

Heavy Metal Biosorption Characteristics of the Submerged Aquatic Plant (*Nasturtium officinale*)

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In the present investigation an aquatic plant, *Nasturtium officinale* was examined for its biosorption ability of heavy metal ions. The results obtained from biosorption experiments were used to understand the driving forces that govern the interaction between metal ions and biosorbent. The experimental biosorption data were fitted to the Scatchard plot, Langmiur and Freundlich isotherms. According to the parameters of the Langmiur isotherm, the maximum biosorption capacities of Cd²⁺ and Co²⁺ were 0.56 and 0.49 mg/g, respectively. In view of Freundlich isotherms, the maximum biosorption capacities of Cd²⁺ and Co²⁺ were 2.23 mg/g for both of metal ions.

Key Words: Biosorption, Heavy metal, Freundlich isotherm, Aquatic plant, *Nasturtium officinale*.

INTRODUCTION

Heavy metals are major pollutants in marine, ground, industrial and even treated wastewaters. Stringent regulations are increasing the demand for new technologies for metal removal from wastewater to attain today's toxicity-driven limits¹.

Heavy metals can be removed from industrial wastewater by a range of physico-chemical treatment technologies such as precipitation, ion exchange, adsorption, electrochemical processes and membrane processes². However, regulatory standards are not always met. Moreover, these technologies are expensive and energy-intensive, driving towards a search of economic alternatives in both developing and developed countries³. The use of biological materials for removing and recovering heavy metals from contaminated industrial effluents has emerged as a potential alternative method to conventional techniques, which may be expensive and ineffective¹. The aquatic plants including dead or living biomass have been used as heavy metal accumulator and, therefore, the use of aquatic plants for the removal of heavy metals from wastewater gained high interest⁴. The use of aquatic plants such as *Myriophyllum spicatum*⁴, *Ceratophyllum demersum*⁵, *Lemna minor*⁶, *Eichhornia crassipes*⁷, *Pistia stratiotes* and *Salvinia herzogii*^{8,9} and *N. officinale*^{10,11} for the removal of heavy metals from wastewater has been investigated by many authors. The literature showed that *N. officinale* could be used for the removal of heavy metals such as Cd and Co.

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The aim of the present study is to investigate the use of *N. officinale* as a biosorbent for the removal of Cd and Co from an aqueous solution.

EXPERIMENTAL

Samples of the plant materials were collected from the Tigris river of Turkey on May of 2008 and were transferred to the laboratory in polyethylene bags. The collected plant materials were washed with dilute hydrochloride acid (3 %) and distilled water to eliminate the adhering foreign materials. Plants of similar size, shape and height were selected and used for the heavy metal uptake studies. Analytical grade cobalt(II) nitrate and cadmium(II) nitrate were used as the metal sources and stock solutions of these metal ions were prepared in deionized water.

General procedure: The biosorption tests were conducted at 25 °C in conical flasks (250 mL) using an orbital shaker in a constant room temperature. The initial pH values were between 5 and 6 during the batch experiments and no pH adjustment was made. Therefore, all the biosorption experiments were carried out at pH values of < 6. *N. officinale* biomass (about 2 g wet weight) was added to each flask, volume was made on 100 mL with the metal solution and placed on the orbital shaker. The initial metal concentrations were 0.1, 0.3, 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 mg/L and the incubation times ranged from 24 to 72 h. The data used to derive the Scatchard plot, Langmuir and Freundlich equations were obtained by using *N. officinale* biomass. After contacting, the contents of the flask were filtered to separate the biomass from the solution.

Detection method: The filtrates mentioned above were then analyzed with an atomic absorption spectrophotometer (ATI Unicam, Model 929) to determine the metal concentrations in the samples. Control experiments were performed for each metal to measure any adsorption onto the glassware. Neither precipitation nor adsorption onto the walls of the flasks were observed. The results of metal analysis were used to calculate the specific adsorption (mg metal adsorbed/g of biomass, dry weight). All the experiments were duplicated and the results presented as mean values. The variation was < 5 %. All the chemicals were used of analytical grade unless state otherwise (Merck). There are three widely accepted and easily linearized adsorption isotherm models used in the literatures which are proposed, respectively, by Langmuir, Freundlich and Scatchard.

RESULTS AND DISCUSSION

The biosorption capacity of a biosorbent which is obtained from the mass balance on the sorbate in a system with solution volume V, is often used to acquire the experimental adsorption isotherms. Under the optimum conditions, the biosorption capacities (q_{eq}) of biosorbent for each concentration of studied metal ions at equilibrium were calculated from the following equation:

$$q_{eq} = \frac{(c_o - c_{eq})V}{X} \quad (1)$$

where c_0 is the initial concentration of solution, c_{eq} , the concentration of solution at equilibrium, V the volume of solution, X the mass of biosorbent.

The nonlinearized adsorption isotherms (q_{eq} versus c_{eq}) of the metal ions on the biosorbents were shown in Fig. 1. These isotherms show that the amount of metal adsorbed increases as its equilibrium concentration increases in solution. As evident from these data, adsorption isotherms of metal ions were steep, indicating a greater affinity of metal ions on the powdered forms of both biosorbents. However, the optimization of a biosorption process using a batch technique requires an understanding of the driving forces that govern the interaction between metal ions and a biosorbent. The Langmuir and Freundlich isotherms were applied to account for these interactions as a first approach. Then, we used the Scatchard plot in order to obtain more compact information about the interaction between metal ions and the biosorbent. The Scatchard linearized form (eqn. 2) of the Langmuir equation used here not only to determine the adsorption parameters, but also to obtain a preliminary prediction about the types of interaction and biosorbent affinity for metal ions.

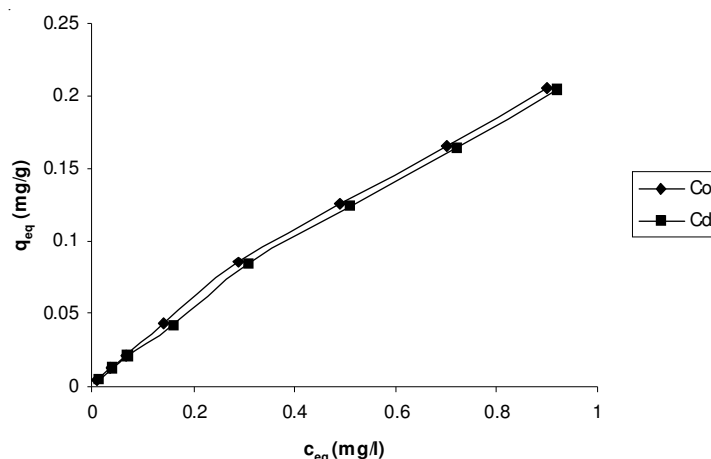


Fig. 1. Non-linear isotherms for the equilibrium binding of metal ions on *N. officinale*

$$\frac{q_{eq}}{c_{eq}} = q_m K_b - q_{eq} K_b \quad (2)$$

where q_{eq} is the amount of metal ion adsorbed per unit weight, c_{eq} is the equilibrium concentration of metal ion, K_b and q_m are the adsorption binding constant and maximum biosorption capacity, respectively. The shape of the plot of q_{eq}/c_{eq} versus q_{eq} is related to the type of interaction of the sorbate with a sorbent. If the Scatchard plot is linear with a negative slope, it is related to independent interaction between the sorbate and the binding sites in the sorbent, which follows the Langmuir model¹². In this work, the Scatchard plots were straight lines but with low regression coefficients (Table-1). This indicates that there was no change in the affinity of the binding sites

for metal ions over the whole range of concentrations studied. The Scatchard plot of the results of equilibrium adsorption indicated the presence of one type of binding site for metal ions on the biosorbent (Fig. 2). Binding constants and correlation coefficients calculated from the Scatchard isotherm results were also given in Table-1. The results show that the adsorptions of Cd and Co on the biosorbent were similar adsorption characteristics. This situation is probably due to a similar affinity of Cd and Co for the active site of the biosorbent.

TABLE-1
ADSORPTION ISOTHERM PARAMETERS FOR Cd AND Co BY USING
Nasturtium officinale AS BIOSORBENT

Metal	Scatchard plot analysis			Langmuir isotherm			Freundlich isotherm		
	K_b	Q_m	r^2	A_s (mg/g)	K_b (L/mg)	r^2	K_F	n	r^2
Cd	0.63	0.53	0.7996	0.56	0.58	0.8603	2.23	1.13	0.9993
Co	0.81	0.46	0.7238	0.49	0.73	0.8662	2.23	1.16	0.9990

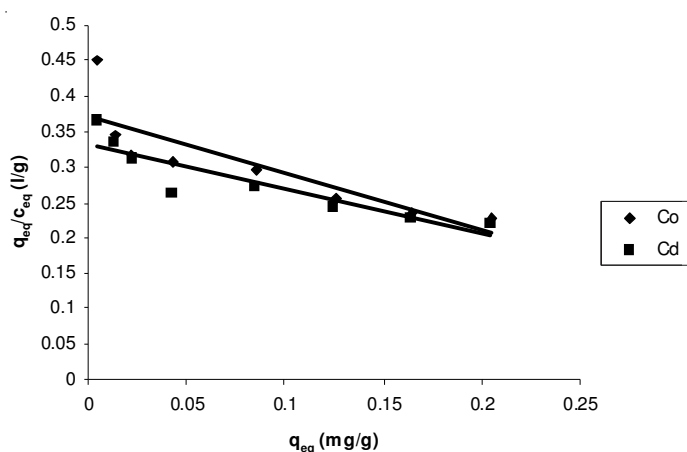


Fig. 2. Scatchard plots for the metal ions adsorption on *N. officinale*

The Scatchard plots have indicated that adsorption of metal ions followed the Langmuir model. However, we tested the adsorption data against the Standard isotherm models, the Langmuir and Freundlich in order to investigate in detail the adsorption characteristics and to compare the adsorption performance of the adsorbents for the biosorption of metal ions. The Langmuir (eqn. 3) and Freundlich (eqn. 4) isotherms are represented by the equations below:

$$\frac{c_{eq}}{q_{eq}} = \frac{1}{K_b A_s} + \frac{c_{eq}}{A_s} \quad (3)$$

$$\ln q_{eq} = \ln K_F + \frac{1}{n} \ln c_{eq} \quad (4)$$

where q_{eq} and c_{eq} are the equilibrium ligand adsorption capacity of the biosorbent and the equilibrium ligand concentration in the aqueous solution, respectively. A_s , K_b , K_F and n are the adsorption isotherm parameters. A_s is the maximum amount of the metal ions per unit weight of biosorbents to form a complete monolayer on the surface bound at high c_{eq} and K_b is a constant related to the affinity of the binding sites. A_s represents a practical limiting adsorption capacity when the surface is fully covered with metal ions and assists in the comparison of adsorption performance, particularly in cases where the biosorbent did not reach its full saturation in experiments. The Langmuir equation is valid for monolayer sorption onto a homogeneous surface with a finite number of identical sites. The empirical Freundlich equation given above is based on a monolayer adsorption by the adsorbent with a heterogeneous energy distribution of active sites. K_F and n (it is desired to be $0.1 < n < 1$) are indicators of adsorption capacity and adsorption intensity, respectively¹³. The Freundlich isotherm is also more widely used but provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model¹⁴.

Table-1 also shows the adsorption constants and correlation coefficients obtained from the Langmuir and Freundlich isotherms at the room temperature using *N. officinale*. As can be seen in this table, high regression correlation coefficients were not obtained from the Langmuir isotherms (Fig. 3). The results showed that the adsorption equilibrium data has fitted to the Freundlich adsorption models (Fig. 4) in the concentration range studied with high correlation coefficient. The n values obtained from calculations presented in Table-1 were in the range between 1.13 and 1.16. These values indicated that the metal ions were favourably adsorbed by *N. officinale* in the present study. The applicability of the Freundlich isotherms to the biosorption of metal ions showed that heterogenous energetic distribution of active sites on the surface of adsorbent conditions exist under the experimental conditions employed.

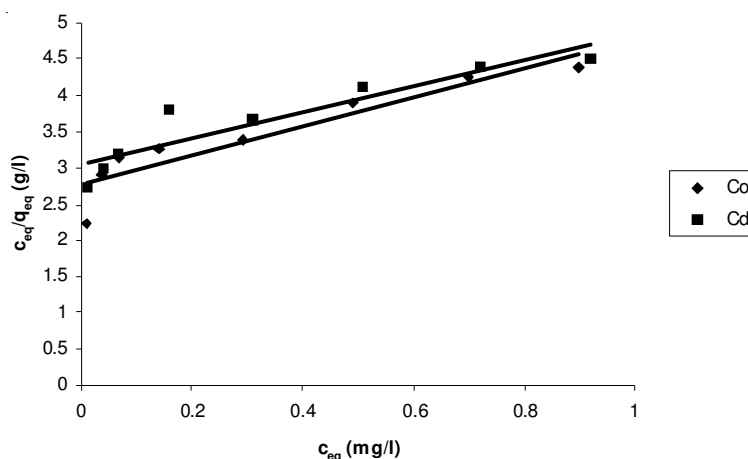


Fig. 3. Langmuir adsorption isotherms of the metal ions adsorption on *N. officinale*

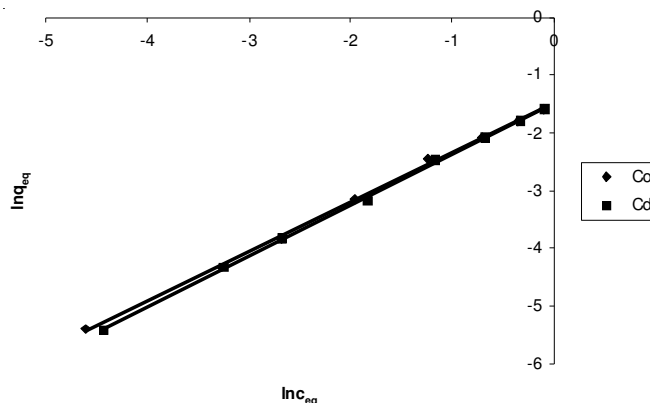


Fig. 4. Freundlich adsorption isotherms of the metal ions adsorption on *N. officinale*

Conclusion

In this study *N. officinale* was used as a biosorbent for Cd and Co removal from aqueous solution. The results showed that initial metal concentration affected the biosorption performance. The adsorption equilibrium data fitted well to the Freundlich isotherms. The maximum biosorption capacities were found of 2.23 for the both of the metals when *N. officinale* was used as a biosorbent. Finally, *N. officinale* can be used as a potential biosorbent for the removal of Cd and Co ions from aqueous solution.

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