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Research Article

Isotherm studies of removal of Cr (III) and Ni (II) by *Spirulina* algae

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Abstract

This study describes the sorption of Chromium (III) and Nickel (II) from aqueous solution by *Spirulina* algae. The batch experiments have been done. The optimum pH and contact time were determined and sorption models were applied. The percentage of removal and distribution coefficients (K_d) were obtained for the sorption process as a function of solution concentration. The sorption process follow Langmuir model. It was shown that the sorption process depend on hydrated ion diameter and charge density. The maximum uptake efficiency of algae was found to be 74% for Cr (III) and 63 % for Ni (II) maximum pH is 6.

Keywords: Heavy metal, isotherms, sorption, *Supirlina* algae.

INTRODUCTION

The removal of heavy metals ions has wide concern due to it serious harmful impacts on all organisms. Different than organic pollutants, the most of them are liable to biological degradation, heavy metal cations do not decay into nontoxic products 1. The existence of heavy metals cations is a main concern because of their harmful to lots of life organisms.

Physicochemical and chemical have conventionally been used for eliminate heavy metals from contaminated wastewater however like these processes have many of disadvantages: they are expensive; they are not effective at dilute solutions of heavy metal. This is why many of safe and economical technologies have been developed to produce low cost alternatives 2. Usually, an adsorbent can be characterized as a low cost adsorbent, if it needs a few modifications, is a plentiful in environment or is a waste matter or is a byproduct or waste matter 3. Currently, big attention has been given to new methods, biosorption, which uses algae, bacteria and other microorganisms to eliminate heavy metals from water solutions 4, 5. Biosorption is the method of sorption by either dead biomass or living biomass and it has various significant advantages as (i) high efficiency in eliminating heavy metals even from very low concentrations (ii)) low cost,(iii) high adsorbing capacity and (iv) the ability of recovering the important metals adsorbed 6. Algae cells can be considered as natural ion-exchange matter as they contain various anionic groups on their surface and this allows them to eliminate heavy metal ions efficiently 7, 8, 9, 10, 11. In this study, the adsorbent used is *Spirulina platensis* powder, in which the adsorption takes place on the surface of the insoluble cell walls. Biosorption methods using blue-green alga *Spirulina platensis* are considered as the potential solution due to their economical efficiency, good absorption capacity and ecofriendliness. The effects of several factors such as pH, initial metal concentration and contact time were studied.

MATERIALS AND METHODS

Biosorbent material:

Spirulina was supplied by the National Institute of Oceanography and Fisheries. Commercial synthetic medium for low-cost mass production of *Spirulina*, in a larger scale with constant aeration at room temperature was used. The algae were harvested from medium solution by plankton cloth mesh, 20 diameters. The collected algal were completely dried in sunlight for 3 weeks and then in oven at 60 °C for

1 week. The dried algae were ground using a domestic mixer. The sieved algae was treated by 0.1 M HCl for 4 h. After washing in distiled water the algal was dried at 70º C for 8 h.

Chemicals and Biosorption experiments:

Stock solutions of chromium trichloriede and nickel chloride were prepared. Five different concentrations of heavy metals with five different weights of dried algal cells at room temperature in a shaker were used. After 1 week, the contents were filtered and the filtrate was analyzed after proper dilutions using a flame Atomic Absorption.

Replicated blank controls were done and different heavy metal concentrations were placed in the bottles for all the metal concentration during the bioremoval efficiency (R) of the algae was considered as

$$q = \frac{(C_i - C_e)}{m} * V \quad (1)$$

Where, q = Bioremoval efficiency (%), C_i = initial concentration of heavy metals. C_e= equilibrium concentration of metals in aqueous solution (mg/L).

RESULTS AND DISCUSSION

Effect of PH:

The pH value of equates solution was studied in range of 1 to 7, further than that were not made because precipitation of the metals as hydroxides would be probable to happen. The effect of pH on sorption of Cr and Ni is presented in Fig. 1. The graph shows that the sorption increases till pH 6 then it decreases.

When the metal dissolve in aqueous solution, the solubility of the metal ions substitutes some of the positive ions established in the active sites, and influences the degree of ionization of the adsorbate during the process. The pH of the solution has a great effect on the adsorption capacity of metals; adsorption capacity was a maximum when pH was 6 and decreased by either the raising or lowering of pH values

under the present range of experimental condition 12. At acidic medium, the metal ion removal was finite in lower pH, and this can be due to competition of the existence of H^+ ions and the Cr (II) or Ni (II) ions on the adsorption sites 13. While the metal ion at high pH was tend to precipitate during hydrolysis.

Effect of contact time:

Time is one of the most important affective factors in all sorption system. Many researchers studied the effect of contact time on adsorption process 14. The effect of time on heavy metals solutions is seen in Fig.2. The sorption was studied for high concentration 100mg/l at different time (5, 10, 20, 30, 60, 80, 90 and 120 min). We can see that the maximum removal of heavy metals was attained at 40 min for Cr and 50 min for Ni.

Sorption isotherms:

There are many sorption isotherms express the equilibrium relation between sorbate and sorbents. Two sorption equations were used to fit the data Freundlich and Langmuir.

Langmuir

The Langmuir model is largely used in various sorption processes sorption supposes 15 that the sorption of heavy metals is a taking place on a monolayer homogenous surface, with no interaction between sorbed ions. The sorption occurs till a whole monolayer of sorbents is completed 16.

The Langmuir model can be expressed as

$$q_e = q_m\left(\frac{bC_e}{1+bC_e}\right) \quad (2)$$

The major parameters of the Langmuir equation, constants b and q_m can be obtained by a linerized form of the Langmuir equation:

$$\frac{1}{q_e} = \frac{1}{bq_n\,C_e} + \frac{1}{q_n} \quad (3)$$

Where, C_e is the equilibrium concentration (mg/l), q_m is the sorption capacity (mg/l) and b is the Langmuir constant related to the free sorption energy (l/mg). The plots of sorption ($1/q_e$) various the equilibrium concentrations ($1/C_e$) are shown in Fig. 3 and the linear isotherms, q_m, b and the coefficient of determinations are presented in (Table 1).

The sorption capacity which is related to complete monolayer coverage showed that the efficiency of sorption of *Spirulina* was Cr >Ni. R^2 values obviously show that Langmuir model fit the data very well.

Freundlich isotherm

Usually the Freundlich sorption isotherm fits the sorption data over a broad range of concentrations. This model provides an explanation including the heterogeneity of the surface and the exponential distribution of active binding sites beside to their energies 17. The Freundlich isotherm is an empirical equation of sorption on a heterogeneous surface, can be determined by the flowing equation

$$q_e = K_d C_e^{1/n} \quad (4)$$

This equation can be linearized to determine the characteristics of Freundlich model as the following form

$$lnq_e = lnK_d + \frac{1}{n}lnC_e \quad (5)$$

The Freundlich adsorption isotherms were also applied to the removal of Cr and Ni, since the adsorption phenomena depend on the charge density of cations, the diameter of hydrate cations is very important. The charge of the Cr ion is the (3^+) and Ni (2^+) ion, the ionic radius of Cr (III) (the smallest diameter) have maximum adsorption. K_d is a Freundlich constant indicates sorption capacity (mg/g) on heterogeneous sites with non-uniform distribution of energy level and the constant 1/n related to the intensity of the sorption. The sorption coefficient k_d that is linked to the energy of sorption for Cr and Ni was determined in table 1.

CONCLUSION

The tradition ways for removal of heavy metal ions in the wastewater are expensive methods. Also they can cause secondary contaminants and are not efficient for low concentrations. In this study the *Spirulina* algae were used to remove chromium and nickel. Adsorption has been shown to be an economically feasible alternative method for removing heavy metals from wastewater. The removal of Cr (III) and Ni (II) ions depend on the sorption process. Hence it increases with increasing the pH parameter of the sorbate. Sorption of Cr (III) and Ni (II) metal ions was fitted with Langmuir model rather than Freundlich model. The studies showed that *Spirulina* can be used as an alternative cheap way and efficient material to remove high toxic heavy metal ions from wastewater.

Table 1
Fitted parameters of adsorption onto *Spirulina* algae

	Cr	**Ni**
Freundlich		
K_d(mg/g)	29.4	7.69
1/n	0.37	0.43
R^2	90	91
Langmuir		
q_m(mg/g)	4.69	2.96
b(l/mg)	0.64	0.73
R^2	99	99

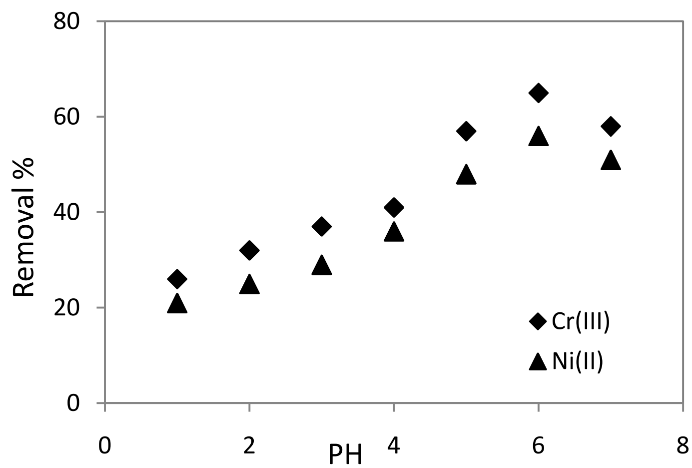

Figure 1
Effect of pH on the sorption of Cr (III) and Ni (II) on to Spirulina algae

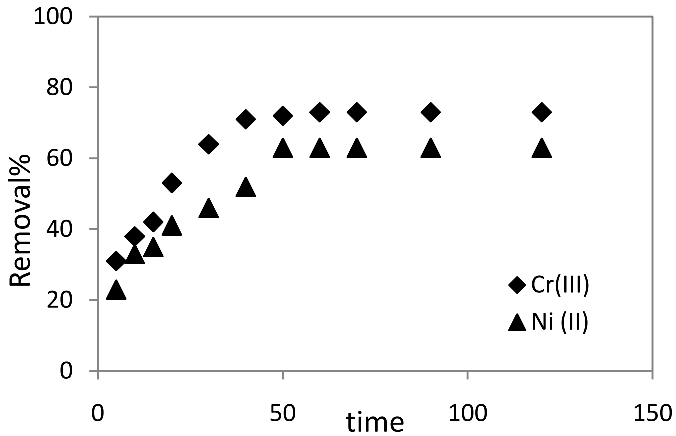

Figure 2
Effect of time on the sorption of Cr (III) and Ni (II) on to Spirulina algae

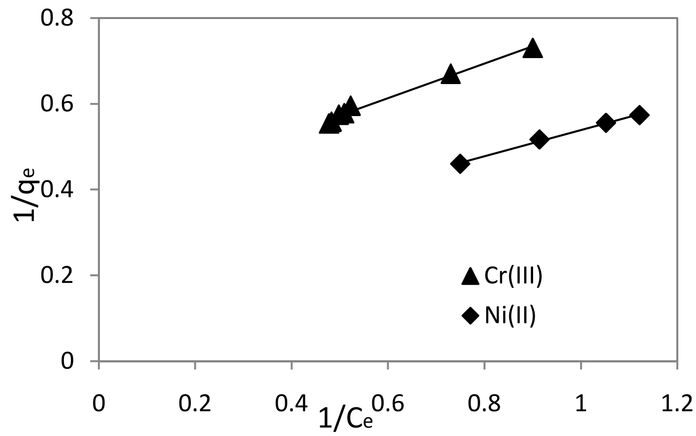

Figure 3
Langmuir isotherm for adsorption of Cr (III) and Ni (II) on to Spirulina algae

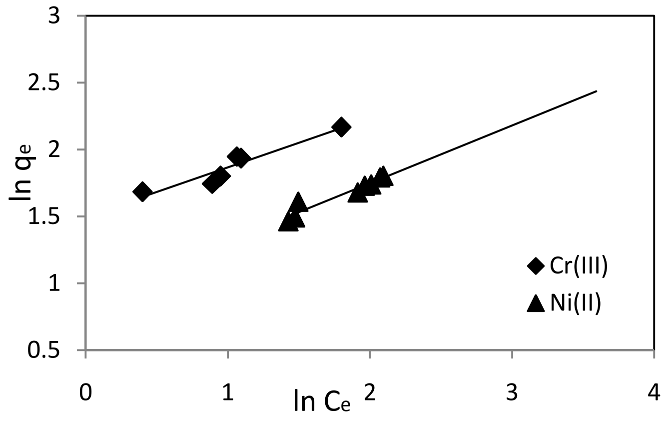

Figure 4
Freundlich isotherm for adsorption of Cr (III) and Ni (II) on to Spirulina algae

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