Journal of Hazardous Materials 164 (2009) 1012–1018

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

The removal of nitrate from aqueous solutions by chitosan hydrogel beads

Sudipta Chatterjee, Seung Han Woo*

Department of Chemical Engineering, Hanbat National University, San 16-1, Deokmyeong-Dong, Yuseong-Gu, Daejeon 305-719, Republic of Korea

ARTICLE INFO

Article history:
Received 8 April 2008
Received in revised form 30 August 2008
Accepted 1 September 2008
Available online 5 September 2008

Keywords:
Adsorption
Chitosan
Hydrogel beads
Nitrate

ABSTRACT

A physico-chemical investigation of the adsorption of nitrate by chitosan hydrobeads was conducted. The adsorption of nitrate by chitosan hydrobeads was increased with a decrease in the pH of the solution. The adsorption process was found to be temperature dependant with an optimum activity at 30 °C. Adsorption capacity was found to decrease with increases in temperature after 30 °C, indicating the exothermic nature of this process. Theoretical correlation of the experimental equilibrium adsorption data for the nitrate–chitosan hydrobeads system was properly explained by the Langmuir isotherm model. This was supported by the fact that homogeneity index was close to unity (0.98–1.08) from Langmuir–Freundlich isotherm model. The maximum adsorption capacity was 92.1 mg/g at 30 °C. The kinetic results corresponded well with the pseudo-second-order rate equation. Intra-particle diffusion also played a significant role at the initial stage of the adsorption process. Thermodynamic parameters such as the Gibbs free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) for the nitrate adsorption were estimated. Results suggest that the adsorption process is a spontaneous, exothermic process that has positive entropy. Desorption of nitrate from the loaded beads was accomplished by increasing the pH of the solution to the alkaline range, and a desorption ratio of 87% was achieved around pH 12.0.

1. Introduction

Water resources are heavily polluted by several nitrogen containing compounds, such as nitrate, nitrite, and ammonium, which may cause severe environmental problems including eutrophication [1]. Nitrate, in particular, causes outbreaks of infectious diseases such as cancer of the alimentary canal and cyanosis among children [2]. Excess nitrate in drinking water may cause blue-baby syndrome, which results from the conversion of haemoglobin into methaemoglobin, which cannot carry oxygen [3].

Therefore, numerous techniques for the removal of nitrate from water samples have been reported. These include biological de-nitrification [4], chemical reduction [5], reverse osmosis, electrodialysis [6], and ion exchange [7]. Biological de-nitrification is not effective at temperatures below 7 °C, and therefore, it may not be useful for treating groundwater. A chemical reduction process requires the addition of chemicals and may release toxic compounds into the environment, especially when H_2 is used as a reductant. Reverse osmosis is too expensive to treat a large amount of wastewater. Compared with these methods, ion exchange is a simple and effective method. But the main problem is that the ion exchange resin is still quite expensive and retains some sulphate and hydrogen carbonate, which induce significant changes in the water composition. It also causes an increase in the chloride concentration of water because the ion exchange resin replaces nitrate with chloride [8].

Adsorption is the process that is used to collect soluble substances in solution on a suitable interface. Adsorption onto activated carbon is a very traditional way to treat wastewater. However, activated carbon is quite expensive and also can be used for nonionic pollutants in most cases. Recently, different low cost adsorbents including some industrial and agricultural wastes such as activated waste sepiolite [1] and modified wheat residue [9] have been used to remove nitrate from water. The biopolymer chitosan has gained importance in environmental biotechnology due to its very high adsorption capacity of dyes and metal ions [10,11]. Moreover, chitosan can be obtained on an industrial scale by chemical deacetylation of crustacean chitin. Chitosan hydrobeads have become a very effective biosorbent for the removal of heavy metals in the field of industrial wastewater treatment [12–14].

The aim of this study is to determine the efficacy of chitosan in the form of hydrobeads to remove nitrate from its aqueous solution and to investigate the interaction between nitrate and chitosan during adsorption.

* Corresponding author. Tel.: +82 42 821 1537; fax: +82 42 821 1593.
E-mail addresses: shwoo@hanbat.ac.kr, shwoo@postech.ac.kr (S.H. Woo).

0304-3894/$ – see front matter © 2008 Published by Elsevier B.V.
doi:10.1016/j.jhazmat.2008.09.001

2. Materials and methods

2.1. Preparation of chitosan beads

Chitosan and all other chemicals used in this study were purchased from Sigma Chemical Co., USA. Ten grams of chitosan was dissolved in 300 ml of 5% acetic acid (v/v) solution and it was diluted to 1 l by stirring overnight. Then it was allowed to stand for another 6 h. Chitosan hydrobeads were prepared by drop-wise addition of this chitosan solution to an alkaline coagulating mixture (H_2O:MeOH:NaOH: 4:5:1, w/w) as described by Mitani et al. [15]. The beads were spherical in shape with an average diameter of 2.5 mm. Prior to use, chitosan beads were kept in water for 30 min with the pH adjusted to that required for different experimental conditions.

2.2. Analysis and data calculation

A stock solution (1.000 g/l) of nitrate was prepared in deionized water and diluted to obtain the desired concentrations of nitrate. The concentration of the nitrate ion in the experimental solution was determined from the calibration curve prepared by measuring the area (μS/cm sec) of the nitrate ion by 790 Personal Ion Chromatography (Metrohm Ion Analysis, Switzerland) using Suppressed CD detector. The analytical column was METROSEP A Supp 5 column (100 mm l × 4.0 mm ID). The sample was eluted (eluent: 3.2 mM Na_2CO_3 + 1.0 mM $NaHCO_3$) at a flow rate of 0.7 ml/min with a retention time of 7.0 min for nitrate detection. The adsorption capacity of chitosan in the form of hydrobeads is calculated using equilibrium studies. The mass balance equation for this process at equilibrium condition is given by

$$q = \frac{(C_0 - C_{eq}) \times V}{W} \quad (1)$$

where q (mg/g) is the adsorbent capacity, C_0 (mg/l) is the initial concentration of nitrate, C_{eq} (mg/l) is the final or equilibrium concentration of nitrate, V is the experimental solution volume (l), and W is the weight of chitosan in the form of hydrobeads (g).

2.3. Effect of pH

The effect of pH on nitrate adsorption process was studied over the pH range 3.0–8.0; and the initial nitrate concentration was fixed at 50, 100, 250, 500, and 1000 mg/l. Then 50 ml of a pH-adjusted nitrate solution with a predetermined initial concentration and 1 g of chitosan hydrobeads with a water content of 96.4% were placed in separate 125 ml Erlenmeyer flasks. The flasks were agitated (120 rpm) at 30 °C for 24 h. At the end of incubation, beads were separated from the solution by filtration and the concentration of the nitrate in the solution was determined.

2.4. Equilibrium adsorption isotherm

The equilibrium adsorption isotherm was used to describe the effect of pH when the initial nitrate concentration was varied from 1 to 1000 mg/l. The pH and temperature of incubation were 5.0 and 30 °C, respectively. The same experiment was also repeated at three different temperatures (viz., 20, 40, and 50 °C).

2.5. Kinetic study

The rate of adsorption of nitrate was studied at different time intervals that were as long as 1440 min using different initial concentrations (100, 250, 500, and 1000 mg/l) at pH 5 and 30 °C. Other experimental conditions were the same as described earlier.

2.6. Desorption study

After performing the equilibrium study with an initial nitrate concentration of 500 mg/l, nitrate-adsorbed chitosan hydrobeads were collected by filtration by thoroughly washing with deionized water. Loaded beads were transferred to different 125 ml Erlenmeyer flasks; each flask contained 50 ml water and the pH was adjusted to 9.0, 10.0, 11.0, and 12.0. The flasks were agitated at 100 rpm for 24 h at 30 °C. The concentration of the eluted nitrate was measured. Desorption of the nitrate from the chitosan beads was evaluated by the following equation.

$$\text{Desorption ratio}\,(\%) = \frac{\text{Amount of desorbed nitrate}}{\text{Amount of adsorbed nitrate}} \times 100 \quad (2)$$

3. Results and discussion

3.1. Effect of pH

The effect of pH on the adsorption of nitrate by chitosan hydrobeads is shown in Fig. 1. Nitrate adsorption was found to increase with a decrease in the pH of the solution because a decrease in the pH of the solution resulted in more protons being available to protonate the chitosan amine group. This resulted in an enhancement of nitrate adsorption by chitosan beads due to increased electrostatic interactions between chitosan's negatively charged nitrate group and positively charged amine group.

The surface charge of chitosan is positive in acidic pH, gradually decreases with increasing in pH and has zero potential at pH 6.4. However, the adsorption at pH 6.4, where the surface charge of chitosan beads is neutral may be due to physical forces. At pH above 6.4, an appreciable amount of nitrate adsorption by chitosan beads indicates the involvement of physical forces.

3.2. Equilibrium adsorption isotherm

The adsorption of nitrate from its aqueous solution by chitosan hydrobeads at different temperatures is presented in Fig. 2. The adsorption of the nitrate was at its maximum at 30 °C. The equilibrium adsorption capacity decreased when the temperature was increased from 30 to 50 °C. This result indicates the exothermic nature of nitrate adsorption onto chitosan beads. A decrease in the nitrate uptake value with the rise in temperature may be due to

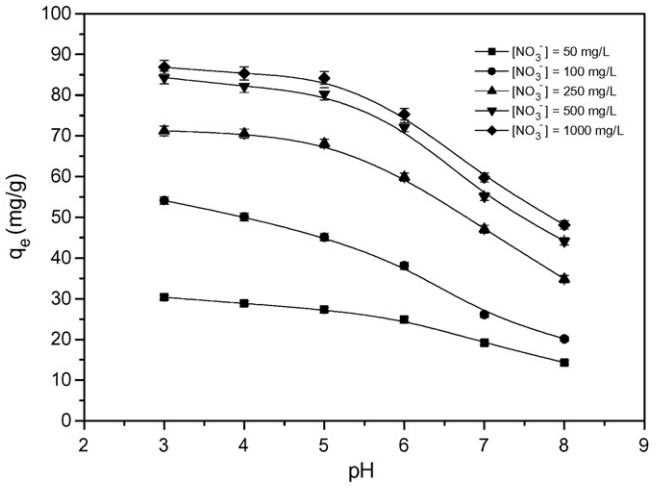

Fig. 1. Effect of pH on nitrate adsorption by chitosan hydrobeads at different initial nitrate concentrations.