*Desalination and Water Treatment*
www.deswater.com

doi: 10.1080/19443994.2014.968213

56 (2015) 3122–3127
December

Taylor & Francis
Taylor & Francis Group

# Solid–liquid equilibrium of glycolic acid with alumina

İsmail İnci[a], Şahika Sena Bayazit[b], Yavuz Selim Aşçi[a,*]

[a]*Engineering Faculty, Chemical Engineering Department, İstanbul University, 34850 Istanbul, Turkey, Tel. +90 212 473 7070/17674; email: isminci@istanbul.edu.tr (İ. İnci), Tel. +90 212 473 7070/17679; email: sasci@istanbul.edu.tr (Y.S. Aşçi)*

[b]*Engineering and Architecture Faculty, Chemical Engineering Department, Beykent University, Ayazağa, Istanbul, Turkey, Tel. +90 212 444 1997/5294; email: senabayazit@beykent.edu.tr (Ş.S. Bayazit)*

Received 6 November 2013; Accepted 7 September 2014

ABSTRACT

This work aims to present novel adsorption equilibrium data for glycolic acid with alumina at aqueous solutions. The adsorption experiments were carried out with aqueous glycolic acid solutions with various initial concentrations (0.38–2.1) mol $L^{-1}$. Adsorbent alumina of (0.2–2) g was used. To show the effect of temperature, also adsorption equilibrium experiments were made at various temperatures (298, 308, and 318K). The equilibrium concentrations of glycolic acid have been found. Removal of glycolic acid was 20.51% as the maximum percentage. The equilibrium data show well fitting with Langmuir isotherm. Also, Elovich model have been applied to adsorption data.

*Keywords:* Adsorption; Glycolic acid; Alumina

## 1. Introduction

Removal and recovery of many different organic acids has an important industrial problem [1]. Many techniques were investigated to recover carboxylic acids from aqueous media [2–5]. One of these techniques is adsorption, which is one of the most efficient techniques in most natural systems. These systems may be physical, biological, or chemical. Adsorption of solids is mostly used in industrial applications with the aim of purification and separation [6]. These solids may be natural and of different synthetic resins

Glycolic acid, also called as hydroxyacetic acid, has been known as smallest α-hydroxy acid. It is an important raw material for different skin cosmetic substances [7]. It is possible to produce glycolic acid from the fermentation broth, or using mineral acid, such as sulfuric acid; glycolic acid can be produced from glycolonitrile hydrolysis. Multicomponent solutions are obtained with these production methods. For fermentation method, concentration of acid obtained in these solution is average, not more than 10% by mass; for glycolonitrile hydrolysate, glycolic acid concentration typically is not more than 40% by mass. Distillation requires a big amount of energy; therefore, separation of acids from product solutions is an important separation problem. On the other hand, distillation is not suitable method to separate acids that are nonvolatile. It is very hard to obtain high distribution coefficients by conventional solvents, as a result of powerful aqueous activity of organic acids [8–10].

Carboxylic group and surface hydroxyls were studied widely by many researchers. Especially, adsorptive separations of carboxylic acids were

*Corresponding author.

Table 1
Effect of initial acid concentration on the adsorption of glycolic acid

| Initial conc. (g $L^{-1}$) | Initial conc. (mol. $L^{-1}$) | Initial conc. (%w/w) | Amount of alumina (g) | Equilibrium conc. $C_e$ (g $L^{-1}$) | Adsorbed acid $Q_e$ (g $mg^{-1}$) | Removal of acid (%) | Temp. (K) |
|---|---|---|---|---|---|---|---|
| 28.9 | 0.38 | 2.82 | 0.6 | 25.8 | 0.026 | 10.72 | 298 |
| 53.24 | 0.7 | 5.27 | 0.6 | 48.8 | 0.037 | 8.33 | |
| 101.15 | 1.33 | 10.04 | 0.6 | 95.3 | 0.049 | 5.78 | |
| 159.71 | 2.1 | 15.96 | 0.6 | 156.3 | 0.028 | 2.13 | |
| 28.9 | 0.38 | 2.82 | 0.6 | 25.6 | 0.028 | 11.41 | 308 |
| 53.24 | 0.7 | 5.27 | 0.6 | 48.9 | 0.036 | 8.15 | |
| 101.15 | 1.33 | 10.04 | 0.6 | 98 | 0.026 | 3.11 | |
| 159.71 | 2.1 | 15.96 | 0.6 | 158.2 | 0.013 | 0.94 | |
| 28.9 | 0.38 | 2.82 | 0.6 | 27.6 | 0.011 | 4.49 | 318 |
| 53.24 | 0.7 | 5.27 | 0.6 | 48.3 | 0.041 | 9.27 | |
| 101.15 | 1.33 | 10.04 | 0.6 | 99.4 | 0.015 | 1.73 | |
| 159.71 | 2.1 | 15.96 | 0.6 | 159.1 | 0.005 | 0.38 | |

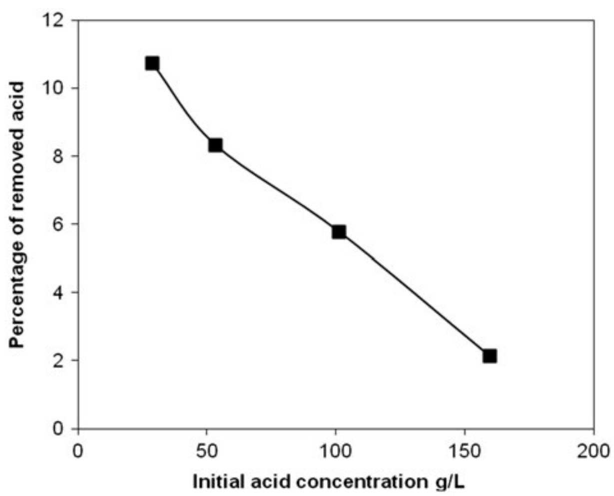


Fig. 1. Plot of the effect of the initial acid concentration on the adsorption of glycolic acid at 298 K.

studied. Oxygens of both acids are attached to the surface of alumina. To explain these interactions chelating and bridging approaches were offered. Bridging approach proposes oxygens on the acid with the inclusion of mutual action are directly to Al–O of alumina by the aim of bonding hydrogen. On the other hand, chelating approach proposes that the group is dissociated. Later this group makes a linkage with Al–O–H. Adsorptive separation of organic acids from dilute solutions by alumina is called as a dissociative adsorption [11,12]. Adsorbed acid molecules onto alumina can affect the surface of alumina. In this interaction, one atom of hydrogen is used between atoms of oxygen of the acid molecule. This interaction is carried out with the formation of hydrogen bond [13].

In this investigation, liquid–solid data of equilibrium of glycolic acid with alumina in aqueous solution has been obtained. Most widely used adsorption isotherms (Freundlich and Langmuir) were plotted by using experimental results. As a kinetic model, Elovich equation was used for kinetic investigation of glycolic acid adsorption by alumina.

## 2. Experimental

Glycolic acid and alumina have been supplied by Merck Co. Purity for all chemicals used in this work are greater than 99.0. Initial concentrations of acid were prepared in four concentrations (0.38, 0.7, 1.33, and 2.1) mol $L^{-1}$. Specified amount of alumina added to 5 mL of glycolic acid solution (10% (w/w)) and shaked for equilibrium in a thermostatic bath. All adsorptive separation experiments have been made in a shaker at (298, 308, and 318K) . Samples were obtained in 10 min of intervals, and analyzed titration with using 0.1 N NaOH; the indicator used in this study was phenolphthalein. As a result of these experiments, the period for equilibrium obtained was 60 min. The samples were shaken for 90 min, and 0.6 g of alumina amount was found as the optimum amount. The impact of initial acid concentration on glycolic acid adsorption was observed at 298 K ± 1 with 0.6 gram of alumina.

Table 2
Effect of amount of adsorbents on the adsorption of glycolic acid

| Initial conc. (g $L^{-1}$) | Initial conc. (mol. $L^{-1}$) | Initial conc. (%w/w) | Amount of alumina (g) | Equilibrium conc. $C_e$ (g $L^{-1}$) | Adsorbed acid $Q_e$ (g $mg^{-1}$) | Removal of acid (%) | Temp. (K) |
|---|---|---|---|---|---|---|---|
| 101.15 | 1.33 | 10.04 | 0.2 | 99.9 | 0.010 | 1.23 | 298 |
| 101.15 | 1.33 | 10.04 | 0.4 | 99.2 | 0.016 | 1.92 | 298 |
| 101.15 | 1.33 | 10.04 | 0.6 | 95.3 | 0.049 | 5.78 | 298 |
| 101.15 | 1.33 | 10.04 | 0.8 | 91.3 | 0.082 | 9.73 | 298 |
| 101.15 | 1.33 | 10.04 | 1.0 | 90.8 | 0.086 | 10.23 | 298 |
| 101.15 | 1.33 | 10.04 | 1.2 | 90.3 | 0.090 | 10.72 | 298 |
| 101.15 | 1.33 | 10.04 | 1.4 | 87.4 | 0.115 | 13.59 | 298 |
| 101.15 | 1.33 | 10.04 | 1.6 | 83.3 | 0.149 | 17.64 | 298 |
| 101.15 | 1.33 | 10.04 | 1.8 | 82.6 | 0.155 | 18.33 | 298 |
| 101.15 | 1.33 | 10.04 | 2.0 | 80.4 | 0.173 | 20.51 | 298 |

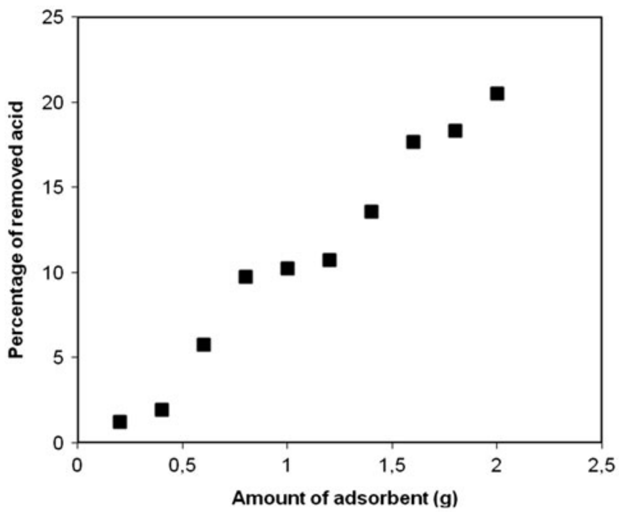


Fig. 2. Plot of the effect of the amount of adsorbents on the adsorption of glycolic acid at 298 K.

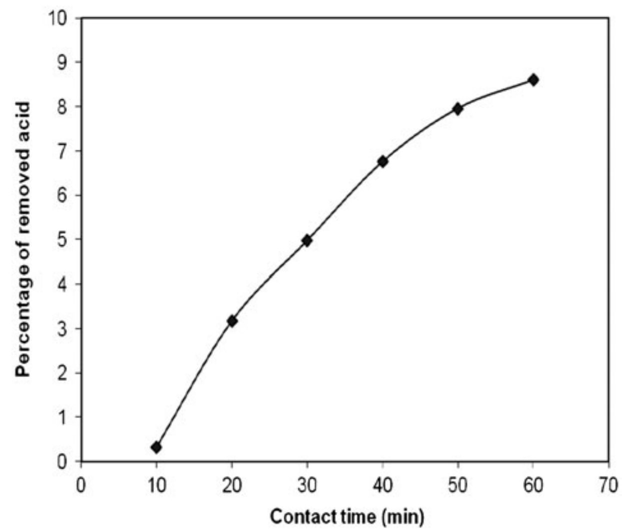


Fig. 3. Plot of the effect of the contact time on the adsorption of glycolic acid.

## 3. Results and discussion

Adsorptive separation investigations were carried out with various initial concentrations of glycolic acid, to show the impact of initial concentration of acid. From Table 1 and Fig. 1, it may be observed that, with rising preliminary concentrations from 0.38 to 2.1 mol $L^{-1}$, glycolic acid adsorbed decreases. In this respect, the removal rate decreased from 10.72 to 2.13% for glycolic acid. The reason of this situation is saturation of surface sites of alumina.

Table 2 and Fig. 2 present effects of alumina amount on adsorption of acid which was studied by changing the alumina amount from 0.2 to 2 g with 1.33 mol $L^{-1}$ of preliminary concentration of glycolic acid at 298 K, respectively. It has been concluded that, as the amount of alumina increases, glycolic acid adsorbed increases. Maximum adsorbent dose has been selected as 2 g, and the maximum adsorption capacities of glycolic acid have been found as 20.51% for this dose (Fig. 3 and Table 3).

To show the influence of contact time on glycolic acid adsorption by alumina, 1.43 mol $mg^{-1}$ of glycolic acid solution has been used for a period of 60 min at 298 K. Alumina dosage used for this purpose was selected as 0.6 g. Glycolic acid uptake of alumina was faster at first, and later it became more slow as the approach reached equilibrium. Between these situations, the adsorption rate has been found to be almost constant. This situation may be explained by the fact that many vacant local sites on alumina surface for

Table 3
Effect of contact time on the adsorption of glycolic acid

| Initial conc. ($g L^{-1}$) | Initial conc. ($mol. L^{-1}$) | Initial conc. (%w/w) | Amount of alumina (g) | Equilibrium conc. $C_e$ ($g L^{-1}$) | Adsorbed acid $Q_e$ ($g mg^{-1}$) | Removal of acid (%) | Time (min) | Temp. (K) |
|---|---|---|---|---|---|---|---|---|
| 108.76 | 1.43 | 10.86 | 0.6 | 108.4 | 0.003 | 0.33 | 10 | 298 |
| 108.76 | 1.43 | 10.86 | 0.6 | 105.3 | 0.029 | 3.18 | 20 | 298 |
| 108.76 | 1.43 | 10.86 | 0.6 | 103.5 | 0.044 | 4.83 | 30 | 298 |
| 108.76 | 1.43 | 10.86 | 0.6 | 101.4 | 0.061 | 6.76 | 40 | 298 |
| 108.76 | 1.43 | 10.86 | 0.6 | 100.1 | 0.072 | 7.96 | 50 | 298 |
| 108.76 | 1.43 | 10.86 | 0.6 | 99.4 | 0.078 | 8.60 | 60 | 298 |

Table 4
Effect of temperature on the adsorption of glycolic acid

| Initial conc. ($g L^{-1}$) | Initial conc. ($mol. L^{-1}$) | Initial conc. (%w/w) | Amount of Alumina (g) | Equilibrium conc. $C_e$ ($g L^{-1}$) | Adsorbed acid $Q_e$ ($g mg^{-1}$) | Removal of acid (%) | Temp. (K) |
|---|---|---|---|---|---|---|---|
| 101.15 | 1.33 | 10.04 | 0.6 | 95.3 | 0.049 | 5.78 | 298 |
| 101.15 | 1.33 | 10.04 | 0.6 | 98.0 | 0.026 | 3.11 | 308 |
| 101.15 | 1.33 | 10.04 | 0.6 | 99.4 | 0.013 | 1.73 | 318 |

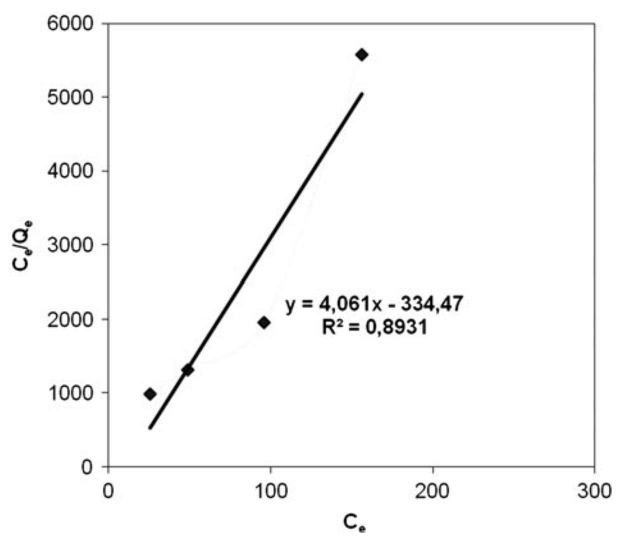


Fig. 4. Plot of the Langmuir isotherm equation for the adsorption of glycolic acid.

glycolic acid adsorption are available at first and after a period, these sites on alumina surface are very hard to occupy as a result of repulsive effects between glycolic acid molecules on alumina and molecules of glycolic acid on water [14].

Temperature effect on adsorption of acid was examined at, 298, 308, and 318 K. Table 4 show results of adsorption in these temperatures. Capacity of adsorbent changes from 0.028 to 0.005 $g mg^{-1}$ as temperature increases from 298 to 318 K is shown in Table 4. This situation shows that obviously the adsorption process is an exothermic.

### 3.1. Adsorption isotherm equations

Most widely used isotherms are Langmuir and Freundlich isotherms. These isotherms were plotted to find isotherm model parameters and adsorption characteristics.

The first isotherm is Langmuir given as the following Eq. (1) [15–17],

$$Q_e = \frac{K_A \cdot Q_0 \cdot C_e}{1 + K_A \cdot C_e} \tag{1}$$

where $Q_e$ and $Q_0$ show the concentrations of glycolic acid on the adsorbent and saturation capacity, respectively

$Q_e$ and $K_A$ may be found using Eqs. (2) and (3).

$$C_e = -K_L + C_e \cdot \frac{Q_0}{Q_e} \tag{2}$$

$$K_L = \frac{1}{K_A} \tag{3}$$

$K_L$ and $Q_0$ values may be found from slope and interception of isotherm in Fig. 4. Langmuir adsorption constants have been obtained using Eqs. (2) and (3). These parameters have been given in Table 5.

The other isotherm applied in this work for glycolic acid adsorption onto alumina is Freundlich isotherm [18–20].

Freundlich isotherm has been calculated from Eq. (4)

$$Q_e = K_f \cdot C_e^{1/n} \tag{4}$$

A logarithmic plot of this equation linearizes this equation, enabling the parameters to be found from Eq. (5). The constant $K_f$ and exponent $n$ are given as,

$$\log Q_e = \log K_f + (1/n) \log C_e \tag{5}$$

Freundlich constant $K_f$ and other parameter $1/n$, at various concentration points can be found from the slope and intercept of log $Q_e$ and log $C_e$ graphs.

From the calculations, it was seen that Langmuir isotherm shows good fitting experimental data for glycolic acid onto alumina with $R^2$ value of 0.9097. However, Freundlich isotherm did not show good results.

### 3.2. The Elovich model equation

The Elovich equation is given as follows Eq. (6) [21],

$$\frac{\mathrm{dQ}}{\mathrm{dt}} = \alpha \cdot \exp(-\beta \cdot Q) \tag{6}$$

In this equation, $\alpha$ is known as initial rate ($\mathrm{mg.g^{-1}.min^{-1}}$). $\beta$ is known as the parameter of desorptive behavior ($\mathrm{g\ mg^{-1}}$). To linearize Elovich model, assumption of $\alpha\beta t \gg t$ is made. Also, using two boundary conditions, Elovich model is given by Eq. (7),

$$Q = \frac{1}{\beta} \cdot \ln(\alpha \cdot \beta) + \frac{1}{\beta} \cdot \ln(t) \tag{7}$$

Table 5
Result of Langmuir isotherm for the adsorbtion of glycolic acid by alumina

| Langmuir isotherm | | | | |
|---|---|---|---|---|
| $1/Q_0$ | $K_L/Q_0$ | $Q_0$ | $K_L$ | $R^2$ |
| 27.976 | 53.354 | 0.036 | 1.907 | 0.9097 |

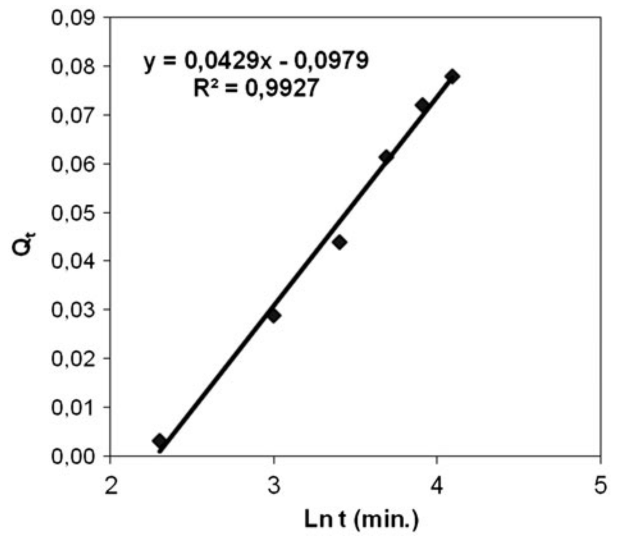


Fig. 5. The linear plot of Elovich model equation glycolic acid.

Table 6
Obtained constant for Elovich equation and pseudo second order kinetic model

| Elovich equation | | |
|---|---|---|
| $\alpha$ | $\beta$ | $R^2$ |
| 0.047 | 23.31 | 0.9927 |

A graph of $q_t$ with respect to ln ($t$) must give a line. This straight line has the slope of ($1/\beta$) and intercept of this line is ($1/\beta$) ln ($\alpha\beta$). The Elovich plotted about glycolic acid adsorption onto alumina is shown in Fig. 5. Constants of Elovich equation for glycolic acid have been given in Table 6.

## 4. Conclusions

In the content of this work, adsorptive separation of glycolic acid using alumina has been studied and influences of equilibrium time, dose of alumina, and preliminary concentration of glycolic acid on the adsorption were examined. It was concluded that removal of alumina increases from 0.010 to 0.173 g $\mathrm{mg^{-1}}$ with increasing dose of alumina from 0.2 to 2 g. Using 2g of alumina, we determine $Q_e$ as 0.173 g $\mathrm{mg^{-1}}$. Nevertheless, the preliminary concentration of acid has not influenced adsorption equilibrium. Adsorptive separation of acid was decreased with rising preliminary concentration of glycolic acid. It was concluded that adsorptive separation decreases with rising temperature. We found that 5.78% recovery was at 298 K. However, at the temperature of 318 K, removal of glycolic acid was 1.73%. It can be observed that alumina adsorption is an efficient method for the separation of glycolic acid from fermentation broth or wastewater streams.

## References


[1] H. Uslu, Linear Solvation Energy Relationship (LSER) modeling and kinetic studies on propionic acid reactive extraction using Alamine 336 in a Toluene solution, Eng. Chem. Res. 45 (2006) 5788–5795.

[2] A.F. Tuyun, H. Uslu, Extraction equilibria of picolinic acid from aqueous solution by tridodecylamine (TDA), Desalination 268 (2010) 134–140.

[3] Y.S. Aşçı, İ.M. Hasdemir, Removal of some carboxylic acids from aqueous solutions by hydrogels, Chem. Eng. Data 53 (2008) 2351–2355.

[4] A. Keshav, K.L. Wasewar, S. Chand, Extraction of propionic acid with tri-n octyl amine in different diluents, Sep. Purif. Technol. 63 (2008) 179–183.

[5] S. Kumar, K.L. Wasewar, B.V. Babu, Intensification of nicotinic acid separation using organophosphorous solvating extractants by reactive extraction, Chem. Eng. Technol. 31 (2008) 1584–1590.

[6] H. Uslu, İ. İnci, Adsorption equilibria of l-(+)-tartaric acid onto alumina, J. Chem. Eng. Data 54 (2009) 1997–2001.

[7] H. Uslu, Ş.İ. Kırbaslar, Ş.S. Bayazit, Adsorption equilibrium data for acetic acid and glycolic acid onto Amberlite IRA-67, J. Chem. Eng. Data 55 (2010) 1295–1299.

[8] A.B. Soni, A. Keshav, V. Verma, S. Suresh, Removal of glycolic acid from aqueous solution using Bagasse Flyash, Int. J. Environ. Res. 6 (2012) 297–308.

[9] A.S. Kertes, C.J. King, Extraction chemistry of fermentation product carboxylic acids, Biotechnol. Bioeng. 28 (1986) 269–282.

[10] Y.S. Aşçı, İ. İnci, Extraction of glycolic acid from aqueous solutions by Amberlite LA-2 in different diluent solvents, J. Chem. Eng. Data 54 (2009) 2791–2794.

[11] İ. İnci, Adsorption equilibria of L (+) tartaric acid onto alumina, J. Chem. Eng. Data 54 (2009) 1997–2001.

[12] Y. Mao, B.M. Fung, A study of the adsorption of acrylic acid and maleic acid from aqueous solutions onto alumina, *J. Colloid Interface Sci.* 191 (1997) 216–221.

[13] I. Inci, Adsorption of glycolic acid by activated carbon, Rev. Chim. 54 (2003) 199–201.

[14] R.K. Rajoriya, B. Prasad, I.M. Mishra, K.L. Wasewar, Adsorption of Benzaldehyde on granular activated carbon: Kinetics, equilibrium, and thermodynamic, Chem. Biochem. Eng. Q. 21 (2007) 219–226.

[15] S. Azizian, Kinetic models of sorption: A theoretical analysis, J. Colloid Interface Sci. 276 (2004) 47–52.

[16] S. Azizian, M. Haerifar, H. Bashiri, Adsorption of methyl violet onto granular activated carbon: Equilibrium, kinetics and modeling, Chem. Eng. J. 146 (2009) 36–41.

[17] I. İnci, Ş.S. Bayazit, Y.S. Aşçi, Separation of succinic acid from aqueous solution by alumina adsorption, J. Chem. Eng. Data 56 (2011) 4449–4453.

[18] Ö. Özcan, I. İnci, Y.S. Asci, Multiwall carbon nanotube for adsorption of acetic acid, J. Chem. Eng. Data 58 (2013) 583–587.

[19] A.R. Iftikhar, H.N. Bhatti, M.A. Hanif, R. Nadeem, Kinetic and thermodynamic aspects of Cu(II) and Cr (III) removal from aqueous solutions using rose waste biomass, J. Hazard. Mater. 161 (2009) 941–947.

[20] N.P. Passe-Coutrin, S. Altenor, D. Cossement, C.J. Jean-Marius, S. Gaspard, Comparison of parameters calculated from the BET and Freundlich isotherms obtained by nitrogen adsorption on activated carbons: A new method for calculating the specific surface area, Microporous Mesoporous Mater. 111 (2008) 517–522.

[21] K. Urano, H. Tachikawa, Process development for removal and recovery of phosphorus from wastewater by a new adsorbent. II. Adsorption rates and breakthrough curves, Ind. Eng. Chem. Res. 30 (1991) 1897–1899.