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Enhanced biosorption of nickel(II) ions by silica-gel-immobilized waste biomass: Biosorption characteristics in batch and dynamic flow mode

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ABSTRACT

Batch and dynamic flow biosorption studies were carried out using the waste biomass entrapped in silica-gel matrix for the removal of nickel(II) ions from synthetic solutions and real wastewater. Batch biosorption conditions were examined with respect to initial pH, S/L ratio, contact time, and initial nickel ion concentration. Zeta potential measurements showed that immobilized biosorbent was negatively charged in the pH range of 3.0–8.0. The immobilized biomass was found to possess relatively high biosorption capacity (98.01 mg g^{-1}), and biosorption equilibrium was established in a short time of operation (5 min). The equilibrium data were followed by Langmuir, Freundlich, and Dubinin–Radushkevich isotherm models. Scanning electron microscope analysis was used to screen the changes on the surface structure of the waste biomass after immobilization and nickel(II) biosorption. Sorbent–sorbate interactions were confirmed by Fourier transform infrared spectroscopy. The applicability of sorbent system was investigated in a continuous mode, and column studies were performed under different flow rate, column size, and biosorbent dosage. Also, the proposed sorbent system was successfully used to remove the nickel ions from industrial wastewater in dynamic flow treatment mode. The results showed that silica-immobilized waste biomass was a low-cost promising sorbent for sequester of nickel(II) ions from synthetic and real wastewater.

1. Introduction

Heavy metals are a group of pollutants that disperse both naturally and by human activities into the environment. Effluents from several industrial operations like electroplating, mining, and metal processing are one of the major contributors to unnatural metal contamination in water sources. Uncontrolled release of heavy metals into the environment can create toxic or inhibitory effect on living systems. Treatment of heavy metals from contaminated effluents using the currently practiced technologies appears to be inadequate and their use is often restricted because of secondary problems with metal-bearing sludge which are extremely difficult to be disposed [1,2].

Therefore environmentally friendly and cost effective new technologies are required for the removal of heavy metals from these waste streams by appropriate treatment before releasing into receiving water bodies. One of the promising alternatives that are receiving more attention is application of biosorption process based on metal–biomass interactions. Microbial and plant origin biomasses were successfully used as biosorbent material in many biosorption studies [3–6].

Biosorption process can use free and immobilized forms of biomasses. Especially, in column applications the use of immobilized form of biomasses provides some advantages, such as improved biosorption capacity and ability to regenerate and separate the biomass from bulk liquid. In addition, easy operation of repeated biosorption–desorption cycles with immobilized biomasses makes the biosorption process potentially more economic and competitive [7–10].

Therefore, some efforts have been made to develop new immobilized biosorbent systems for detoxifying the heavy metals from contaminated waters. Some natural or synthetic polymeric materials including alginates, carrageenan, agar, polyacrylates, silica gel, etc. [11,12] are commonly used as immobilization matrix. Silica gel is a nontoxic, inert, and efficient support and is generated by decreasing the pH value of alkali silicate solution to less than 10. Reactive sites of silica gel exist in large number, and therefore, the number of immobilized organic molecules is high, which results in good sorption capacity for metal ions [11,13–15].

In a recent study, we reported that the waste biomass of *Phaseolus vulgaris* L. can remove a textile dye AR57 [16] from aqueous media as the most potent biosorbent with the high biosorp-

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tion capacity (215.13 mg g^{-1}). However, no studies have thus far reported about the biosorption potential of this waste biomass for heavy metal removal from contaminated solutions. In this present study, we show that the waste biomass of *P. vulgaris* L. derived from canned food plant is capable of nickel(II) biosorption, and its nickel removal capacity was enhanced by immobilization with silica-gel matrix. Biosorption conditions of immobilized biomass were screened by varying the pH, sorbent dosage, contact time and initial metal ion concentration. The mechanism of the biosorption and the surface structure of the biomass were examined by FTIR and scanning electron microscope (SEM) analysis, respectively. Biosorption performance of the immobilized biomass was investigated in continuous mode in addition to determination of various isotherm parameters. Finally, its application for nickel biosorption in real wastewater conditions was also tested in a column.

2. Materials and methods

2.1. Preparation of the biosorbent

The biosorbent used in this study, *Phaseolus vulgaris* L., was provided as a waste biomass, from a canned food factory in Bartın, Turkey. It had been washed with deionized water three times, and dried at 80 °C, to obtain a constant weight. Next, it was grounded and sieved, using an ASTM Standard sieve, to select the particle sizes of 100 mesh and used for immobilization. An immobilization procedure previously described by Lopez et al. [17] was used with some modifications. About 10 g of silica gel was dissolved in 100 mL of 7% (w/v) aqueous solution of potassium hydroxide by heating. After cooling to 20 °C, 100 mL of suspension containing 5 g of biomass in deionized water was added and mixed. A measured amount of phosphoric acid solution (20%) was added, enough to provide the gel formation. The resulting gel was dried at 333 K for 12 h in an oven and subsequently used as a sorbent material in powdered form. Blank silica gel was prepared similarly without having waste biomass and tested for its nickel sorption capacity.

2.2. Biosorption in batch scale

The batch biosorption experiments were performed by mixing 0.1 g of immobilized biomass in 50 mL of synthetic solutions at 100 mg Ni(II) L^{-1} for the determination of optimum pH value. The pH of the solutions was adjusted to different values with 0.1 N nitric acid (HNO_3) and 0.1 N sodium hydroxide (NaOH). The mixtures were mixed on a magnetic stirrer at a rate of 200 rpm. The best amount of biomass was determined by changing the biomass dosage between 0.02 and 0.2 g in 50 mL of solution. The equilibrium time was studied within the time interval of 5–120 min, and the temperature of the solution was controlled at 25 ± 2 °C. Suspended solids were separated from the biosorption medium by centrifugation at 4500 rpm for 3 min and nickel(II) ion concentrations were then measured using Flame atomic absorption spectrophotometer. The equilibrium data were analyzed by some isotherm models by changing the initial nickel(II) ion concentration from 75 to 500 mg L^{-1} for immobilized biosorbent.

2.3. Biosorption isotherms

Analysis of equilibrium data is important for developing an equation that can be used to compare different biosorbents under different operational conditions and to design and optimize an operating procedure. The isotherm models are widely used parameters to examine the relationship between biosorption capacity and sorbate concentration at equilibrium. Among the various sorption isotherm models, Langmuir, Freundlich, and Dubinin–Radushkevich models are widely used for fitting the data.

2.3.1. Langmuir isotherm

The Langmuir isotherm model has been successfully applied to many biosorption processes and the basic Langmuir theory is that biosorption takes place at specific homogeneous sites within the biosorbent [18]. The Langmuir equation [19] is

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \left(\frac{1}{q_{max}K_L}\right)\frac{1}{C_e} \tag{1}$$

where q_e and q_{max} are the equilibrium and monolayer biosorption capacities of the biosorbent (mol g^{-1}), respectively, C_e is the equilibrium Ni(II) concentration in the solution (mol L^{-1}) and K_L is the Langmuir constant (L mol^{-1}) related to the free energy of biosorption.

The Langmuir constant, K_L, can be used to determine the suitability of the biosorbent to sorbate by using Hall separation factor (R_L, dimensionless) and R_L can be calculated as follows [20]:

$$R_L = \frac{1}{1 + K_L C_o} \tag{2}$$

where C_o is the highest initial sorbate concentration (mol L^{-1}).

2.3.2. Freundlich isothrem

The Freundlich equation is an empirical expression based on biosorption on a heterogeneous surface. The Freundlich [21] model is represented by the equation:

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{3}$$

where K_F (L g^{-1}) is Freundlich constant related to biosorption capacity of biosorbent and n (dimensionless) is Freundlich exponent indicating the biosorption intensity [21,22].

2.3.3. Dubinin–Radushkevich isotherm

Since the Freundlich and Langmuir isotherm models do not give any idea about the mechanism of biosorption, the equilibrium data are tested with the D–R isotherm model. Dubinin and Radushkevich [23] have reported that the characteristic biosorption curve is related to the porous structure of the sorbent. The Dubinin–Radushkevich (D-R) equation is generally expressed as follows:

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \tag{4}$$

where $\varepsilon = RT\ln(1 + 1/C_e)$ (Polanyi potential), q_m is the biosorption capacity (mol g^{-1}), β is the constant related to the biosorption energy, R is the gas constant (8.314 kJ mol^{-1}) and T is the absolute temperature (K).

Polanyi sorption theory assumed [24] fixed volume of sorption space close to the sorbent surface and existence of sorption potential over these spaces. The mean free energy of biosorption (E) can be calculated from the Eq. (5).

$$E = \frac{1}{(2\beta)^{1/2}} \tag{5}$$

2.4. Fixed-bed column studies

These experiments were performed in small-scale cylindrical fixed-bed columns. A known quantity of immobilized biomass was packed between two layers of glass wool into the column. Ni(II) ion solution was pumped from bottom to top through the column at a desired flow rate by a peristaltic pump (Ismatec ecoline). All the column studies were performed at room temperature of