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Removal of copper from aqueous solution by *Retama raetam* Forssk. growing in Algerian Sahara

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ABSTRACT

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. The Saharan plant *Retama raetam* (Fabaceae family) was used as locally available adsorbent for removal of copper ions from aqueous solution. Various biosorption parameters such as initial metal concentration, pH and temperature on the capacity of copper biosorption were investigated. The relation between the phytochemical composition (polyphenol, alkaloids, terpenoids, carbohydrates) of the aerial parts of *Retama raetam* and the percent of adsorption for copper ion was examined.

Keywords: Biosorption; *Retama raetam*; Copper; Wastewater; Phytochemical; Sahara

1. Introduction

Toxicological effects of heavy metals on the environment and drinking water are well recognized. Due to their persistence in nature, increased susceptibility to disease in man and animal (hepatic, kidney, nerves and the immune system damage and block functional vital groups), it becomes essential to search for different methods to reduce water pollution and to remove heavy metals from wastewaters [1–7]. 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, anemia, and an increase in lung cancer among exposed workers is associated with continued inhalation of copper-containing sprays [8].

Thus, several approaches have been studied and developed for the effective removal of heavy metals using biosorbents like peat, fly ash, algae, soya beans, hull leaf mould, sea weeds, coconut husk, sago waste, peanut hulls, hazelnuts, bagasse, rice hulls, sugar beet pulp, plant 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 [9–19].

Continuing our effort on the valorisation of Algerian Sahara plants as biomaterials for the biosorption of toxic heavy metals from water [20], we report herein our results in this field. To our knowledge, no information is available for heavy metals biosorption from aqueous solutions by the aerial parts of the Saharan plant *Retama raetam* (Fabaceae). So, the objective of this study was to utilize the locally available plant *Retama raetam* as an adsorbent for

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removal of copper ions from aqueous solution. Effects of operating conditions like initial metal concentration, pH and temperature on copper biosorption were investigated. The relation between the phytochemical composition (polyphenol, alkaloids, terpenoids, carbohydrates) of the aerial parts of *Retama raetam* and the percent of adsorption for copper ion were examined.

2. Materials and methods

2.1. Biosorbent preparation

The aerial parts of *Retama raetam* used were collected from its natural habitat, i.e. from El Bayadh region (South Algeria) in April 2006. The biomass was washed with distilled water several times to remove soil-associated particles and water soluble materials. The dried biomaterials ground in a mortar to powder and sieved into a size ranging from 125 to 250 μm and 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 solid copper sulfate ($CuSO_4{\cdot}5H_2O$) in distilled water. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) solutions were used to adjust the solution pH. Blank runs, with only the sorbent in 100 mL of distilled water, were conducted at similar conditions to understand the pH change of the solution during sorption experiments. 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. After agitation, the solid was removed by filtration through a filter paper (Whatman GF/A). The final 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 and the average results are presented in this study.

3. Results and discussion

3.1. Effect of initial copper ion concentration

According to our recent works [20], we have determined the optimum time of biosorption for different initial concentrations (varied between 50 and 300 mg l^{-1}). Then, biosorbed copper ion concentrations increased with time and reached equilibrium after 4 h for all initial copper ion concentrations tested, an increase of removal time to 24 h did not show notable effects.

Table 1

Variation of percent copper removal and biosorbed copper concentrations with the initial copper ion concentration at the end of 4 h, pH 5, T = 25°C

Initial Cu^{2+} concentration C_0 (mg l^{-1})	Final Cu^{2+} concentration C (mg l^{-1})	Percent Cu^{2+} removal (%)	Biosorbed Cu^{2+} concentration q (mg g^{-1})
50	6	88	44
100	21	79	79
150	48	68	102
200	90	55	110
250	137	45	113
300	186	38	114

We noted that variations of equilibrium solid phase Cu^{2+} concentration (qe, mg Cu g biomass^{-1}) with initial Cu^{2+} increased with increasing initial Cu^{2+} concentration (Table 1). At pH 5, the percent copper ion removal decreased from 88% to 38% and the final Cu^{2+} concentration increased from 6 mg l^{-1} to 186 mg l^{-1} when the initial Cu^{2+} concentration was raised from 50 mg l^{-1} to 300 mg l^{-1}. At low initial Cu^{2+} concentrations, such as 50 mg l^{-1} and 100 mg l^{-1}, all copper ions were biosorbed onto binding sites on *R. raetam* plant surfaces. However, at high initial copper ion concentrations, such as 250 mg l^{-1} and 300 mg l^{-1}, a large fraction of binding sites on biomass surfaces were occupied by copper ions [20].

3.2. Effect of solution pH

The pH of the solution is the most important controlling parameter in the biosorption process, can significantly influence the removal of heavy metals [3]. Several studies were done to determine the effect of pH on the sorption of copper(II) by using a variety of different sorbent types, and optimum sorption capacities of copper ions have been reported at pH values of 5 [14,20–22], 6 [3,12,23,24] and 7 [14,25,26].

Keeping the same experiment conditions with 100 mg/L of copper ions solution as mentioned previously (time = 4 h, T = 25°C), pH of solution was varied from 3 to 7

Data on variations of percent copper removal and biosorbed copper concentration by the *R. raetam* under different pH values are summarized in Table 2 and Fig. 1.

The greatest increase in the biosorption rate of Cu^{2+} ions on the *R. raetam* plant 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 circumstances of extreme acidic conditions. At pH 3–7 there are three species present in the solution [3]: Cu^{2+}, $CuOH^+$ and $Cu(OH)_2$. These species are adsorbed an electrostatically interaction at the surface of the biomass. As the pH decrease, the sur-

Table 2
Effects of pH on percent copper removal and biosorbed copper concentration. Initial Cu^{2+} concentration C_0 = 100 mg l^{-1}, T = 25°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	91	9	9
4	42	58	58
5	21	79	79
6	30	70	70
7	33	67	67

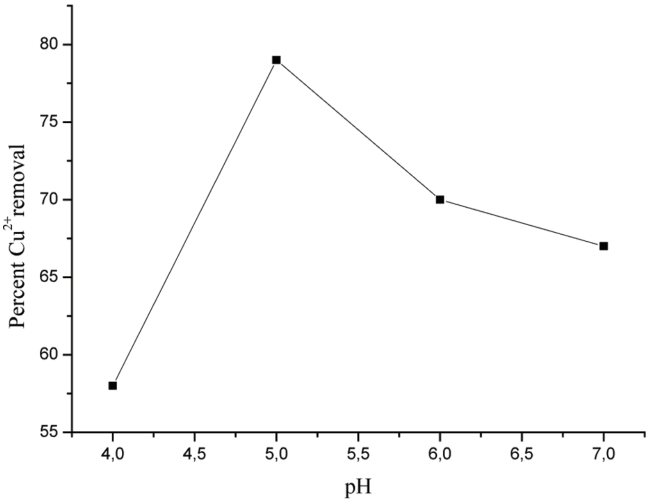

Fig. 1. Effects of pH on percent Cu^{2+} removal by *Retama raetam* plant.

face of the *R. raetam* plant exhibits an increasing positive characteristic.

H^+ ions present at a higher concentration in the reaction mixture and compete with Cu^{2+} ions for the biosorption sites resulting in the reduced 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, mainly Cu^{2+}, would be expected to interact more strongly with the negatively charged binding sites in the sorbent [20,27,28].

3.3. *Effect of solution temperature*

According to our previous sutdies on desert plant *Acacia raddiana* [20], we have found the same effect of the temperature on the biosorption of copper cations by *R. raetam* plant. The sorption of copper cations increased slightly with the increase in temperature up to 50°C and then started decreasing. The temperature higher than 30°C caused a change in the texture of the biomass and thus reduced its sorption capacity (Table 3). Usually the physical sorption reaction is exothermic and preferred at a lower temperature [27].

Table 3
The biosorption quantity of Cu^{2+} onto *R. raetam* plant at different temperature. Initial Cu^{2+} concentration C_0 = 100 mg l^{-1}, pH 5, 4 h

T (°C)	Final Cu^{2+} concentration C (mg l^{-1})	Percent Cu^{2+} removal (%)
25	21	79
30	21	79
40	39	61
50	58	42
60	79	21

3.4. *Phytochemical characterization of aerial parts of* R. raetam

Retama raetam Forssk., locally named as -R'tm- is a glabrescent large shrub belonging to the Fabaceae family. It is common in the Northern Africa and East Mediterranean region [29–32]. In Algeria, it is largely located in Sahara and arid steppe regions. The plant flowers from March to April and plays an important ecological role, it is widely used in dune stabilisation and soil fixation (Fig. 2). In Algerian Sahara, *R. raetam* provides food for many desert animals and is largely recommended by

Fig. 2. *Retama raetam* in its natural habitat (El Bayadh region, March 2007).

traditional herbal healers for treatment of various illness as diabetes, hypertension and gastro-intestinal disorders [33–35].

According to our previous phytochemical screening of the aerial parts of *R. raetam*, we reported the presence an important quantities of flavonoids, tritepenoids saponin, alkaloids, phytosterol, cellulose, hemicellulose and lignin [31,33]. It has been reported that the plant contains various flavones and glycosides flavonoids [36,37]. It is known that these natural compounds present in the cell wall are the most important sorption sites. Therefore, the importance of these natural compounds is that they contain functional groups as hydroxyl, carboxylic, carbonyl and amine groups which are important sorption sites for the binding of metal ions [26,38]. Thus, biosorption of copper ion occurs as a result of ion exchange or complex formation between metal ions and functional groups (hydroxyl, amine, carboxyl) on the cell surface of the biomass.

4. Conclusions

This study showed that the aerial parts of *Retama raetam* can be used as an inexpensive biosorbent and as suitable alternatives for the removal of copper ions from wastewater. The process of biosorption was dependent on the initial concentrations of adsorbate (Cu^{2+} ions), pH and temperature, respectively. The optimal pH was 5 and the temperature was 25–30°C. Copper cation biosorption obtained was nearly 88%, and the equilibrium was reached in 4 h.

Thus, biosorption of copper ions occurs as a result of ion exchange or complex formation between metal ions and functional groups (hydroxyl, amine, carboxyl) on the cell surface of the biomass. Additional work will be required in order to determine the biosorption of other heavy metal ions and to determine the mechanism of copper sorption by *Retama raetam* plant.

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References

[1] M. Horsfall, A.A. Abia and A.I. Spiff, Afr. J.Biotechnol., 2 (2003) 360–364.

[2] S.P. Mishra, D. Tiwari, R.S. Dubey and M. Mishra, Bioresour. Technol., 63 (1998) 1–5.

[3] M. Ajmal, A.H. Khan, S. Ahmad and A. Ahmad, Water Res., 32(10) (1998) 3085–3091.

[4] X.-S. Wang and Y. Qin, Process Biochem., 40(2) (2005) 677–680.

[5] A. Leusch, Z.R. Holan and B. Volesky, J. Chem.Technol. Biotechnol., 62 (1995) 279–288.

[6] N. Rangsayatorn, P. Pokethitiyook, E.S. Upatham and G.R. Lanza, Environ. Int., 30 (2004) 57–63.

[7] N. Meunier, J. Laroulandie, J.F. Blais and R.D. Tyagi, Biores. Technol., 90 (2003) 255–263.

[8] W. Jianlong, Z. Xinmin, D. Decai and Z. Ding, J. Biotechnol., 87 (2001) 273–277.

[9] M.N.V. Prasad and H. Freitas, Environm. Pollution, 110 (2000) 277–283.

[10] H. Benaıssa and M.A. Elouchdi, Chem. Eng. Processing, 46 (2007) 614–622.

[11] J.P. Chen, W.R. Chen and R.C. Hsu, J. Ferment. Bioeng., 81(5) (1996) 458–463.

[12] N. Chubar, J.R. Carvalho and M.J.-N. Correia, Colloids Surf. A: Physicochem. Eng. Aspects, 230 (2004) 57–65.

[13] R.C. Vaishya and S.C. Prasad, Indian J. Environ. Prot., 11(4) (1991) 284–289.

[14] B. Yu, Y. Zhang, A. Shukla, S. Shukla and K.L. Dorris, J.Hazard. Mater., B80 (2000) 33–42.

[15] M.A. Ferro-Garcia, J. Rivera-Ultrilla, J. Rodriguez-Gordillo and I. Bautista-Toledo, Carbon, 26(3) (1988) 363–373.

[16] M.S. Tanyildizi, A. Ozer and F. Tumen, Bilimleri Dergisi, 11(2) (1999) 145–154.

[17] I. Villaescusa, M. Martinez and N. Miralles, J. Chem. Technol. Biotechnol., 75 (2000) 1–5.

[18] Z. Al-Qodah, Desalination, 196 (2006) 164–176.

[19] S. Larous, A.-H. Meniai and M. Bencheikh Lehocine, Desalination, 185 (2005) 483–490.

[20] M.F. Talhi, A. Cheriti, N. Belboukhari and C. Roussel, CMTDE-2007, Tunisia.

[21] P. Kaewsarn, Chemosphere, 47 (2002) 1081–1085.

[22] Y.S. Ho and G. McKay, Adsorption, 5 (1999) 409–417.

[23] U. Danis, Y. Kaya and O.F. Algur, Fresenius Environ. Bull., 10(4) (2001) 363–367.

[24] F. Beolchini, F. Pagnanelli, L. Toro and F. Veglio, Water Res., 40(1) (2006) 144–152.

[25] M. Alkan and M. Dogan, J. Colloid. Interf. Sci., 243 (2001) 280–291.

[26] S. R. Popuri, A. Jammala, K.V.N. Suresh Reddy and K. Abburi, Electr. J. Biotech., 10(3) (2007) 358–367.

[27] Y. Nuhoglu and E. Oguz, Process Biochem., 38 (2003) 1627–1631.

[28] U. Forstner and G.T.W. Wittmann, Metal Pollution in the Aquatic Environment, Springer, Berlin–Heidelberg–New York, 1981.

[29] P. Quezel and S. Santa, Nouvelle flore de l'Algérie et des régions désertiques méridionales, Tome I et II, Paris, Ed. CNRS, 1962 et 1963.

[30] A. Chehma, Catalogue des plantes spontanées du sahara septentrional algérien, Ain Mila, Ed. Dar el Houda, 2006.

[31] A. Cheriti, Plantes médicinales du sud ouest algérien: Ethnopharmacologie, CRSTRA, Algiers, 2000.

[32] M. Mahdhi, A. Nzoue, P. de Lajudie and M. Mars, Prog. Natural Sci., 18 (2008) 43–49.

[33] A. Cheriti, N. Belboukhari and S. Hacini, Ir. J. Pharm. Res., 3(2) (2004) 51.

[34] Ibn Baytar, El djamia limoufradet el Adouia, Ed Dar El Koutob Elmia, Beirut, 1992.

[35] A. Cheriti, N. Belboukhari, K. Sekkoum and S. Hacini, J. Algerien des regions arides, 5 (2006) 7–10.

[36] M. Kassem, S.A. Mosharrafa, N.A.M. Saleh and S.M. Abdel-Wahab, Fitoterapia, 71 (2000) 649–654.

[37] A.E. El-Sherbeiny, H.I. El-Sissi, M.A. Nawwar and M.A. El-Ansari, Planta Med., 34 (1978) 335.

[38] B. Volesky and Z.R. Holan, Biotechnology Progress, 11 (1995) 235–250.