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Evaluation of the Activated Carbon Prepared of Algae Marine *Gracilaria* for the Biosorption of Ni (II) from Aqueous Solutions

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Abstract: Biosorption of heavy metals can be an effective process for the removal and recovery of heavy metal ions from aqueous solutions. In this study, the batch removal of nickel (II) ions from aqueous solution under different experimental conditions using activated carbon prepared of red alga *Gracilaria* was investigated in this study. The nickel (II) uptake was dependent on initial pH and initial nickel concentration, with pH 5 being the optimum value. The equilibrium data were fitted using Langmuir and Freundlich isotherm model, with the maximum nickel (II) uptake of 99.03% determined at a pH of 5. At various initial nickel (II) concentrations (30-70 mg/L), If the adsorption is design correctly, it will be attractive. sorption equilibrium was attained between 15 and 120 min. The nickel (II) uptake by activated carbon was best described by Pseudo-second order rate model. This study, shows the usage of activated carbon as a valuable material for the removal of Ni from aqueous solution wastewater and a better substitute to be used in activated marine red algae.

Key words: Nickel · *Gracilaria* · Activated carbon · Langmuir and Freundlich · Removal · Alga · isotherm model

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 limits [1].

If the adsorption is design correctly,it will attractive method for the removal of solutes from effluents [2].

Where the concentrations of the heavy metal ions are relatively low, biosorption is an alternative technology in which an increased amount of study is focused [3]. Biosorption utilizes the ability of the biological materials to accumulate heavy metals from aqueous solutions by either metabolically mediated or purely physico-chemical pathways of uptake [4]. Marine algae are biological resources which are available in large quantities in many parts of the world. Surface adsorption is qualifying to be an important basis for the treatment of toxic nickel contaminated water [5]. Activated carbon has undubitably been the most popular adsorbent used in wastewater treatment throughout the world and still used for a new activated carbon. The aim of the present work was to test the ability of an activated carbon from *Gracilaria* to remove nickel (II) ions from aqueous solution.

MATERIALS AND METHODS

Preparation of Biomass: The biomass used was the red seaweed *Gracilaria*. It was collected from the Persian Gulf on Queshm Island. Before use, it was washed several times with tap water to remove the sand particles and dirt. Then clean alga was sun dried for 5 days. Dry biomass was milled and an average of 0.5 mm particles was used for biosorption experiments.

Activated Carbon: The dried red alga *Gracilaria* 112 g was added in small portion to 90 mL fume cupboard of 97% H_2SO_4 and the resulting mixture was kept for 24 h at room temperature, followed by refluxing in fume hood for 4 h. After cooling, reaction mixture was washed repeatedly with deionized water and soaked in 2% $NaHCO_3$ solution to remove any remaining acid,and pH of

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the activated carbon reached 7 and was dried in an oven at 150°C for 46 h.

Chemicals: The synthetics solutions were all prepared by use of deionized water and analytical grade salt o. $NiCl_2$. $6H_2O$ (97%) (Merck supplied). Adsorption of Ni was studied using different dosages of activated carbon in 30 mL, solution of (30-70 ml) of initial concentration and initial pH 5.0. All the adsorption experiments were carried out at room temperature (23 2 C). $NiCl_2$. $6H_2O$ (97%). The pH of sample solution was adjusted with 1M HCL or 1 M NaOH during the equilibrium period, at the obtained optimal values for heavy metal.Using agitation speed (200 rpm) for 2 h. Then, the solution was filtered and the filtrate was measured for ion content (C_e) by an atomic adsorption spectroscopy (GBC-932).

RESULTS AND DISCUSSION

Effect of Agitation Time: The equilibrium time required for biosorption of on activated carbon is obtained by studying adsorption of nickel at various initial concentrations and fixed amount of activated carbon at different time intervals. The effect of contact time on biosorption has been shown in Fig. (1). The uptake of Ni^{+2} ions increased quickly and after 15 min, the change become slow. However, an increase in retention time for 15 to 120 min results in a decrease in the remaining concentration of heavy metals.

Effect of pH on Biosorption: The effect of pH on Ni (II) biosorption on activated carbon is studied at room temperature by varying the pH of Ni (II) solution activated carbon suspension from 1 to 11. The uptake of Ni (II) showed an increase with increasing pH from 1 to 5.0. The uptake of Ni (II) in pH 1, 2, 3, 4, 5 was obtained in 64.00%, 65.80%, 67.91% and 81.32%, respectively. The lower uptake at higher pH value is probably due to the formation of anionic hydroxide complexes [6]. Because of this effect, at higher pH values, the ligands such as carboxylate and sulfonate groups could uptake fewer metal ions [7].

Effect of Metal ion Concentration on Biosorption: By increasing initial concentration, the uptake was decreased. This was due to the saturation of the sorption sites on adsorbents.The maximum uptake of nickel with initial concentrations, 30, 50 and 70 mg L at pH 5.0 and after 60 min was in the ranges of 99.03, 97.99 and 95.12%.

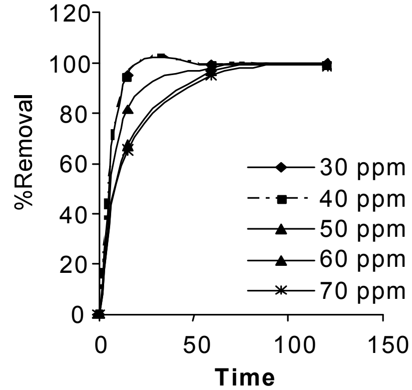

Fig. 1: The effect of time on percentage of removal for different Ni^{2+} Concentration at pH 5.0 and room temperature using 0.6g of activated carbon

Equilibrium Studies: The equilibrium adsorption isotherm is fundamentally important in the design of adsorption systems. Equilibrium studies in adsorption give the capacity of adsorbent. It is described by adsorption isotherm characterized by certain constants whose values express the surface properties and affinity of the adsorbent. Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, usually being the ratio between the quantity adsorbed and that remaining in the solution at a fixed temperature at equilibrium [8]. In order to investigate the adsorption isotherm, two equilibrium mode

Langmuir Isotherm: The Langmuir adsorption isotherm is probably the most widely applied adsorption isotherm. A basic assumption of the Langmuir theory is that adsorption takes place at specific homogeneous sites within the adsorbent. The saturated monolayer isotherm can be represented as [9].

$$q_e = b.q_{max}.C_e/1+ b.C_e \quad (1)$$

Where q_e is the amount of metal ion adsorbed (mg g^{-1}), C_e is the equilibrium concentration (mg L^{-1}), q is the maximum adsorption capacity and b is an affinity constant.

Freundlich Isotherm: The empirical Freundlich equation based on a monolayer adsorption by the adsorbent with a heterogeneous energy distribution of active sites is given below by Eq (2).

$$q_e= K_f.\ C_e^{1/n} \quad (2)$$

Table 1: Isotherm parameters obtained for biosorption of nickel using activated carbon

Isotherm model	0.4 g	0.6 g
Langmuir		
Qm(mg g^{-1})	2.686	2.305
b (L mg^{-1})	0.673	1.100
R^2	0.924	0.993
Freundlich		
1/n	0.144	0.175
KF (mg g^{-1})(L mg^{-1})$^{1/n}$	1.595	1.322
R	0.979	0.982

Table 2:Parameters obtained for Second-order kinetic model

Parameter		Second-order kinetic model			
Activated carbon	Initial Ni concentration (mg L^{-1})	q_e (experimental)	K_2	q_e (calculated)	R^2
0.6 g	30	1.41	37.93	1.01	1.00
0.6 g	40	1.28	49.21	1.01	1.00
0.6 g	50	1.33	14.86	1.03	0.99
0.6 g	60	1.41	7.76	1.06	0.99
0.6 g	70	1.62	6.870	1.12	0.99

Where K_f and n are the Freundlich constants [10]. The results showed that the data could be well modeled according to the Langmuir and Freundlich adsorption isotherm. These isotherm constants for Ni^{+2} are presented in Table 1.

Adsorption Kinetics Studies: The kinetic of adsorption describes the rate of nickel ions uptake on activated carbon, which controls the equilibrium time. The adsorption kinetics of Ni (II) biosorption on algae follows second order rate expression given by:

$$dq_t/ d_t= K2(q_e-q_t)^2 \qquad (3)$$

Where K is the equilibrium rate constant (g / mg min). q and q are the sorption capacity at equilibrium at time t. The integrated form of Eq (3) becomes:

$$1/ (q_e-q_t) = 1/ (q_e) + K_2t \qquad (4)$$

This has linear form:

$$t / q_t= 1/ K_2. q_e^2+ (1/ q_e)t \qquad (5)$$

A plot of t / q versus t indicates a straight line of slope (1/ q) and an intercept of (1/ K_2. q_e^2) [11,12]. This isotherm constants are presented in Table 2. This result suggest that the sorption of Ni^{+2} ions followed the second-order kinetic model, which relied on the assumption that biosorption could be the rate-limiting step.

CONCLUSIONS

In this study, adsorption of Ni (II) on activated carbon prepare of alga (*Gracilaria*) has been investigated. The data obtained through this work supports the view that the activated carbon is an effective low cost adsorbent for the removal of nickel from aqueous solution. Different dosage of biosorbent did not have an effect on the results, but 0.6 g of biosorbent was showed higher uptake. Sorption rate would be increased by increasing retention. The adsorption of metal ions is dependent on the amount of concentration of metal ion and retention time and pH of the metal solution. The equilibrium adsorption data are correlated by Langmuir and Freundlich isotherm equation. The adsorption kinetic data can be described by the second-order kinetic models. These methods are become less the great amount of indiscriminate effluent carries out around the small industry concerns.

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