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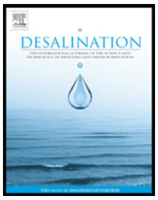

Bio-sorption of cadmium and nickel ions using *Spirulina platensis*: Kinetic and equilibrium studies

Abuzer Çelekli [a,*], Hüseyin Bozkurt [b]

[a] *Department of Biology, Faculty of Art and Science, University of Gaziantep, 27310, Gaziantep, Turkey*
[b] *Department of Food Engineering, Faculty of Engineering, University of Gaziantep, 27310, Gaziantep, Turkey*

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ABSTRACT

The present study dealt with sorption of cadmium (Cd^{2+}) and nickel (Ni^{2+}) ions on *Spirulina platensis* as a function of contact time, initial metal concentration, and pH regimes. Characterization of this adsorbent was confirmed by FTIR spectrum. Rapid sorption of both metal's ions was observed during the first 60 min of contact time and favored at pH_i 5. The sorption of these metal's ions could be described by Langmuir isotherm that maximum sorptions (73.64 mg g^{-1} for Cd^{2+} and 69.04 mg g^{-1} for Ni^{2+}) are related to saturated monolayer of adsorbate molecules on the surface. Sorption kinetics of Cd^{2+} and Ni^{2+} ions on *S. platensis* was better described by pseudo second-order model. This sorption could be explained by the intra-particle diffusion, which was composed of more than one sorption processes. The cyanobacterium showed remarkable performance for removing of Cd^{2+} and Ni^{2+} ions as an eco-friendly process.

1. Introduction

Metal pollution is one of the most important environmental problems due to disposal of hazardous effluent into natural waters [1–3]. Various industries (such as mining and smelting of metalliferous, electroplating, battery manufacture, textile, refinery and petrochemical, leather, pesticides, and chemicals) produce and discharge wastewater containing metals into receiving water, which cause a serious environmental problem [3,4]. Heavy metals are non-biodegradable and tend to accumulate in photosynthetic organisms and transfer pollutants to consumers, including humans, leading to various diseases and disorder [4,5].

Cadmium and nickel ions are usually encountered together in industrial wastewaters from mine drainage, paint and ink formulation units, plating plants and porcelain enameling etc. [6]. Combination of cadmium with hydroxyl radicals, superoxide anions, nitric oxide and peroxides in various organs can cause cancers such as the lung, kidney, pancreas, prostate, and liver [7,8]. Besides, it is known that that cadmium is accumulated in the kidney causing malfunction such as overdose resultin in spilling of proteins in the urine and disruption of protein metabolism [2]. An essential amount of nickel may be benefit organisms as a component in a number of enzymes, participating in important metabolic reactions (methane biogenesis, hydrogen metabolism, ureolysis, and acidogenesis) [4]. However, an over permissible value of nickel exposure causes various diseases, such as renal edema, lung cancer, pulmonary fibrosis, skin dermatitis, and gastrointestinal discomfort [4,6].

Effluent from the plating plants vary from 10 to 80 mg L^{-1} and about 14.6–20.2 mg L^{-1} nickel and cadmium, respectively [2]. The conventional methods, such as chemical precipitation, ion exchange, reverse osmosis, filtration, and electrochemical treatment have been suggested for removing of metal ions from wastewaters and effluents [3,6,9]. However, these methods are generally costly, have limited applicability, and produce waste containing hazardous materials. Besides, chemical precipitation and electrochemical treatment could be ineffective when applied for the removal of metal ions from dilute solutions, especially in the range of 10–100 mg L^{-1} [3,6,9]. Also, large quantities of residual sludge from these processes are required to be treated.

In order to decrease cost of treatment, researches have been focused on finding inexpensive, effective, and natural alternative techniques such as using of adsorbents. Among the numerous techniques for removing metal ions, the sorption process is one of the cheep, effective, and eco-friendly techniques that has been successfully employed for wastewaters treatments. Biological biomasses such as algae, yeast, fungi, and bacteria etc. have attracted attention as a low-cost treatment technology for sequestering of heavy metal ions from wastewaters [5,8,10,11].

Biomaterial surfaces can be regarded as a mosaic of different functional groups which are responsible for binding of metal ions, including amide ($—NH_2$), carboxylate ($—COO^-$), thiols ($—SH$), phosphate (PO_4^{3-}), and hydroxide ($—OH$) [3–5]. Their intensity depends mainly on the kind, number, affinity and distribution on biopolymers. Therefore, the identification of functional groups is very important for understanding the mechanisms which are responsible for binding of certain metal ions.

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* Corresponding author. Tel.: +90 3423171925; fax: +90 3423601032.
E-mail addresses: celekli.a@gmail.com (A. Çelekli), hbozkurt@gantep.edu.tr (H. Bozkurt).

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Nomenclature

a_{R-P}	Redlich-Peterson isotherm constant $(\mathrm{L\,mg^{-1}})^{\beta}$
b	Langmuir constant $(\mathrm{L\,mg^{-1}})$
β	exponent in Redlich–Peterson isotherm
C_{eq}	metal concentration at equilibrium $(\mathrm{mg\,L^{-1}})$
C_o	initial metal concentration $(\mathrm{mg\,L^{-1}})$
C_t	metal concentration at t time $(\mathrm{mg\,L^{-1}})$
k_1	pseudo first-order rate constant of the sorption $(\mathrm{g/mg\,min^{-1}})$
k_2	pseudo second-order rate constant of the sorption $(\mathrm{g/mg\,min^{-1}})$
k_i	intra-particle diffusion rate constant of the sorption $(\mathrm{mg/g\,min^{0.5}})$
K_F	Freundlich sorption capacity $[(\mathrm{mg\,g^{-1}})(\mathrm{mg\,L^{-1}})^{-\frac{1}{n}}]$
K_{R-P}	Redlich–Peterson isotherm constant $(\mathrm{L\,mg^{-1}})$
l	intra-particle diffusion intercept $(\mathrm{mg\,L^{-1}})$
M	dry weight of adsorbent (g)
N	the number of experimental point
n	Freundlich sorption intensity
p	significance level obtained from ANOVA
$\mathrm{pH_{zpc}}$	the zero point charge of the adsorbent
$\mathrm{pH_i}$	the initial pH of sorption solution
R^2	correlation coefficient
q_{eq}	amount of adsorbed metal per unit weight of biomass at equilibrium $(\mathrm{mg\,g^{-1}})$
q_{exp}	experimental amount of adsorbed metal per unit weight of biomass $(\mathrm{mg\,g^{-1}})$
q_{cal}	calculated amount of adsorbed metal per unit weight of biomass $(\mathrm{mg\,g^{-1}})$
q_m	maximum metal sorption capacity from Langmuir model $(\mathrm{mg\,g^{-1}})$
q_t	amount of adsorbed metal per unit weight of biomass at time t $(\mathrm{mg\,g^{-1}})$
SSE	the Sum of Squares Error
t	time (min)
V	volume of the metal solution (L)
χ^2	Chi-square test statistic

In this study, cadmium (Cd^{2+}) and nickel (Ni^{2+}) ions were selected as the target metals, since they are mainly encountered in industrial wastewaters due to their intensive use in industries. The objective of this study was to remove Cd^{2+} and Ni^{2+} ions from aqueous solution by dried biomass of *Spirulina platensis* as a function of contact time, initial metal concentration, and pH regimes in a batch system. The sorption capacities of this adsorbent were predicted by use of the equilibrium and kinetic models. Furthermore, error functions were carried out to determine the best model.

2. Materials and methods

2.1. Microorganism as adsorbent

The cyanobacterium used in the study, *Spirulina platensis* [12] was inoculated on the Schlösser's medium [13]. This blue green alga was maintained in Erlenmeyer flasks placed on an orbital shaker at 90 rpm under 2.0 klux continuous illumination using cool, white fluorescent lamps. In the stationary phase of growth, biomass of *S. platensis* was harvested by use of centrifugation at 6000 rpm for 6 min. After that pellet was washed twice with distilled water, centrifuged, and then dried at 80 °C for 24 h to obtain its dried biomass. After that, it was grinded and sieved to select the particles between 75 and 100 µm mesh sizes, and stored in plastic bottles.

The infrared spectrum of nature and metal laden adsorbents was obtained by the use of a Fourier transform infrared (FTIR) spectrometer (Perkin–Elmer Spectrum 100 FTIR Spectrometer) equipped with an Attenuated Total Reflection (ATR) accessory (Perkin Elmer) to identify the functional groups responsible for the sorption.

2.2. Sorption studies

Standard concentrate solutions of Cd^{2+} and Ni^{2+} were purchased from Sigma-Aldrich (Sigma-Aldrich Chemie GmbH, Germany). The solutions of metals ions were prepared by diluting Cd^{2+} and Ni^{2+} standard concentrate solutions in distilled water. Initial metal concentrations were adjusted to 25, 50, 75, 100, and 200 mg L^{-1} for the sorption process, respectively.

The sorption studies were carried out in 250 mL Erlenmeyer flask containing 100 mL of solution. This sorption solution consisted of ten milliliters adsorbent suspension (1.0 g L^{-1}) and 90 mL of metal ion solution at a known initial Cd^{2+} or Ni^{2+} concentration, both at the desired initial pH (2, 3, 4, and 5). The initial pH ($\mathrm{pH_i}$) of each solution was adjusted to the desired value with diluted or concentrated HCl and/or NaOH solutions before mixing the adsorbate or adsorbent suspension. The flasks were agitated on the orbital shaker at 150 rpm for 360 min, which was more than ample time for sorption equilibrium.

Samples were taken at 0, 5, 10, 15, 30, 60, 120, 180, 240, 300, and 360 min. They were centrifuged at 6000 rpm for 5 min to precipitate the suspended adsorbent, and the supernatant liquid was analyzed for the residual metal ion concentrations using flame atomic adsorption spectrophotometer (Perkin Elmer AA 400, USA) at 228.7 and 232.0 nm for Cd^{2+} and Ni^{2+}, respectively. Experiments were repeated two times and average values are given in the present study. Blank experiments were conducted without the adsorbent.

The amount of metal ions per unit of adsorbent at time t (q_t; mg g^{-1}) and at equilibrium (q_{eq}, g^{-1}) were calculated by using Eqs. (1) and (2), respectively.

$$q_t = \frac{(C_o - C_t) \times V}{M} \tag{1}$$

$$q_{eq} = \frac{\left(C_o - C_{eq}\right) \times V}{M} \tag{2}$$

where, C_o, C_t, and C_{eq} (mg L^{-1}) represent concentrations of metal ions at initial, at t time, and at equilibrium in the solution, respectively. V is the volume of solution (L), and M is the mass of adsorbent (g).

Table 1
Equations of models and error functions.

	Equation and number	References
Kinetic models		
Pseudo first-order kinetics	$log(q_e - q_t) = \ logq_e - \left(\frac{k_1}{2.303}t\right)$ (3)	[14]
Pseudo second-order kinetics	$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{t}{q_{eq}}$ (4)	[15]
Intra-particle diffusion	$q_t = k_i t^{0.5} + I$ (5)	[16]
Equilibrium models		
Langmuir	$q_{eq} = \frac{bq_o C_{eq}}{1 + bC_{eq}}$ (6)	[17]
	$R_L = \frac{1}{1 + bC_o}$ (7)	[18]
Freundlich	$q_{eq} = K_F C_{eq}^{1/n}$ (8)	[19]
Redlich–Peterson	$q_{eq} = \frac{K_{RP} C_{eq}}{1 + a_{RP} C_{eq}^{\beta}}$ (9)	[20]
Error functions		
Chi-square statistic	$\chi^2 = \sum_{i=1}^{m} \left[\left(q_{\ exp} - q_{cal}\right)^2 / q_{cal}\right]$ (10)	[21]
The sums of squares error	$SSE = \sqrt{\frac{\sum\left(q_{\ exp} - q_{cal}\right)^2}{N}}$ (11)	[21]

Symbols of models and error functions are given in the Nomenclature section.