of a mercury sorbent prepared from leaves of castor tree [*Ricinus communis* L.] (a cheap, readily available plant in many countries) and to study the effect of several parameters (pH, contact time, initial metal concentration and foreign ions effect) on the biosorption efficiency of mercury from aqueous solution.

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2. Materials and methods

2.1. Reagents

All chemicals were of analytical grade. Glassware were socked in 10% (v/v) nitric acid for at least 24 h and then rinsed with 1% (v/v) nitric acid, three times and subsequently five to six times with double distilled water.

Mercury stock standard solution (1000 mg/L) was prepared from a ready made $HgCl_2$ standard (Mindex Limited, UK). Working mercury solutions were prepared just before used by appropriate dilutions of stock solution. (0.1 M) HCl and (0.1 M) NaOH solutions were used for adjusting the initial pH of solutions. Solutions of dithizone (1.56×10^{-3} M) (RIEDEL-DE HAEVAR, Germany), (4.5 M) H_2SO_4 (Analyticals CARLOERBA, Milano, Italy) and triple distilled 1,4-dioxane (RIEDEL-DE HAEVAR, Germany) were used.

2.2. Preparation of biosorbent

The biosorbent in this study was leaves of castor tree [*Ricinus communis* L.], which were collected from different places around Tripoli, Libya. The leaves were cleaned with double distilled water, dried at 60 °C and finally ground in a mortar and sieved through a 125–150 μm mesh.

2.3. Experimental procedure

Adsorption operations were carried out by batch method using conical flasks with continuous shaking at room temperature and different optimized parameters [pH (from 2 to 8), contact time (from 5 to 180 min), initial concentrations (from 5 to 100 mg/L of Hg(II)), and effect of foreign ions] were studied.

The effects of contact time, initial pH and initial mercury concentration were investigated by varying any one of the process parameters and keeping the other parameters constant.

For kinetic studies of Hg adsorption, amount of castor leaves powder (1.0 g) was suspended in 1000 ml of an aqueous solution containing 100 mg/L of mercury(II) (from $HgCl_2$). The pH of each solution was adjusted to the chosen pH (pH 5.5). The mixture was stirred, and then the unadsorbed mercury in solution was checked by taking aliquots at the considered time. Mercury content was analyzed spectrophotometrically (6505 UV/Vis Spectrophotometer, JENWAY) at 488 nm, following a procedure adapted by Ahmed et al. using dithizone [20].

Adsorption isotherm experiments were carried out at different pH values (2–8). Different concentrations of Hg(II) were prepared (5–100 mg/L), a volume of 100 ml of mercury solution was then mixed with 0.25 g of biomass and stirred for 120 min until equilibrium was reached. The mercury content in supernatant solution was filtered through a filter paper (Whatman 42) and analyzed.

The amount of Hg(II) adsorbed (Q_e) in mg/g at equilibrium was computed by using the following equation:

$$Q_e = \frac{(C_0 - C_e)V}{1000m},$$

where C_0 and C_e are the Hg(II) concentrations in mg/L initially and at equilibrium, respectively, V is the volume of Hg(II) solutions in ml, and m is the weight of sorbent in grams.

2.4. Sorption in column

Selected weight (1.0 g) of castor leaves was suspended in double distilled water and shaken for 30 min then transferred to the column (1.0 cm × 25 cm). The pH was adjusted at 5.5 by addition of (0.1 M) NaOH. Twenty-five milliliters aliquots of (100 mg/L) Hg(II) solutions were fed to the column at a flow rate of 2.0 ml/min, effluents were collected separately. The column was rinsed by 75 ml of double distilled water at a flow rate 4 ml/min. The unadsorbed mercury in effluents was determined spectrophotometrically.

2.5. The desorption of mercury from sorbent

A selected weight (0.25 g) of biomass containing Hg was investigated at room temperature using mechanically shaken 10 ml aliquots of (1.0–6.0 M HCl). The shaking time was fixed at 30 min. The mixture was filtered and washed by double distilled water three times. The pH of supernatant solution was adjusted at 5.5 and made up to 100 cm^3 volumetrically, then the mercury in solution was determined and the desorbed mercury was calculated.

$$\text{Desorption yield} = \frac{A}{B},$$

where A is the amount of mercury desorbed per effluent and B is the amount of mercury loaded on sorbent.

3. Results and discussion

3.1. Effect of initial pH on biosorption

The initial pH of the aliquot samples ranged between 2 and 8 (Fig. 1). Aliquots of 100 ml of 100 mg/L Hg(II) solutions were shaken for 120 min with 0.25 g of biomass at various initial pH (which was adjusted before and during the experiment). As shown in Fig. 1 the initial pH values (from 5.5 to 8) had no effect on the adsorption of mercury. The adsorption

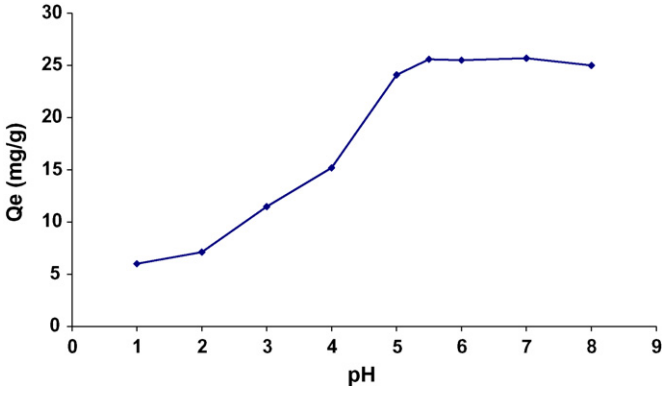

Fig. 1. Effect of pH on the sorption of mercury(II) (100 ml of 100 mg/L of Hg(II), 120 min and 0.25 g of castor leaves powder).

capacity (Q_e) of Hg(II) between pH 4 and pH 5.5 showed a slight increase (19 mg/g and 25.6 mg/g, respectively), while no significant increase was detected beyond pH 5.5. So the workers decided to fix the pH at this value throughout the following experiments. Similar action was taken by other workers for similar situations [17–19,21].

Different functional groups such as (carboxylate group) on plant surface can play an important role for the sorption of mercury. Similar work on parsley [19] reported that carboxylate groups represent a major role in the binding of mercury. At lower pH values (pH < 4) H^+ ions may bind with negatively charged groups on plant surface, which showed low sorption of mercury. Herrero et al. [18] suggested that the H^+ ions and Hg(II) compete with each other in binding with acid sites on seaweed surface at low pH. On the other hand, they showed that most of dissolved mercury appears as neutral species ($HgCl_2$, Hg(OH)Cl and $Hg(OH)_2$). The workers feel that a similar situation occurs in this case, where the carboxylate groups seem to be the attracting sites on caster leaves. Moreover, some evidences from preliminary IR investigations done by the team support this assumption. However, one cannot conclude positively on this assumption until full IR investigation results are at hand.

3.2. Contact time

The effect of time on the sorption of mercury(II) by castor leaves was studied. Fig. 2 demonstrates that the biosorption efficiency of mercury(II) increased rapidly during the first 5 min and remained nearly constant after 40 min of adsorption. The mercury sorption was relatively fast, suggesting that the system reached the final equilibrium plateau within 60 min. The increase of contact time beyond 60 min has no significant effect on biosorption efficiency. Most of the mercury sorption was during the first 20 min. This probably is due to the availability of so many sorption sites at the beginning of experiments. Similar results have been reported in literature for different biomass sorbents. Karunasagar et al. [19] noted that most of Hg(II) was removed by coriander (china parsley) within 45 min of stirring time, however, Zeroual et al. [17] indicated that the ideal time for adsorption of Hg(II) by *Ulva lactuca* is 120 min. Other parameters such as surface charge capacity, composition of sorbent,

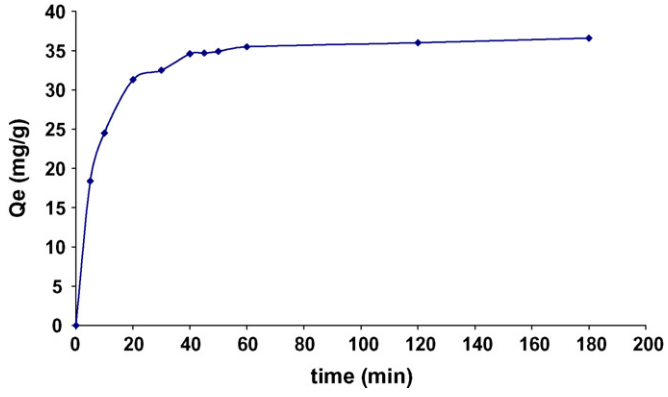

Fig. 2. Effect of time on the sorption of mercury(II) (1000 ml of 100 mg/L of Hg(II), pH 5.5 and 1.0 g of castor leaves powder).

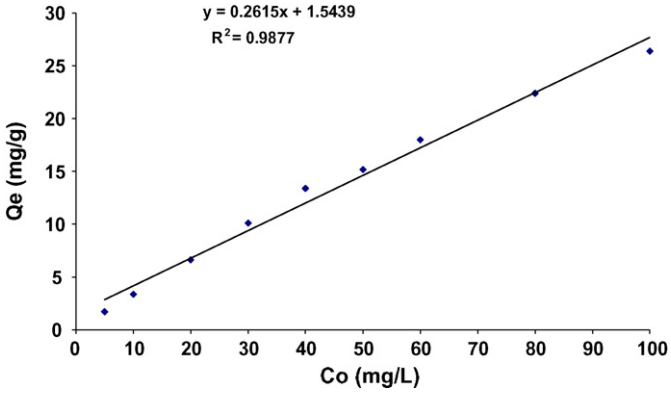

Fig. 3. Effect of initial concentration on adsorption of Hg(II) on castor leaves powder (0.25 g of material, 100 ml of solution, at pH 5.5, for 60 min).

metal affinity and experimental conditions play a role in the adsorption mechanism.

3.3. Effect of initial concentration of mercury(II) on biosorption

Fig. 3 shows percentage of mercury(II) removal as a function of initial concentration with 0.25 g of sorbent (pH 5.5 and 60 min). Although, the total uptake of mercury increased with the increase of Hg concentration, the adsorption capacity (Q_e) per 0.25 g of biomass after 60 min ranged from (1.71 mg of Hg(II)/g) for an initial concentration (5 mg/L) to (26.4 mg of Hg(II)/g) for an initial concentration (100 mg/L). The results (Fig. 3) show that as the initial concentration of mercury is increased, the capacity of material (Q_e mg of mercury(II) per gram of material) increases. This result gave evidence of the great ability of material to remove mercury from aqueous solutions in accordance with Karunasagar [19].

3.4. Adsorption isotherms

Langmuir and Freundlich models are frequently used for estimating the quantification of the biosorptive capacity of a biosorbent [12,14]. Langmuir model is appropriate for monolayer adsorption onto a homogeneous surface with invariable adsorption energy, however, the Freundlich equation hypothesizes a heterogeneous surface and considers that molecules attached to surface site will have an effect on the next sites [22].

The Langmuir isotherm is represented by the following equation:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max} b} + \frac{C_e}{Q_{max}},$$

where C_e is the equilibrium concentration (mg/L), Q_e is the amount of mercury adsorbed (mg/g), and Q_{max} and b are Langmuir constants related to the adsorption capacity and energy, respectively.

The data from this study (Fig. 4) show that when C_e/Q_e is plotted against C_e, a straight line was obtained. This indicates that the Langmuir isotherm was followed under the present conditions with $R^2 = 0.9813$ (Table 1).

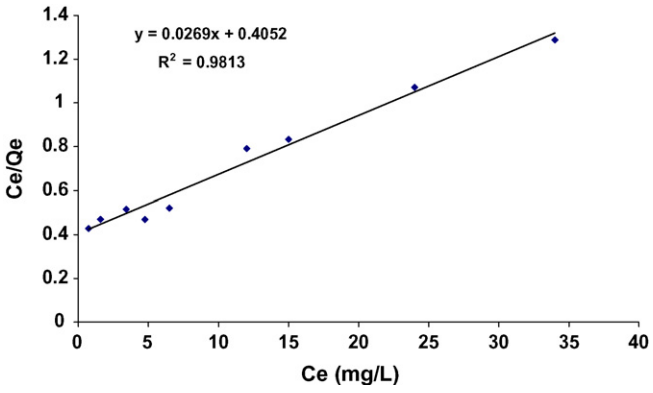

Fig. 4. Mercury(II) sorption isotherm based on Langmuir model, using castor leaves as a biosorbent (at room temperature, pH 5.5).

Table 1
Langmuir and Freundlich constants

Langmuir constant	
Q_{max} (mg/g)	37.2
b (mg/L)$^{-1}$	0.066
R^2	0.9813
Freundlich constant	
K	2.61
n	1.41
R^2	0.9667

On the other hand, the Freundlich equation is represented by the following:

$$\mathrm{Log}\,Q_e = \mathrm{Log}k + \frac{1}{n}(\mathrm{Log}C_e),$$

where C_e is the equilibrium concentration (mg/L), Q_e is the amount of mercury adsorbed (mg/g), k and n are Freundlich constants. The constant (n) gives an indication of the favorability and k the capacity of the adsorbent (Table 1). Application of Freundlich equation in this study showed reasonably good results and a straight line was obtained with $R^2 = 0.9667$ with a slop $(1/n) = 0.7093$ (Fig. 5). Thus, one can conclude that both isotherms are applicable to the findings of this study.

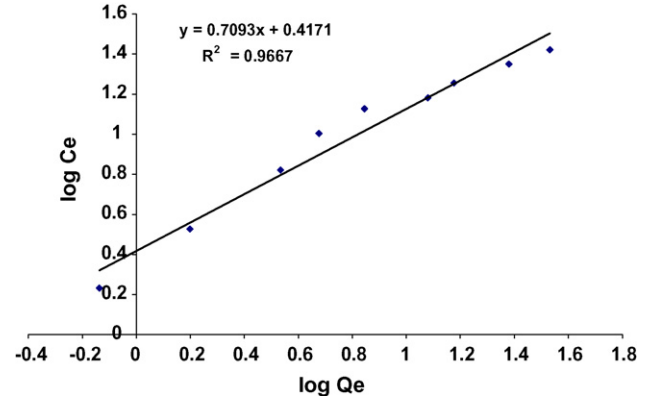

Fig. 5. Mercury(II) sorption isotherm based on Freundlich model, using castor leaves as a biosorbent (at room temperature, pH 5.5).

Table 2
Desorption Hg(II) (0.25 g of biomass containing 7.5 mg of Hg(II) with 10 ml of HCl)

HCl concentration (M)	Desorption percent (A/B)
1	60
2	76
3	84
4	98
5	98
6	99

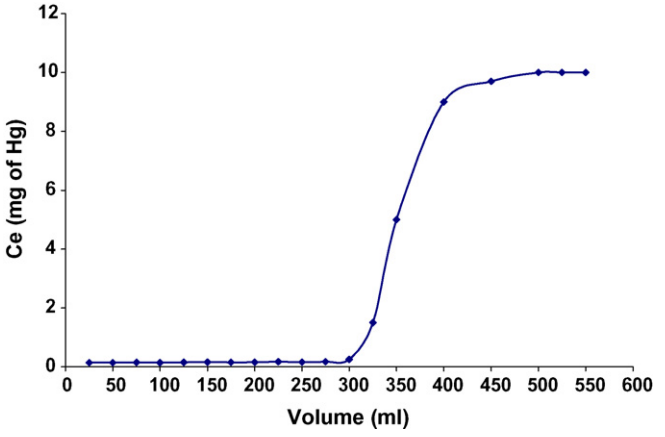

Fig. 6. Adsorption breakthrough curve for mercury removal (1 g of biomass, flow rate 2 ml/min, column 1 cm, initial concentration is 100 mg/L of Hg(II) and C_e is the final concentration at pH 5.5).

3.5. Desorption studies

Desorption of mercury from Hg(II)-loaded biomass was treated by HCl as desorption agent. From the results of this study, more than 60% (0.25 g of biomass containing 7.5 mg of Hg(II) with 10 ml of HCl) desorption of mercury occurred at 1 M of HCl, however, the complete desorption (>98%) was preformed with 4 M of HCl. Table 2 shows the results of mercury desorption. Similar desorption results were reported by Chinese parsley sorbent [19] that the complete desorption was found between 4 M and 6 M of HCl. The acid treatment did not alter the surface sites of the biomass with almost the same binding capacity [21].

3.6. Column studies

Aliquots of mercury solution (25 ml of 100 mg/L of Hg(II), pH 5.5) were passed through a column (contains 1 g of biomass) at flow rate 2 ml/min. The effluent of solution was collected and the remaining concentration of mercury in solution was determined. The results in this study show that more than 96% of mercury was adsorbed by the material in column. Adsorption breakthrough represented in Fig. 6. The breakthrough curve was obtained by plotting remaining mercury(II) in solution (C_e mg of Hg(II)) against the number of ml volumes. About 350 ml of Hg(II) solution (100 mg/L) was passed through the column before breakthrough. The Q_{max} was calculated to be 35.5 mg/g, and this value was very close to that obtained for batch equilibrium experiments (37.2 mg/g).

The mercury in column then was desorbed with 4 M HCl (20 ml) and the column was rinsed with 75 ml double distilled water. It was observed that more than 98% of mercury(II) was desorbed from biomass in column. Several adsorption–desorption cycles could be employed. These results suggest that castor leaves can be used for pre-concentration, determination and extraction of mercury from contaminated water at ultra low levels of mercury.

3.7. Effect of the foreign ions on mercury adsorption

As an application tap water (pH 7.8, $Na^+ = 40$, $K^+ = 10$, $Mg^+ = 34$, $Ca^{2+} = 76$, $Cl^- = 85.5$ and $SO_4{}^{2-} = 120$ mg/L) spiked with Hg(II) (20 mg/L) was used. The results here show that more than 86% of mercury was adsorbed on the biomass and there was no limited effect on adsorption of mercury from foreign ions in water. On the other hand, the mercury adsorption experiments were carried out in the presence of some heavy metals (Pb, Cr, Cu and Cd) with higher concentration than mercury (100 mg/L of mercury and 250 or 500 mg/L of heavy metal ions) for the study of foreign ions effect. Cr(II), Cu(II) and Cd(II) ions appear to slightly decrease the mercury sorption, whereas Pb(II) ions slightly increase it (108% increase). Similar results were reported by Herrero et al. [18].

4. Conclusion

The results obtained in this study demonstrated that castor leaves [*Ricinus communis* L.] can be used as an excellent biosorbent to remove mercury(II) from wastewaters with good efficiency and low cost. Several parameters were studied and maximum adsorption was found to occur at a pH range of 5.5–8 within 60 min contact. Biosorption efficiencies were increased with increasing contact time and initial metal concentration, maximum capacity of material was observed 37.2 mg/g of material. Furthermore, it can be concluded that castor leaves hold great potential to be an effective biosorbent for removal of mercury and other heavy metals from contaminated waters.

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