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Biosorption of copper ions from aqueous solutions using the desert tree *Acacia raddiana*

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ABSTRACT

Biosorption of heavy metals from aqueous solutions is a relatively new technology for the treatment of industrial wastewater, which utilize naturally occurring biomass derived from waste materials. Desert tree *Acacia raddiana* bark was evaluated as a new biosorbent for removal of copper ions from aqueous solution. Effect of operating conditions, like initial metal concentration, pH and temperature, on copper biosorption were investigated. The process of biosorption has nearly reached equilibrium in 04 hours and the maximum copper cations biosorption capacity of *Acacia raddiana* bark obtained was 82.63 mg/g at pH 5 and temperature around 25–30°C. The relation between the chemical composition of the bark part of this desert tree and the percent of adsorption for copper ion was examined.

Keywords: Heavy metal; Sorption; Wastewater; *Acacia raddiana*; Sahara

1. Introduction

Increased knowledge about toxicological effects of heavy metals on the environment and in drinking water is well recognized and therefore, it is inevitable to search for different methods to reduce water pollution [1–2]. Due to their persistence in nature and to the increased susceptibility to disease in man and animal (hepatic, kidney, nerves and the immune system damage and block functional vital groups, etc.), it becomes essential to remove them from wastewaters. Conventional wastewater treatment including sludge separation, chemical precipitation, electrochemical process, membrane separation, reverse osmotic treatment, ion-exchange and solvent extraction are often expensive, require high energy, have low selectivity and are impractical when they are used to treat the wastewaters with heavy metal ions amount lower than 100 mg l^{-1} [3–6].

Biosorption of heavy metals from aqueous solutions is a relatively new technology for the treatment of industrial wastewater, which utilize naturally occurring biomass derived from waste materials. The major advantages of biosorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive biosorbent. Thus, several approaches have been studied and developed for the effective removal of heavy metals using biosorbents like peat, fly ash, algae, soya bean, hulls leaf mould, sea weeds, coconut husk, sago waste, peanut hull, hazelnut, bagasse, rice hull, sugar beet pulp, plants biomass and bituminous coal. It has also been observed that these biosorbents need further modifications to increase the active binding sites and also made them readily available for sorption [3,4,7–14].

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Table 1
Variation of biosorbed copper ion concentration with time for different initial copper ion concentrations, pH 5.0, $T = 25 \pm 0.1°C$

Initial Cu^{2+} concentration C_0 (mg l^{-1})	Biosorbed Cu^{2+} concentration, q_e (mg g^{-1})							
	Time (h)	01	02	03	04	05	07	24
50		31	39	45	47	47	47	46
100		70	78	82	86	86	86	86
150		92	100	104	108	108	108	107
200		98	106	110	114	114	114	114
250		99	107	111	115	115	115	115
300		101	109	113	117	117	117	117

Copper, like all heavy metals, is potentially toxic. The excessive intake of copper results in its accumulation in the liver causing gastrointestinal problems, kidney damage and anaemia. Besides, an increase in lung cancer among exposed workers is associated with continued inhalation of copper-containing sprays [15].

Continuing our effort on the valorization of Algerian Sahara plants, in this investigation, we attempt to use the bark of the desert tree *Acacia raddiana* as low-cost biomaterials for the biosorption of toxic heavy metals from water and a suitable for application in small industries and for sustainable development.

To our knowledge, no information is available for heavy metals biosorption from aqueous solutions by the bark of this desert tree. So, the objective of this study was to utilize the locally available *Acacia raddiana* bark as an adsorbent for removal of copper ion from aqueous solution. Effects of operating conditions like initial metal concentration, pH and temperature, on copper biosorption were investigated.

The relation between the chemical composition of the bark part of *Acacia raddiana* and the percent of adsorption for copper ion was examined.

2. Materials and methods

2.1. Biosorbent preparation

Bark of tree *Acacia raddiana* used in this work was collected from Saoura desert (Bechar, Algeria) in May 2005. The biomass was washed with distilled water several times to remove soil-associated particles and water soluble materials. The dried bark, ground in a mortar to powder and sieved into a size ranging from 125 to 250 μm, was stored in a desiccator until use for the biosorption process.

2.2. Biosorption studies

All chemicals used in this study were of analytical grade and solutions were prepared using double distilled water. Cu^{2+} solution was prepared by dissolving copper sulfate in distilled water. Hydrochloric acid and sodium hydroxide solutions were used to adjust the solution pH. The pH was measured using Hanna pH meter at the beginning and at the end of the experiments.

Batch experiments were carried out by shaking 100 mg of biosorbent mixed with 100 ml of copper sulfate solution of known concentration in 200 ml Erlenmeyer flasks stirred at constant speed in a magnetic shaker in a thermostatic bath. After, the solid was removed by filtration through a filter paper (Whatman GF/A). Blank runs, with only the sorbent in 100 mL of double distilled water, were conducted at similar conditions. The equilibrium metal concentration in the filtrates as well as in the initial solution was analyzed using atomic adsorption spectrophotometer (Perkin Elmer Analyst 700). Each experiment was carried out in duplicate.

3. Results and discussion

3.1. Effect of initial copper ions concentration

We have determined the optimum time of biosorption for different initial concentrations. Biosorbed copper ion concentrations increased with time and reached equilibrium after 4 h for all initial copper ion concentrations tested. An increase of time up to 24 h did not show notable effects as shown in Table 1.

An important parameters in biosorption of heavy metal ions is the equilibrium solid phase metal ion concentration. We noted that q_e, the Cu^{2+} equilibrium concentration in solid phase (mg Cu g biomass^{-1}), increased rising initial Cu^{2+} concentration. Copper ion percent removal decreased from 94% to 39% (Fig. 1) and the final Cu^{2+} concentration increased from 3 to 183 mg l^{-1} (Fig. 2) when the initial Cu^{2+} concentration was raised from 50 to 300 mg l^{-1} at constant pH 5.0. At low initial Cu^{2+} concentrations, such as 50 and 100 mg l^{-1}, all copper ions were biosorbed onto binding sites

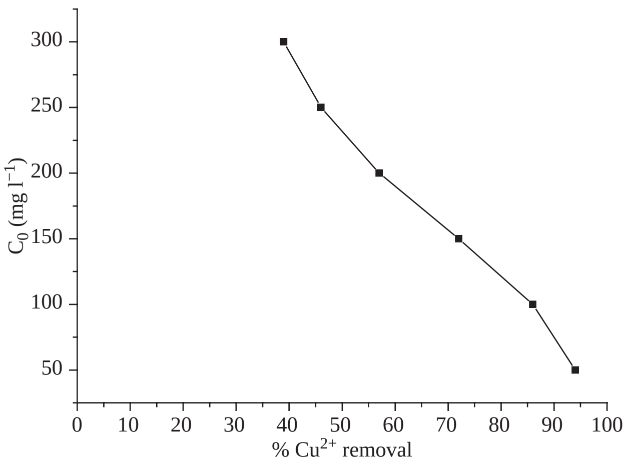

Fig. 1. Variation of percent copper removal with the initial copper ion concentration at the end of 4 h, pH 5, $T = 25 \pm 0.1$°C.

on *Acacia raddiana* bark surfaces. However, at high initial copper ion concentrations, such as 250 and 300 mg l^{-1}, a large fraction of binding sites on biomass surfaces were occupied by copper ions.

3.2. Effect of pH

The pH of the solution is the most important parameter that in the biosorption process can significantly influence the removal of heavy metals [2]. The effect of pH on the sorption of copper (II) have been studied using different sorbent types and optimum sorption capacities have been reported at pH values of 5 [11,16], 6 [2,17] and 7 [10,18].

Following the previously mentioned experimental conditions a 100 mg/L copper ions solution was treated at pH values from 3 to 7.

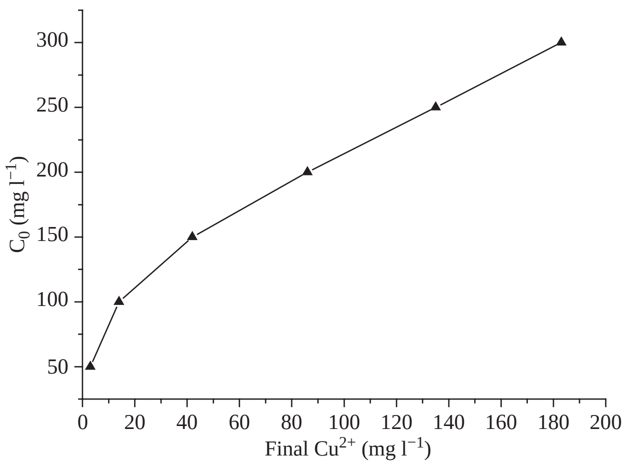

Fig. 2. Variation of final Cu^{2+} concentration with the initial copper ion concentration at the end of 4 h, pH 5, $T = 25 \pm 0.1$°C.

Table 2
Effects of initial pH on percent copper removal and biosorbed copper concentration. Initial Cu^{2+}concentration $C_0 = 100$ mg l^{-1}, $T = 25 \pm 0.1$°C, 4 h

pH	Final Cu^{2+} concentration C (mg l^{-1})	Percent Cu^{2+} Removal	Biosorbed Cu^{2+} concentration q (mg g^{-1})
3	89	11	11
4	36	64	64
5	14	86	86
6	15	85	85
7	17	83	83

Table 2 shows that removal of copper ions by the *Acacia raddiana* bark increased until pH 5.0 to remain nearly constant in the pH range 5.0–7.0.

The greatest increase in the biosorption rate of copper ions on the *Acacia raddiana* bark was observed at pH 5. At lower pH, H^+ ions compete with copper cation for the exchange sites in the system. The heavy metal cations are completely released under extreme acidic conditions. At pH 3–7, there are three species present in solution [2], Cu^{2+}, $CuOH^+$ and $Cu(OH)_2$. These species are adsorbed through electrostatical interaction at the surface of the biomass. As the pH decrease, the surface of the *Acacia raddiana* bark exhibits an increasing positive characteristic. H^+ ions, present at a high concentration in the reaction mixture, compete with Cu^{2+} ions for the biosorption sites reducing uptake of copper cation. At higher pH values, precipitation of $Cu(OH)_2$ occurred and both sorption and precipitation would be the effective mechanisms to remove the copper ions in aqueous solution. At around pH 5, copper cations, would be expected to interact more strongly with the negatively charged binding sites in the sorbent [19].

3.3. Effect of temperature

Keeping all other parameters constant temperature was varied from 25 to 60°C. Table 3 shows that the removal of copper ions depends on temperature. The sorption of copper cations increased slightly with the increase in temperature up to 30°C and then started decreasing. The temperature higher than 50°C caused a change in the texture of the biomass and thus reduced its sorption capacity. Usually the physical sorption reaction is exothermic and preferred at lower temperature [19].

3.4. Biosorption isotherms

The distribution of metal ions between liquid and solid phases is generally described by using Langmuir, Freundlich and Dubinin-Radushkevich biosorption

Table 3
The biosorption quantity of Copper ions onto *Acacia raddiana* bark at different temperature Initial Cu^{2+}concentration $C_0 = 100$ mg l^{-1}, pH 5.0, 4 h

T °C	Final Cu^{2+} concentration C (mg l^{-1})	Percent Cu^{2+} removal	Biosorbed Cu^{2+} concentration q (mg g^{-1})
25	14	86	86
30	14	86	86
40	37	63	63
50	62	38	38
60	76	24	24

isotherm models. The two most common isotherm equations have been tested in the present study. So, the biosorption data were analyzed according to the linear form of the Langmuir (Eq. 1) and Freundlich (Eq. 2) isotherms.

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m}, \qquad (1)$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e, \qquad (2)$$

where q_e is the amount of metal ion sorbed at equilibrium per unit weight of sorbent (mg/g), C_e the equilibrium concentration of metal ion in the solution (mg/L), q_m and b the Langmuir model constants indicate, respectively, the monolayer sorption capacity and the constant related to the free energy of sorption. The Freundlich model constants K_F and n indicate respectively the relative sorption capacity of the sorbent and the intensity of the sorption. The plot of C_e/q_e versus C_e and log q_e versus log C_e, gives a straight line of slope, which will permit us to obtain the constants from their intercepts and slopes. The isotherms were found to be linear over the entire concentration range studied with a good linear regression coefficient for Langmuir and Freundlich models respectively ($R^2 = 0.985$) and ($R^2 = 0.917$). The parameters of both models determined by least squares fit of the experimental biosorption data are presented in Table 4.

Fig. 3 shows the comparison of the experimental equilibrium data and the theoretical isotherm predicted by the Langmuir and Freundlich models. It was observed that Langmuir acceptably fit the experimental results with an acceptable coefficient. The maximum sorption capacity q_m of the *Acacia raddiana* bark was 82.63 mg/g which indicates that this biosobent is a quite good and attractive in treatment of diluted ions copper solutions.

Table 4
Parameters of the Langmuir and Freundlich isotherms for the biosorption of Copper ions onto *Acacia raddiana* bark

Langmuir			Freundlich		
q_m (mg/g)	B	R^2	K_F	N	R^2
82.63	0.073	0.985	8.75	1.54	0.917

3.5. Chemical characterization of Acacia's bark

In Algerian Sahara, *Acacia raddiana* tree (Fig. 4) provide food and shelter for many desert animals and is a major source of livestock feed and firewood for the native people [20].

In a previous study, we reported the phytochemical screening of the bark's acacia and the presence an important quantities of polyphenolic compounds (Flavonoids, Tannin) and another natural substances such as: tritepenoids saponin, cellulose, hemicellulose and lignin [21,22]. It's known that these natural compounds present in the cell wall are the most important sorption sites. Therefore, the important of these natural compounds is that they contain hydroxyl, carboxylic, carbonyl, groups which are important sites for metal sorption [23].

4. Conclusions

Biosorpion of copper ions from aqueous solution onto *Acacia raddiana* bark was investigated as functions of important parameters, such as contact time, concentrations of adsorbate (Cu^{2+} ions), solution pH and temperature.

The process of biosorption has nearly reached equilibrium in 04 hours and the biosorption of metals was pH and temperature dependent, respectively optimal pH was 5 and temperature was 25–30°C. Results

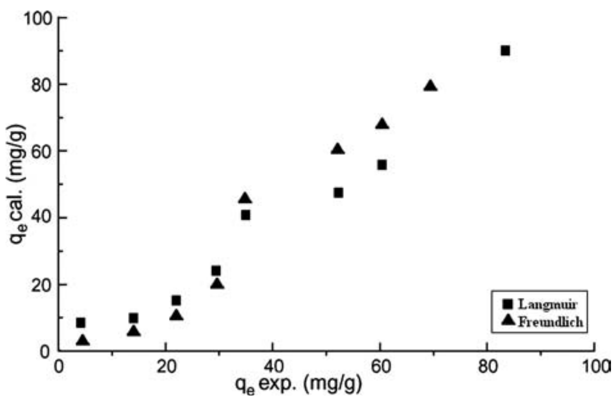

Fig. 3. Comparison of Langmuir and Freundlich models with experiment data of copper sorption by Acacia raddiana bark.

Fig. 4. *Acacia raddiana in* its natural habitat (Oued Saoura, Algerian Sahara).

indicated that the Langmuir model gave an acceptable fit to the experimental data than the Freundlich model. Copper cations biosorption capacity of *Acacia raddiana* bark was found to be 82.63 mg/g.

Therefore, the present study demonstrates the possibility of usage of inexpensive biosorbent, *Acacia raddiana* bark as suitable alternatives for the removal of copper ions from wastewater.

Finally, additional work will be required in order to determine the biosorption of other heavy metals ions, and to determine the mechanism of copper sorption by this sorbent biomaterial.

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