Adsorption of Boron from Aqueous Solutions by Sepiolite: II. Column Studies

D. Kavak, N. Öztürk

Osmangazi University, Faculty of Engineering and Architecture, Department of Chemical Engineering, 26480, Eskişehir

ABSTRACT: A continuous fixed bed study was carried out by using HCl activated waste sepiolite (AWS) as an adsorbent for the removal of boron from aqueous solutions. The breakthrough curve was obtained and the capacity value for column study was calculated by graphical integration as 219.01 mg/g for AWS. The Thomas and the Yoon-Nelson models were applied to experimental data predict the breakthrough curves and to determine the characteristic parameters of the column useful for process design. Desorption test performed with 2.46 M H_2SO_4.

1. INTRODUCTION

Boric acid and boron salts have extensive industrial use m the manufacture of glass and porcelain, in wire drawing, the production of leather, carpets, cosmetics and photographic chemicals, for fiteproofmg fabrics, and weatherproofing wood. Boron compounds are used in certain fertilizers for the treatment of boron deficient soils. Boric acid, which has mild bactericidal and fungicidal properties, is used as disinfectant and as food preservative. Borax is widely used in welding and brazing of metals, and more recently, boron compounds have found applications for hand cleansing, high-energy fuels, cutting fluids and catalysts (Şahin, 2002). During the production of boron compounds, many of these are introduced into the environment in the form of waste. For this reason boron must be removed from wastewater (Öztürk et al., 2002).

Adsorption is a separation process in which certain components of a fluid phase are transferred to the surface of a solid adsorbent. Over the last few decades adsorption has gained importance as a purification and separation process on an industrial scale (Öztürk et al., 2003, Kopaç and Kocabaş, 2002). Activated carbon is currently the most widely used adsorbent for wastewater treatment, but recognizing the high cost of activated carbon, many investigators have studied the feasibility of cheap, commercially available materials as its possible replacements (Morais et al., 1999).

Waste sepiolite obtained during the production of ornaments and tobacco pipes by carving was preferred as adsorbent. The relatively low cost of sepiolite guarantee its continued utilisation in the future, and most of the world sepiolite reserves are found in Turkey/Eskişehir (nearly 70%) (Balcı and Dinçel, 2002; Saniz and Nuhoğlu, 1992). In adsorption, adsorbent surface area must be large. Surface area can be increased by activation (Kıpçak, 1999; Radojevic et al., 2002). During acid activation, the proton (H^4) of the acids replaces part of the Mg^{2*} ions located in the octahedral sheet of sepiolite.

In this study, boron removal from aqueous solutions by column adsorption method was investigated by using HCl activated waste sepiolite (AWS). The Thomas and Yoon-Nelson models were applied to column study. Column capacities were calculated.

2. EXPERIMENTAL WORK

Sepiolite was obtained from carving waste, in Eskişehir (Margı) area. Non activated waste sepiolite (NAWS) was activated with 400 mL, 0.75 M HCl in a reactor under reflux condenser at 75°C for 4 h. Adsorbent were dried at 105°C for 2 h and screened before being used. Adsorbent particle sizes used in adsorption experiments were between 71 and 80 urn. Surface areas of waste sepiolites calculated from Langmuir equation were determined by measurements of the adsorption of N_2 in a NOVA 2200 at 77 K. Surface areas of NAWS and AWS were given in m^2/g: 516.3, 519.06, respectively.

The aqueous solution of H3BO3 was prepared by using the analytical grade Merck product. The solution was prepared in such a manner that the initial boron concentration adsorption experiments was held at 600 mg/L. pH was measured with pH meter (Consort P903).

A glass column (0.7 cm ED and 15 cm length) was filled with 0.5 g of AWS on glass wool support. Boron solution (600 mg/L B) at 20°C and pH 10 was delivered downflow to the column using a peristaltic pump (ATTO SJ 1211 model) at a 0.15 mL/min flow rate. To obtain breakthrough curve the effluent was collected as 1.5 cm^3 fractions with a fraction collector (Spectra/chrom CF-1) and analysed. Boron was determined using HACH DR-2000 Spectrophotometer by carmine method. Column studies were terminated when the column reached exhaustion. The desorption studies carried out after the column adsorption studies were conducted at 20°C and 0.15 ml/min flow rate. The adsorbed boron was desorbed from AWS by using 2 M H_2SO_4 solution.

3. RESULTS AND DISCUSSION

The performance of packed beds is described through the concept of the breakthrough curve. The breakthrough curve shows the loading behaviour of boron to be removed from solution in a fixed bed and is usually expressed in terms of adsorbed boron concentration $(C_{ad}$ =inlet boron concentration (C_0) - outlet boron concentration (C_e)) or normalised concentration defined as the ratio of effluent boron concentration to inlet boron concentration $\left(C/_{C_r}\right)$ as a function of time or volume of effluent for a given bed height (Aksu and Gönen, 2004). The area under the breakthrough curve obtained by integrating the adsorbed concentration $(C_{ad}$; mg/L) versus the throughput volume (V ; L) plot can be used to find the total adsorbed boron quantity (maximum column capacity). Total adsorbed boron quantity $(q_0$; mg/g) in the column for a given feed concentration and flow rate is calculated from Eq. (1)

$$q_o = \int_0^{V_T} \frac{(C_0 - C_e)dV}{m} \tag{D}$$

where VT is the volume of effluent collected upon exhaustion of the bed and m is the mass of the adsorbent (g). The capacity value q_0 was obtained by graphical integration as 219.01 mg/g. The height of the mass transfer zone hz is given by the relation (Agyei et al., 2002):

$$h_Z = h_T\left[\left(V_Z/_{V_T} - 0.5V_Z\right)\right] \tag{2}$$

$$V_Z = V_T - V_E \tag{3}$$

where hj is the bed height and Vg is the volume of effluent collected up to breakthrough. The value of hz was calculated as 0.53 cm for boron removal by AWS at studied column.

3.1. Application of the Thomas Model

Successful design of a column adsorption process requires prediction of the concentration-time profile or breakthrough curve for the effluent. The maximum adsorption capacity of an adsorbent is also needed in design. Traditionally, The Thomas model is used to fulfil the purpose. The model has

the following form (Mathialagan and Viraragravan, 2002).

$$\frac{C_e}{C_o} = \frac{1}{1+\exp\left[\dfrac{K_T(q_o m - C_o V)}{\theta}\right]} \qquad (4)$$

where K_T is the Thomas rate constant (L/min.mg) and θ is the volumetric flow rate (L/min). The linearized form of the Thomas model is as follows:

$$\ln\left(\frac{C_o}{C_e}-1\right) = \frac{K_T q_o m}{\theta} - \frac{K_T C_o}{\theta} V \qquad (5)$$

The kinetic coefficient KT and the adsorption capacity of the bed q_o can be determined from a plot of $\ln\left[\left(C_o/C_e\right)-1\right]$ against t at a given flow rate.

The Thomas equation coefficients for boron adsorption by AWS were $Kr= 2.5 \ 10^5$ L/min.mg and $q_o= 219.53$ mg/g. The value of q_o is a measure of the adsorption capacity at the AWS for boron. The theoretical predictions based on the model parameters are compared in Fig. 1 with the observed data.

3.2. Application of the Yoon and Nelson Model

This model is based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent. The Yoon and Nelson model not only is less complicated than other models, but also requires no detailed data concerning the characteristics of adsorbate, the type of adsorbent, and the physical properties of adsorption bed.

The Yoon and Nelson equation regarding to a single component system is expressed as (Aksu and Gönen, 2004):

$$\frac{C_e}{C_o} = \frac{1}{1+\exp[k(\tau-t)]} \qquad (6)$$

where k is the rate constant (L/min); τ, the time required for 50 % adsorbate breakthrough (min) and t is the breakthrough (sampling) time (min). The linearized form of the Yoon and Nelson Model is as follows:

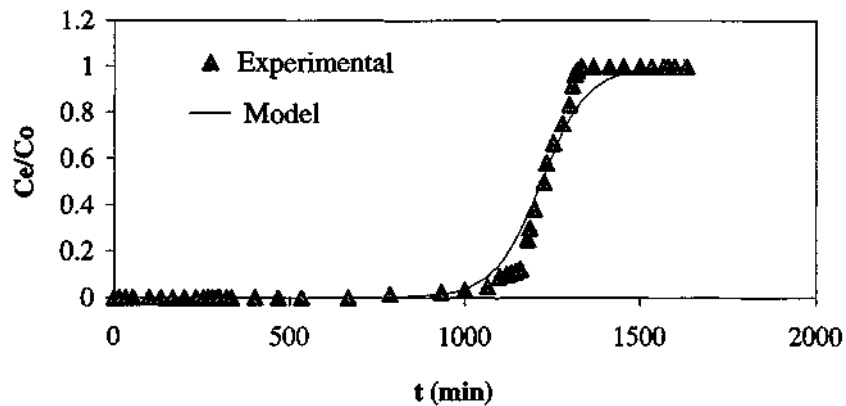$$\ln\frac{C_e}{C_o-C_e} = kt - \tau k \qquad (7)$$

Figure 1. Comparison of the experimental and predicted breakthrough curves for AWS according to Thomas model (at 20°C, pH 10 and C_0 600 mg/L).

The calculation of theoretical breakthrough curves for a single-component system requires the determination of the parameters k and r for the adsorbate of interest. These values may be determined from available experimental data. The approach involves a plot of $\ln[C_e/(C_o - C_e)]$ versus sampling time (0 according to Eq, (7). The model parameters for boron adsorption by AWS were $k=$ 0.019 L/min and r =1197.5 min. Alternatively, r can also be obtained at the adsorption time when $\ln\left[C_e/(C_o - C_e)\right]$ is zero because of the fact that by definition T is the adsorption time when C_e is the one-half of *Co.*

These values were used to calculate the breakthrough curve. The theoretical curves were given with the corresponding experimental data in Fig. 2.

The derivation for Eq. (6) was based on the definition that 50% breakthrough of the adsorption process occurs at r. Accordingly, the bed should be completely saturated at *2r.* Due to the symmetrical nature of breakthrough curve, the amount of boron adsorbed by the AWS is one half of the total boron entering the adsorption column within the 2 7 period. Hence the following equation can be written (Lin and Wang, 2002).

$$q_o = \frac{1}{2}C_o\theta(2\tau) = C_o\theta\tau \qquad (8)$$

The above equation establishes the relation among the adsorption capacity of the column *(q₀),* inlet concentration (C_0), liquid flow rate *(0)* and the 50% breakthrough time (T). *q₀* was calculated as 215.55 mg/g using Yoon and Nelson model.

3.3. Desorption Studies

Figure 3 shows the desorption behaviour of boron. Desorption tests with 2M H_2S0_4 produced 2.46 % desorption.

4. CONCLUSION

The column capacity value was obtained by graphical integration as 219.01 mg/g for AWS. The Thomas and the Yoon-Nelson models were applied to data obtained from experimental studies performed on fixed column to predict the breakthrough curves and to determine the column kinetic parameters. The capacity values were obtained as 219.53 mg/g and 215.55 mg/g using the Thomas and the Yoon-Nelson models, respectively, for AWS. Very low desorption of boron suggests that chemisorption might be the major mode of boron removal by the adsorbent.
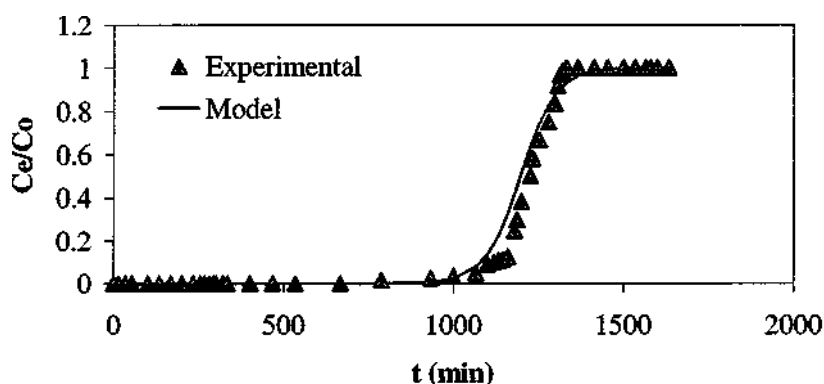
Figure 2. Companson of the experimental and predicted breakthrough curves for AWS according to Yoon-Nelson model (at 20°C, pH 10 and C_o 600 mg/L).
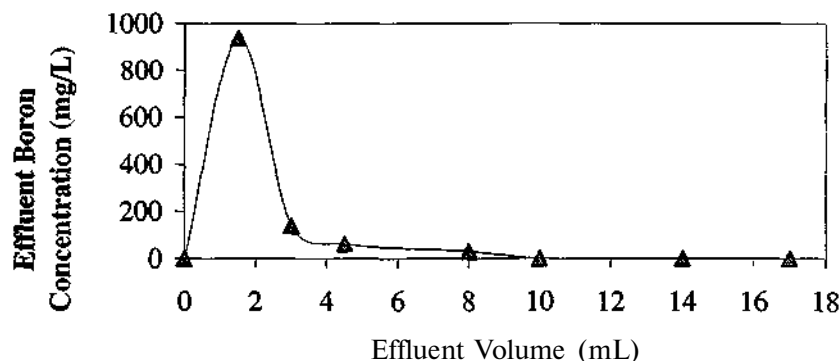

Figure 3. Desorption of boron.

REFERENCES

Agyei, N.M., Strydom, CA. Potgieter, J.H. 2000. *The removal of phosphate ions from aqueous solution by fly ash, slag, ordinary portland cement and related blends,* Cement and Concrete Research, No. 32,1889-1897.

Aksu, Z., Gönen, F. 2004. *Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves,* Process Biochemistry, No.39,599-613.

Balcı, S., Dınçel, Y. 2002. *Ammonium ion adsorption with sepiolite: use of transient uptake method,* Chemical Engineering and Processing, No. 41,127-133.

Kıpçak, Î., 1999. Investigation of Dissolution Kinetics of Magnesium from Sepiolite in Acid Medium, M.Sc. Thesis, Osmangazi University, Chemical Engineering Department, Eskişehir, Turkey, (in Turkish).

Kopaç, T., Kocabaş, S. 2002. *Adsorption equilibrium and breakthrough analysis for sulfur dioxide adsorption on silica gel,* Chemical Engineering and Processing, No. 41, 223-230.

Lin, S.H., Wang, C.S., 2002. *Treatment of high-strenght phenolic wastewater by a new two-step method,* Journal of Hazardous Materials, No. 90, 205-216.

Mathialagan, T., Viraraghavan, T. 2002. *Adsorption of cadmium from aqueous solutions by perlite,* Journal of Hazardous Materials, No. 94, 291-303.

Morais, L.C., Freitas, O.M Gonçalves, E.P. Vasconcelos, L.T. Gonzalez Beça, *C.G* 1999. *Reactive dyes removal from wastewaters by adsorption on Eucalyptus Bark: Variables that define the process,* Water Research, No.33(4), 979-988.

Öztürk, N., Kavak, D. Özdemir, M. 2002. *Boron removal from aqueous solution by adsorption onto activated carbon and alumina using experimental design,* International Solid Waste Association World Environmental Congress&Exhibition, G. Kocasoy, T. Atabarut and Î. Nuhoglu (Eds.), 1907-1914, Istanbul, Turkey.

Öztürk, N., Kavak, D. 2003. *Boron removal from aqueous solutions by adsorption using full factorial design,* Fresenius Environmental Bulletin, No.l2(12), 1450-1456.

Radojevic, M., Jovic, V. Karaulic, D. Vitorovic, D. 2002. *Study of sepiolite from Goles (Kasuvo, Yugoslavia). II. Acid Activation,* J. Serb. Chem. Sos., No.67(7), 499-506.

D Kavak, N. Özturk

Saniz, K., Nuhoğlu, I. 1992. Industrial raw material beds and mining 338-343, Anadolu University, Eskişehir, Turkey.

Şahin, S., 2002. *A mathematical relationship for the explanation of ion exchange for boron adsorption,* Desalination, No. 143,35-43.