

Modelling of Fixed Bed Column Adsorption of Cationic Surfactant on Silica Gel

Suman Koner and Asok Adak^{1*}

Department of Civil Engineering, Jalpaiguri Government Engineering College, Jalpaiguri – 735102, India

¹Department of Civil Engineering, Bengal Engineering and Science University, Shibpur, Howrah – 711103, India

✉ asokadak@gmail.com

Received August 22, 2009; revised and accepted September 10, 2010

Abstract: The adsorption of cationic surfactant (CS) on silica gel in a continuous flow type packed bed reactor was studied in detail. The column having 2.5 cm internal diameter, with different bed depth such as 30, 40, 50 and 60 cm were used. The initial CS concentration was 2000 mg/l and the flow rate through the packed bed was 10 ml/min. The data generated from column study was analysed using bed depth service time (BDST) model. Different column design parameters like depth of exchange zone, time required for exchange zone to move its own height, adsorption rate, adsorption capacity, etc. were calculated. The adsorption rate constant (K) and adsorption capacity (N_o) were found to be 0.00122 1/mg-h and 32,330 mg/l respectively. Effect of flow rate and initial concentration were also studied. Desorption of CS from the silica gel surface was possible using 18% HCl.

Key words: Silica gel, cetyltrimethylammonium bromide, adsorption, column study, breakthrough curve.

Introduction

A surfactant may briefly be defined as a material that can greatly reduce the surface tension of water when used in very low concentrations. This molecule is made up of two distinct groups, viz., water soluble (hydrophilic) and water insoluble (hydrophobic). Cationic surfactants (CS) are those which carry a positive charge in the active portion of the molecule. These are compounds with a positive charged nitrogen atom and at least one hydrophobic, long-chain substituent in the molecule. Important CS includes quaternary ammonium compounds, imidazolinium derivatives or pyridinium compounds. An example of quaternary ammonium based CS is cetyltrimethylammonium bromide (CTAB). CS has large applications in various fields like fabric softeners, textile industry, road construction, mining, hair conditioning, cosmetics, disinfectants, biocides, emulsifiers, etc. (Puchta, 1984; Agarwal et al., 2004).

Such widespread use of CS causes its massive discharge into the environment leading to an environmental concern. To protect public health, elimination of CS from wastewater has thus become very important. The reduction of these contaminants has received considerable attention in recent years (Wee and Kennedy, 1982; Sabah et al., 2002). Common technologies that reduce the CS from water environment includes ozonation or advanced oxidation process (Ikehata and El-Din, 2004), adsorption (Li et al., 2008; Upadhyay et al., 2007; Zhu and Ma, 2007; Saleh, 2006; Golub and Koopal, 2004; Sabah et al., 2002; Mikhailova and Gerashchenko, 2001) and biological process (Merretting-bruns and Jelen, 2009; Garcia et al., 2000; Sullivan, 1983).

Removal by the ozonation was found to be costly and difficult for field application. As most of the cationic surfactants are biocidal, biological process would not be effective in high concentration (>20 mg/l) (Li et al., 2008). Hence, adsorption appears to be most effective process

*Corresponding Author

that can be easily applied in the field. Among the various adsorbents, the use of natural clay minerals like zeolite, bentonite, sepiolite, etc. (Li et al., 2008; Zhu and Ma, 2007; Sabah et al., 2002) have drawn much interest since these are abundant and also cheap commodities. However, the industrial application requires answers to some basic questions: ability of regeneration and ease of application in the field (Saleh, 2006). Aerosil (a high purity non porous silica gel) was used for adsorption of cationic surfactant (Golub and Koopal, 2004; Mikhailova and Gerashshenko, 2001) from water environment, however in these studies the works were limited to describe the adsorption process by self-consistent-mean-field approximation lattice model and to develop the adsorption isotherm at different physico-chemical behaviour of aerosil. The application of silica gel for removal of cationic surfactant from industrial wastewater in continuous flow type packed bed reactor is still unexplored. Hence, the present research aims to examine the potential of silica gel for being used as an adsorbent for the removal of CS from water environment. In the present study, CTAB was used as a representative of quaternary ammonium based cationic surfactants, since many researchers have considered the same (Li et al, 2008; Zhu and Ma, 2008; Agarwal et al., 2004; Mikhailova and Gerashshenko, 2001). Thus, the broad objectives of the study are: (i) to analyse the adsorption columns with the help of BDST model, and (ii) regeneration of adsorbent and its reuse for CS removal. The authors feel that this is the first report where the engineering applications of silica gel for CS removal from wastewater was studied.

Materials and Methods

Reagents

Orange II (Hi-Media, India), cetyltrimethylammonium bromide (Hi-Media, India) and Chloroform (Merck, India) were used as received. All other chemicals used in this study were of high purity and used without further purification. All the chemicals were of Analytical Reagent Grade.

Adsorbent

Silica gel was supplied by Merck, India and used without further grinding and sieving. The granulation of silica gel was 60–120 mesh (Indian Standard) and the corresponding particle size range was 0.125 to 0.250 mm. The zero point charge of silica gel is reported to be 2. The BET surface area and pore volume of silica gel were 278.4 m²/g and 0.68 ml/g respectively.

Instrumentation

A high precision electrical balance (CP 225D, Sartorius GMBH) was used for weighing. Digital pH meter (PB-11, Sartorius GMBH) was used for pH measurements. A spectrophotometer (UV-1800, Rayleigh, Beiging) was used for absorbance measurement.

Analytical Method

Spectrophotometric method was used for the determination of CS in the concentration range 0–12 mg/l (Few and Ottewill, 1956). Orange II (0.4×10^{-3} M) chemically known as p-(β -naphthol-azo) benzene sulphonic acid as ion pairing agent with CS and chloroform as an extraction solvent were used. The relation between absorbance and concentration at 485 nm wavelength has been determined as Absorbance = $0.0399 \times \text{Concentration (mg/l)} + 0.0377$ ($R^2 = 0.9965$).

Experimental Studies

Fixed bed column studies were conducted using columns having 2.5 cm internal diameter and 100 cm length. The columns were packed with silica gel between two supporting layers of glass wool. The bed depths were taken as 30, 40, 50 and 60 cm. The schematic diagram of the column study is shown in Figure 1. The column was charged with CS bearing wastewater in the up flow mode with a volumetric flow rate of 10 ml/min ($\sim 1.22 \text{ m}^3/\text{m}^2/\text{hr}$). The initial concentration of CS was 2000 mg/l. The study considering such high concentration was carried out by many researchers (Li et al., 2009; Zhu and Ma, 2008). The samples were collected at certain time intervals and were analysed for remaining CS concentration. Experiment was conducted with an initial CS concentration of 4000 mg/l, flow rate of 10 ml/min and bed depth of 30 cm. Effect of flow rate was also studied, where columns were run with flow rates of 15 ml/min,

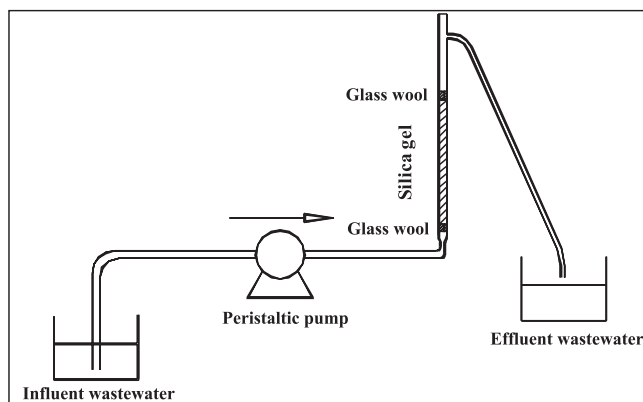


Figure 1: Schematic diagram of lab-scale column study.

with the bed depth of 30 cm and initial CS concentration of 2000 mg/l. In all the cases the temperature was $27 \pm 2^\circ\text{C}$ and the pH was 6.9 ± 0.1 . The regeneration of exhausted silica gel was studied using dilute HCl.

Results and Discussion

Behaviour of Adsorption Column

Fixed bed column studies were conducted using columns having 2.5 cm internal diameter and 100 cm length. The columns were packed with Silica gel at different depths 30, 40, 50 and 60 cm. The column was charged with CS-spiked distilled water in the up flow mode with a volumetric flow rate of 10 ml/min ($\sim 1.22 \text{ m}^3/\text{m}^2/\text{hr}$). The initial concentration of CS was 2000 mg/l. The breakthrough curves were shown in Figure 2. The breakthrough times (corresponding to $C/C_0 = 0.1$) were found to be 3.0, 4.5, 5.75 and 7.0 h for 30, 40, 50 and 60 cm bed depth respectively. The exhaust times (corresponding to $C/C_0 = 0.9$) were 6.0, 7.75, 9.25 and 10.0 h respectively. The corresponding volumes of wastewater treated at breakthrough point were 1.80, 2.70, 3.45 and 4.2 l respectively and at exhaust point 3.60, 4.65, 5.55 and 6.00 l respectively. Different parameters for column have been calculated from the above data.

The time required for the exchange zone to move the length of its own height up/down the column once it has become established is

$$t_z = \frac{V_E - V_B}{Q_w} \quad (1)$$

where V_E = total volume of wastewater treated to the point of exhaustion (l), V_B = total volume of wastewater treated to the point of breakthrough (l), Q_w = wastewater flow rate (l/h).

The time required for the exchange zone to become established and move completely out of the bed is

$$t_E = \frac{V_E}{Q_w} \quad (2)$$

Rate at which the exchange zone is moving up or down through the bed is

$$U_z = \frac{h_z}{t_z} = \frac{h}{t_E - t_f} \quad (3)$$

where h_z = height of exchange zone (cm), h = total bed depth (cm), t_f = time required for the exchange zone to initially form (h).

Rearranging equation 3 provides an expression for the height of the exchange zone as given below.

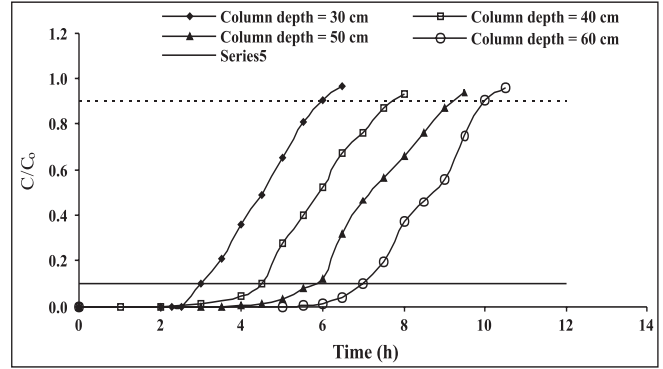


Figure 2: The breakthrough curves of CTAB removal by silica gel packed columns of different bed depth.

$$h_z = \frac{h(t_z)}{t_E - t_f} \quad (4)$$

The value of t_f can be calculated as follows.

$$t_f = (1 - F)t_z \quad (5)$$

At breakthrough the fraction of adsorbate present in the adsorption zone still possessing ability to remove solute is

$$F = \frac{S_z}{S_{\max}} = \frac{\int_{V_B}^{V_E} (C_0 - C) dV}{C_0 (V_E - V_B)} \quad (6)$$

where C_0 = initial solute concentration (mg/l), S_z = amount of solute that has been removed by the adsorption zone from breakthrough to exhaustion, S_{\max} = amount of solute removed by the adsorption zone if completely exhausted.

The percentage of the total column saturated at breakthrough is

$$\% \text{ saturation} = \frac{h + (F - 1)h_z}{h} \times 100 \quad (7)$$

The values of the important design parameters for 30, 40, 50 and 60 cm bed depth were calculated and shown in Table 1.

Table 1: Important column behaviour parameters

Parameter	Bed depth = 30 cm	Bed depth = 40 cm	Bed depth = 50 cm	Bed depth = 60 cm
t_z (h)	3.00	3.25	3.50	3.00
h_z (cm)	20.05	21.80	23.75	21.00
U_z (cm/h)	6.68	6.70	6.78	6.98
Bed saturation (%)	66.30	70.10	74.44	83.54

Evaluation of Adsorption Column Design

Parameters

Data collected during laboratory and pilot plant tests serve as the basis for the design of full-scale adsorption columns. A number of mathematical models have been developed for the use in design. Among various models, model proposed by Bohart and Adam (1920) is widely used. The equation, which is based on surface reaction rate theory, can be represented as follows:

$$\ln\left(\frac{C_o}{C_B} - 1\right) = \ln\left(e^{\frac{KN_o x}{V}} - 1\right) - KC_o t \quad (8)$$

where C_o = initial concentration of solute (mg/l), C_B = desired concentration of solute at breakthrough (mg/l), K = adsorption rate constant (l/mg-h), N_o = adsorption capacity (l/mg), x = bed depth of column, V = linear flow velocity of feed to bed (cm/h), t = service time of column under above conditions (h).

The equation can be rearranged to yield an expression for service time, t . Realizing that $e^{\frac{KN_o x}{V}} \gg 1$, the above equation simplifies to

$$\ln\left(\frac{C_o}{C_B} - 1\right) = \ln e^{\frac{KN_o x}{V}} - KC_o t \quad (9)$$

Solving the above equation for t ,

$$t = \frac{N_o}{C_o V} x - \frac{1}{C_o K} \ln\left(\frac{C_o}{C_B} - 1\right) \quad (10)$$

The form of the Bohart-Adams equation, shown as equation (10) can be used to determine the service time, t , of a column of bed depth, x , given the values of N_o , C_o and K which must be determined for laboratory columns operated over a range of velocity values, V .

At least nine individual column tests must be conducted to collect the laboratory data required for the Bohart-Adams approach, an expensive and time-consuming task. A technique has been presented by Hutchins (1973), which requires only three column tests to collect the necessary data. In this technique, called the bed depth service time (BDST) approach, the Bohart-Adams equation is expressed as

$$t = ax + b \quad (11)$$

where

$$a = \text{slope} = \frac{N_o}{C_o V} \quad (12)$$

$$b = \text{intercept} = \frac{1}{KC_o} \ln\left(\frac{C_o}{C_B} - 1\right) \quad (13)$$

As it is already mentioned, the breakthrough times (corresponding to $C/C_o = 0.1$) were found to be 3.0, 4.5, 5.75 and 7.0 h for 30, 40, 50 and 60 cm bed depth respectively and the exhaust times (corresponding to $C/C_o = 0.9$) were found to be 6.0, 7.75, 9.25 and 10.0 h respectively. Figure 3 showed the depth vs. service time plot for 10% and 90% saturation of column. The equations of these lines were as follows:

For 90% saturation

$$t = 0.135x + 2.175 \quad (14)$$

For 10% saturation

$$t = 0.125x - 0.9 \quad (15)$$

From the slope it was found that these lines were parallel and the horizontal distance between the lines was found to be 23.8 cm. This horizontal distance is called the height of exchange zone. Theoretically this value was found to be 20.05 cm and 23.75 cm. (Table 1).

From the slope and the intercept of the 10% saturation line design parameters like K and N_o could be found out using equations 12 and 13. The values of K and N_o were found to be 0.00122 l/mg-h and 32330 mg/l respectively. The value of K and N_o indicated that the silica gel is highly efficient for the removal of CS from water environment.

Design of Adsorption Column

The column design parameters as obtained earlier could be used for the design of adsorption column for practical purpose. According to BDST approach, if a value is determined for one flow rate, values for the other flow rates can be calculated by multiplying the original slope a by the ratio of the original and the new flow rates. It is not necessary to adjust b value, since this term is assumed to be insignificantly affected by changing flow rates.

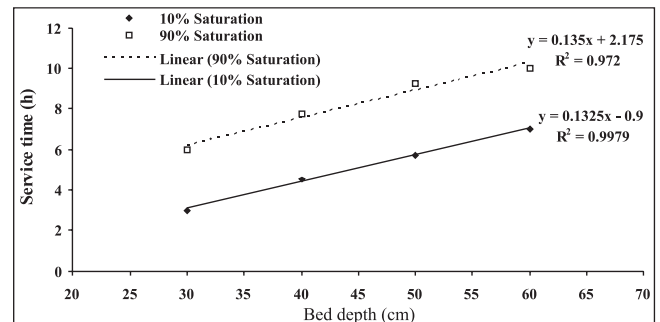


Figure 3: BDST curve of CTAB removal.

It is also proposed that the data collected for one influent solute concentration can be adjusted by the BDST technique and used to design systems for treating other influent solute concentrations. If a laboratory test is conducted at solute concentration C_1 , yielding an equation of the form

$$t = a_1x + b_1 \quad (16)$$

then it is possible to predict the equation for concentration C_2 as follows:

$$a_2 = a_1 \frac{C_1}{C_2} \quad (17)$$

$$b_2 = b_1 \left(\frac{C_1}{C_2} \right) \frac{\ln \left(\frac{C_2}{C_F} - 1 \right)}{\ln \left(\frac{C_1}{C_B} - 1 \right)} \quad (18)$$

where a_1 = slope at concentration C_1 , a_2 = slope at concentration C_2 , b_1 = intercept at concentration C_1 , b_2 = intercept at concentration C_2 , C_F = effluent concentration at influent concentration C_2 , C_B = effluent concentration at influent concentration C_1 .

Design of Adsorption Column for Different Flow Rate

Column was run with flow rate of 15 ml/min, whereas original flow rate was 10 ml/min. The initial CS concentration was kept constant at 2000 mg/l. The bed depth and column diameter were 30 and 2.5 cm respectively. The breakthrough time (corresponding to 10% of influent concentration) was found to be 110 minutes (Figure 4). The revised value of a was calculated from flow rate ratio and the value was found to be 0.0883.

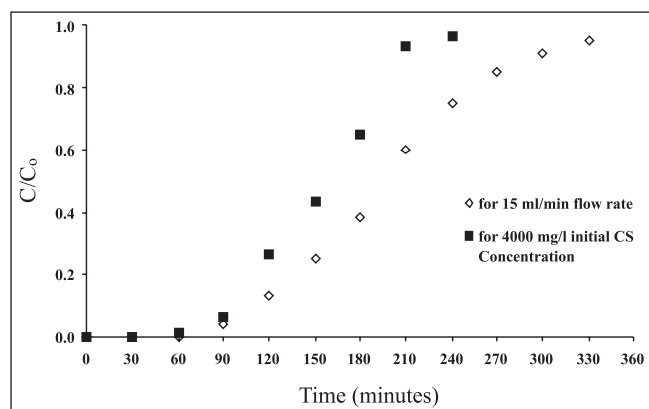


Figure 4: The breakthrough curves of CTAB removal by silica gel packed columns of different flow rate and initial concentration.

The value of intercept was -0.90 . From these values of a and b , the service time for 30 cm column was calculated and this was 105 minutes. These values were comparable with the experimental values.

Design of Adsorption Column for Different Initial Concentration

Column was run with initial CS concentration of 4000 mg/l, whereas original CS concentration was 2000 mg/l. The flow rate was kept at 10 ml/min. The bed depth and column diameter were 30 and 2.5 cm respectively. The breakthrough time was found to be 87 minutes (Figure 4). The breakthrough concentration was taken as 200 mg/l, which was taken for 2000 mg/l initial CS concentration. The values of a_2 and b_2 calculated from equation 17 and 18 were 0.06625 and 0.6030 respectively. From these values of a and b , the service time for 30 cm column was calculated and this was 83 minutes. This value was comparable with the experimental values.

Regeneration of Exhausted Silica Gel

The regeneration of the exhausted silica gel was carried out in batch mode. 50 gm of exhausted silica gel was taken in 100 ml 18% hydrochloric acid (500 g/l) (pH less than 1) and shaken for two hours at 150 rpm. After that it was taken out from the hydrochloric acid solution and thoroughly washed with tap water and finally distilled water. Regenerated silica gel was again used for further uptake of CTAB in batch mode. The efficiency of regenerated silica gel was found to be slightly less ($\sim 3\%$ – 4%) than the fresh material.

Conclusion

Silica gel was found to be very efficient media for the removal of CS from wastewater. The column of 2.5 cm internal diameter and having bed depths of 30, 40, 50 and 60 cm could treat 1.80, 2.70, 3.45 and 4.2 l of CS bearing wastewater (CS concentration 2000 mg/l) respectively at breakthrough. The adsorption bed was ~ 66 – 83% saturated at exhaust point. The height of the adsorption zone was 20.05–23.75 cm and the rate at which it moved its own height was found to be 6.68–6.98 cm/h. The adsorption rate constant (K) and adsorption capacity (N_o) were found to be 0.00122 l/mg–h and 32,330 mg/l respectively. Effect of flow rate and initial concentration was studied. The increase in flow rate decreased the breakthrough time. The initial CS concentration also had the similar effect. Desorption of CS from the silica gel surface was possible using 18% HCl.

Acknowledgement

We are thankful to the SERC Division, Department of Science and Technology (DST), New Delhi, India, for the financial support for this work.

References

- Agarwal, K., Agnihotri, G., Shrivastava, K., Mundahara, G.L., Patel, K.S. and P. Hoffman (2004). Determination of cationic surfactants in environmental samples by flow injection analysis. *Microchimica Acta*, **147**: 273–278.
- Bohart, G.S. and E.Q. Adam (1920). Some aspects of behaviour of charcoal with respect to chlorine. *Journal of American Chemical Society*, **42**: 523–544.
- Few, A.V. and R.H. Ottewill (1956). A spectrophotometric method for the determination of cationic detergents. *Journal of Colloid Science*, **11**: 34–38.
- Garcia, M.T., Campos, E., Sanchez-Leal, J. and I. Ribosa (2000). Anaerobic degradation and toxicity of commercial cationic surfactant in anaerobic screening tests. *Chemosphere*, **41**: 705–710.
- Golub, T.P. and L.K. Koopal (2004). Adsorption of cationic surfactants on silica surface: 2. comparison of theory with experiment. *Colloid Journal*, **66**: 44–47.
- Hutchins, R.A. (1973). New simplified design of activated carbon system. *American Journal of Chemical Engineering*, **80**: 133–138.
- Ikehata, K. and M.G. El-Din (2004). Degradation of recalcitrant surfactants in wastewater by ozonation and advanced oxidation processes: A Review. *Ozone: Science and Engineering*, **26**: 327–343.
- Li, Z., Yuansheng, D. and H. Hanlie (2008). Transport of micelles of cationic surfactants through clinoptilolite zeolite. *Microporous and Mesoporous Material*, **116**: 473–477.
- Merretting-bruns, U. and E. Jelen (2009). Anaerobic biodegradation of detergent surfactants. *Materials*, **2**: 181–206.
- Mikhailova, I.V. and I.I. Gerashchenko (2001). Adsorption of cationic surfactants on highly dispersed silica. *Colloid Journal*, **63**: 437–440.
- Puchta, R. (1984). Cationic surfactants in laundry detergents and laundry aftertreatment aids. *Journal of American Oil Chemists' Society*, **61**: 367–376.
- Sabah, E., Turan, M. and M.S. Celik (2002). Adsorption mechanism of cationic surfactant onto acid- and heat-activated sepiolites. *Water Research*, **36**: 3957–3964.
- Saleh, M.M. (2006). On the removal of cationic surfactant from dilute stream by granular charcoal. *Water Research*, **40**: 1052–1060.
- Sullivan, D.E. (1983). Biodegradation of cationic surfactant in activated sludge. *Water Research*, **17**: 1145–1151.
- Upadhyay, A., Acosta, E.J., Scamerhorn, J.F. and D.A. Sabatini (2007). Adsorption of anionic-cationic surfactant mixtures on metal oxide surfaces. *J. Surfactant and Detergent*, **10**: 269–277.
- Wee, V.T. and J.M. Kennedy (1982). Determination of trace levels of quaternary ammonium compounds in river water by liquid chromatography with conductometric detection. *Analytical Chemistry*, **54**: 1631–1633.
- Zhu, L. and J. Ma (2008). Simultaneous removal of acid dye and cationic surfactant from water by bentonite in one-step process. *Chemical Engineering Journal*, **139**: 503–509.