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BIOREMOVAL OF Cu(II) FROM AQUEOUS SOLUTION BY BIOSORBENT FROM THE DESERT *TAMARIX APHYLLA* BARK

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ABSTRACT

The biosorption of Cu(II) ion from aqueous solutions using a new biosorbent obtained from the bark of the desert tree *Tamarix aphylla*, has been studied. The effect of initial metal concentration (50–250 mg L^{-1}), pH (3-7) and temperature (25-60 °C), on Copper biosorption were investigated. Equilibrium at 25ºC was reached after 4 h and Copper cations biosorption in excess of 82% was obtained at pH 6. The relation between the chemical composition of the biomass from *Tamarix aphylla* (flavonoids, tannins, saponins, terpenoids, carbohydrates, coumarins, alkaloids….....) and the percent of adsorption for Copper ion was examined.

Keywords: Biosorption; Heavy metal; Copper; Wastewater; *Tamarix aphylla;* Tamaricaceae.

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1. INTRODUCTION

The environment is exposed to different anthropogenic pollutants generated by human activities (industrial, agricultural and domestic). Heavy metals such as Antimony (Sb), Arsenic (As), Cadmium (Cd), Chromium (Cr), Cobalt (Co), Copper (Cu), Iron (Fe), Lead (Pb), Manganese (Mn), Mercury (Hg), Nickel (Ni), Selenium (Se), Silver (Ag), Tin (Sn) and Zinc (Zn) do not degrade, persist in nature and could easily accumulate throughout the trophic chain, increased susceptibility to disease in man and animal (hepatic, kidney, nerves and the immune system damage and block functional vital groups…..) [1-4].

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]. Thus, it becomes essential to study new and alternative technologies to remove trace metals from wastewater. It is well known that conventional wastewater treatment (sludge separation, chemical precipitation, electrochemical process, membrane separation, reverse osmotic treatment, ion-exchange and solvent extraction) are often expensive with low selectivity and are impractical when the heavy metal ions amount in solution is lower than 100 mg L^{-1} [5-7].

It has been reported that some metals at trace amounts are essential to human and many other living species and are essential nutrients that are required for various biochemical and physiological functions [8], but can become highly toxic when reaching an excessively large doses concentrations. In the Dangerous Substances Directive (2006/11/EC) of the European Union, Copper has been registered as a List 2 Dangerous Substance and is classified with Zinc, Arsenic, Chromium and Cobalt as the most frequently reported RBSPs (river basin-specific pollutants) causing failures of ecological status [9].

Copper, like all heavy metals, is potentially toxic. The maximum allowable level of copper in drinking water considered safe by the World Health Organisation is 1,5 mg L^{-1} [10-12]. 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 [1, 13].

Biosorption of heavy metals from aqueous solutions by using biosorbent from biomass is a relatively new technology for the treatment of industrial wastewater. Several natural biosorbents have been studied and developed for the effective removal of heavy metals like peat, fly ash, algae, soya bean, coconut husk, sago waste, peanut hull, hazelnut, bagasse, rice hull and plants biomass [1, 13-18].

In Algeria, especially the desert region is increasingly confronted with the problem of the scarcity of water. The region is characterized by irregular rainfall with a generally variable pattern of distribution and the major environmental issues include: soil erosion; desertification, petroleum refining wastes, and other industrial effluents are leading to the environmental pollution [19, 20].

Continuing our studies on the valorization of Algerian Sahara plants as biomaterials for the biosorption of toxic heavy metals from water [1, 13-15], We present here our results on the use of the locally available desert tree *Tamarix aphylla*. To our knowledge, no information is available for heavy metals biosorption from aqueous solutions by the bark of this desert tree. Thus, effects of operating conditions like initial metal concentration, pH and temperature, on Copper biosorption were investigated. The relation between the phytochemical composition (flavonoids, tannins, saponins, terpenoids, carbohydrates, coumarins, alkaloids…...) of *Tamarix aphylla* bark and the percent of adsorption for copper ion was examined.

2. RESULTS AND DISCUSSION

2.1. Effect of initial Copper ions concentration

The biosorption capacity is governed by a series of properties, such as pore and particle size distribution, specific surface area, cation exchange capacity, pH, temperature and surface functional groups of biosorbent [1, 21].

As shown in Table 1, we noted that biosorbed Cu(II) ion concentrations increased with time and reached equilibrium after 4 h for all initial Copper ion concentrations tested. An increase of time up to 15 h did not show notable effects.

Table1. Variation of biosorbed Cu (II) concentration with time for different initial concentrations, pH 6, T = 25 °C

Initial Cu^{2+} concentration C_0 (mg L^{-1})	Biosorbed Cu^{2+} concentration , q_e (mg Cu^{2+}. g biomass^{-1})							
	Time(h)	**01**	**02**	**03**	**04**	**05**	**09**	**15**
50		26	34	40	42	42	42	42
100		66	74	78	82	82	82	82
150		89	97	101	105	105	105	105
200		93	101	105	109	109	109	109
250		95	103	107	111	111	111	111

The equilibrium solid phase metal ion concentration is an important parameters in biosorption. The heavy metal ions Cu(II) concentrations were varied between 50 and 250 mg L^{-1} at constant pH 6, as indicate in Table 2. Cu^{2+} ion percent removal decreased from 84% to 44,4%. We observed that the biosorption characteristic indicates that the surface saturation is dependent on the initial metal ion concentrations. Thus, at low initial Cu^{2+} concentrations, such as 50 mg L^{-1} to 150 mg L^{-1}, the majority of Copper ions were biosorbed onto binding sites on *Tamarix aphylla* bark surfaces and adsorption sites took up the available metal more quickly. However, at high initial Copper ion concentrations, such as 200 mg L^{-1} and 250 mg L^{-1}, a large fraction of binding sites on biomass surfaces were occupied by Cu(II) ions and metals need to diffuse into the biomass surface by intra-particular diffusion and greatly hydrolyzed ions will diffuse at a slower rate [13-15, 22].

Table 2. Variation of percent Cu(II) removal with the initial concentration at the end of 4h, pH 6, T = 25°C

Initial Cu^{2+} concentration C_0 (mg L $^{-1}$)	Final Cu^{2+} concentration C (mg L $^{-1}$)	Biosorbed Cu^{2+} concentration q_e (mg g $^{-1}$)	% Cu^{2+} removal
50	8	42	84
100	18	82	82
150	45	105	70
200	91	109	54,5
250	139	111	44,4

2.2. Effect of pH

It has been reported in literature that the pH of the solution is the most important parameter in the biosorption process to remove heavy metals [1, 4, 13, 14]. The result in table 3, indicate that removal of Cu(II) by the *Tamarix aphylla* bark increased with pH, when we treated a 100 mg/L Cu(II) ions solution at pH values from 3 to 7.

Table 3. Effects of initial pH on percent Cu(II) removal concentration.

Initial Cu^{2+}concentration C_0 = 100 mg L^{-1}, T = 25 °C, 04h

pH	Final Cu^{2+} concentration C (mg L^{-1})	Biosorbed Cu^{2+} concentration q_e (mg g $^{-1}$)	% Cu^{2+} removal
3	90	10	10
4	42	58	58
5	24	76	76
6	18	82	82
7	29	71	71

The best increase in the biosorption rate of Cu(II) ions on the *Tamarix aphylla* bark was observed at pH 6, but at lower pH, 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.. As the pH decrease, the surface of the *Tamarix aphylla* bark exhibits an increasing positive characteristic. At around pH 6, Cu(II) cations, would be expected to interact more strongly with the negatively charged binding sites in the biosorbent [13, 23, 24]

2.3. Effect of temperature

Following the previously mentioned parameters in experimental conditions, constant temperature was varied from 25ºC to 60ºC. Biosorption of Cu^{2+} depends on temperature, which increased slightly with the increase in temperature up to 30ºC and then started decreasing (Table 4). The temperature higher than 50ºC caused a change in the texture of the biomass and thus reduced its sorption capacity. Our result is in accordance with literature which indicate that the physical sorption reaction is exothermic and preferred at lower temperature [13-15, 23, 24].

Table 4. Biosorption quantity of Cu^{2+} at different temperature Initial Cu^{2+}concentration C_0 = 100 mg L^{-1}, pH 6, 04h

T °C	Final Cu^{2+} concentration C (mg L^{-1})	% Cu^{2+} removal
25	22	82
30	22	82
40	45	63
50	68	25
60	81	11

2.4. Chemical Characterization of *Tamarix aphylla* bark

Tamarix aphylla (vernacular name**:** *Tlaya, Ethel, Laarich*) belongs to Tamaricaceae family is a tree, mostly growing along watercourses in arid areas. It is very resistant to saline and alkaline soils. It is found in North Africa, in the Middle East and Asia. Botanically the specie has a rounded crown of many stout branches with drooping twigs. It reaches a height of 10–18 m and may attain a diameter of 0.8 m. The leaves are gray-green, having long scales which overlap closely on the twigs. Flowers are small, pink in color, and arranged in spike-like racemes. The fruit is a small capsule with three valves. The plant flowers from spring through the summer [25, 26].

Tamarix aphylla leaves have been used as traditional remedies for the treatment of various diseases such as rheumatism, diarrhea and gingivitis and used as antidiabetic, diuretic, anthelmintic, antihaemorrhoid. The plant has been used to cure dromedary galls and as antimicrobial agents [27-30]. The specie is found to be rich in polyphenolic compounds such as flavonoids, phenolic acids, tannins and coumarins [31, 32].

By applied of classical phytochemical screening on the bark's *Tamarix aphylla*, we found that the bark contains a significant amount of flavonoids, tannin and another natural substance such as: tritepenoids saponin, tritepenoids, cellulose, coumarins and trace of alkaloids. 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 potential binding sites for the sequestration of metal ions [1, 33]. In another hand, polysaccharides are important components of the cell wall of bark's tree containing ionisable functional groups such as carboxyl, phosphoric, amine, and hydroxyl groups. They can constitute up to 40% of the dry matter and have a great affinity for divalent cations [34-36]. So, the biosorption of Cu(II) cation 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 derived from the desert tree *Tamarix aphylla* bark.

3. EXPERIMENTAL

Bark of tree *Tamarix aphylla* used in this work was collected from Bechar (South, Algeria) in February 2017. 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.

All chemicals used in this study were of analytical grade and solutions were prepared using double distilled water. Experiments were performed according to our previous works to determine the effect of various parameters (contact times, initial metal concentration, pH and temperature) on the biosorption of Cu^{2+} onto *Tamarix aphylla* bark. [13-15].

4. CONCLUSION

In this study, batch adsorption experiments for the bioremoval of Cu(II) from aqueous solution by biosorbent from the desert *Tamarix aphylla* bark was carried as functions of important parameters (contact time, concentrations of adsorbate, solution pH and temperature). In the light of results obtained, the desert biomass of *Tamarix aphylla* bark could be used as an efficient and inexpensive biosorbent for the removal of Cu(II) ions from aqueous solutions in excess of 82% at 04 hours. The process of biosorption was pH and temperature dependent, respectively optimal pH was 6 and temperature was 25-30ºC.

Finally, additional work will be required in order to study the biosorption of other heavy metals ions by this eco-friendly biomaterial.

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