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Developing a new model to predict mass transfer coefficient of salicylic acid adsorption onto IRA-93: Experimental and modeling

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Abstract−An experimental breakthrough curve for Salicylic acid in an adsorption recovery process was determined by an anion-exchange resin IRA-93. The volumetric mass transfer coefficients were calculated by employing constant wave propagation theory. Meanwhile, the effects of volumetric feed flow rates on this break through curve and mass transfer coefficients at different flow rates were also studied in order to develop three new models to predict mass transfer coefficient. The results demonstrated that by the increase in the feed flow rates, the amount of adsorption reduces. However, while the volumetric feed flow rates increase the overall volumetric mass transfer coefficients will increase. This grows the feeling that the feed flow rate should be optimized. The optimum flow rate for the adsorption was found to be 7 mg/*l* in this study. In addition, three new models to predict the mass transfer coefficient in respect of feed rates were developed in this research work which showed very high fittings with R^2>0.99. These models could fully support the experimental data obtained.

Key words: Modeling, Predict Mass Transfer Coefficient Ion-exchange Resin, IRA-93, Salicylic Acid, Breakthrough Curve, Constant Wave Propagation Theory

INTRODUCTION

Phenols are probably the most extensively studied compounds in the field of wastewater treatment, as they are persistent pollutants with high toxicity that are released in the wastewater of a considerable number of industries [1-3]. Different techniques are used for the removal of phenolic compounds from wastewater [3,4]. Adsorption of phenolic compounds on different polymeric adsorbents has been studied by various researchers [5-9]. Salicylic acid is a drug compound which is usually produced from phenol [10]. Applications of salicylic acid are such as cosmetics, wart-removing medicines, to externally treat fungus infections, as an acne topic treatment and to increase the cell turnover as a component of skin creams. This compound is also employed as food preservative besides its usage in plant protection against insects and pathogens. Thus, this compound is present as a main pollutant of wastewaters produced by different industries. Salicylic acid has also been found to be available in the wastewater from households, schools, hotels, business complexes so-called as gray wastewater, as well as some types of industries where no contributions from toilets, bidets or heavily polluted process water are included [11,12].

To properly design and operate fix-bed adsorption processes, the fix-bed dynamics must be well known. These dynamics are the pollutant breakthrough curves which should be fully recognized. Although a variety of models are available to predict the fixed-bed dynamics, the non-linear wave propagation theory provides a simple method to estimate the column breakthrough times for any types of adsorption isotherms. Due to some assumptions, infinite mass-transfer rate and local equilibrium, of the non-linear wave propagation theory cannot always be applicable for fixed-bed operations. Thus, a constant pattern wave approach has been proposed to predict the breakthrough curves of fixed-bed adsorption processes using either Langmuir or Freundlich adsorption isotherms. The constant-pattern wave approach was adopted in order to model the breakthrough curves of fixed-bed processes for removing organic pollutants such as phenols, p-nitrophenol and acid dye.

This research work focuses on the adsorption of salicylic acid onto IRA-93 as an anion-exchange resin to investigate the effects of feed flow rate on breakthrough curves and the calculation of mass transfer coefficient by employing the constant wave propagation theory and the effect of flow rates on these coefficients. Meanwhile, three new models with EViews software were developed to predict the effect of feed rate on mass transfer coefficient.

1. Theory

To properly evaluate the fix-bed adsorption process, the breakthrough curves should be determined experimentally or by mathematical models. Recently, various mass-transfer models have been found for prediction of the fixed bed dynamics [13-18], among which the mathematical model based on non-linear wave propagation theory has been used widely [18].

In the language of wave propagation theory, [19] the introduction of the feed generates a self-sharpening wave. Because of the finite mass-transfer rate, the self sharpening wave will eventually evolve into a constant pattern traveling at a constant velocity, u_C. In the constant-pattern wave, the ratio of the pollutant concentrations in the stationary and mobile phases is constant [16]:

$$\frac{q}{C}=\frac{q_F}{C_F} \tag{2}$$

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Where C_F is the feed pollutant concentration in the mobile phase and q_F is its associated equilibrium concentration in the stationary phase. The adsorption rate of the pollutant can be described by the linear driving force model in terms of the overall liquid-phase mass-transfer coefficient [16]:

$$\frac{\rho \partial q}{\partial t} = K_L a(C - C^*) \tag{3}$$

Where C^* is the mobile-phase concentration in equilibrium with the stationary-phase concentration q, and a, is the mass-transfer area per unit volume of the bed, while, K_L stands for the overall liquid-phase mass-transfer coefficient. The volumetric mass-transfer coefficient in the liquid phase is demonstrated by K_La.

Also in the constant-pattern wave, the mobile-phase concentration can be expressed as a unique function of the adjusted time defined as $\tau = t - z/uC$. The adsorption rate expressed in terms of the adjusted time is:

$$\frac{\rho \partial q}{\partial \tau} = K_L a(C - C^*) \tag{4}$$

When q is substituted with qFC/CF in Eq. (4) and the general adsorption isotherm model of power-law type is used, $q = kC^n$ leads to the Eq. (5) which can be used to predict the breakthrough curve:

$$t = t_{0.5} + \frac{\rho k C_F^{n-1}}{K_L a}\left[\int_{1/2}^{X} \frac{1}{X - X^{1/n}} dX\right] \tag{5}$$

Where;

X is the dimensionless effluent concentration, $X = C/C_F$ and $t_{0.5}$, the half-time for X=0.5.

In Eq. (5) the parameter $t_{0.5}$ can be directly read from the experimental data and the parameter K_La can be determined from the tangent slope of the x versus t curve at X=0.5.

$$\left(\frac{dX}{dt}\right)_{X=0.5} = \frac{K_L a}{\rho k C_F^{n-1}}(X - X^{1/n}) \tag{6}$$

MATERIAL AND METHODS

1. Experimental

Experiments were carried out in both batch and column tests. The adsorption isotherms of Salicylic acid onto IRA-93 at various initial concentrations were experimentally determined by batch tests. Series of column tests were performed to determine the breakthrough curves behavior at four different flow rates on IRA-93 and investigating the volumetric mass transfer coefficient as well.

2. Chemicals and Adsorbents

Salicylic acid ($C_7H_6O_3$) was purchased from Sigma-Aldrich (Spain). The desired concentrations of the solutions were prepared by using degassed and distilled water. The experiments were performed by using Amberlite IRA-93 as a weak-basic anionic resin. Table 1 summarizes the data supplied by the manufacturers on the physical characteristics of the resin studied.

3. Adsorbent Preparation

IRA-93 was based on polystyrene cross-linked with 10% divinyl benzene supplied by Aldrich. The resin was attained in Cl^- form. In the experiments, the Cl^- form resin was converted into OH^- using 100 cm^3 of 1M NaOH solution for 10 cm^3 of resin. The moisturized adsorbents were stored in sealed flasks to avoid drying.

Table 1. Characteristics of IRA-93 as the adsorbent employed

Adsorbent	IRA-93
Description	Gel type I weak base anion exchange resin.
Polymer structure	Cross-linked polystyrene, macro porous
Appearance	Semi-transparent spherical beads
Functional group	$-N(CH_3)_2 \cdot H_2O$
Ionic form as shipped	Free base
Mesh size (US Std.)	16-50
Total exchange capacity, form, wet, volumetric Cl^-	1.4 meq/mL

4. Batch Adsorption Studies

Adsorption equilibrium experiments were done by contacting the corresponding amount of adsorbent with 40 mL of salicylic acid in a 100 mL Erlenmeyer flask. To determine the adsorption isotherms parameters, the initial concentrations of salicylic acid solutions were varied within the range of 400 to 800 ppm with the intervals of 100 at a constant weight of IRA-93. The flasks were then placed in a shaker at 150 rpm in room temperature of 25±2 °C for 48 h to reach equilibrium. The solution was separated from the adsorbent after the desired time, and the final concentration of salicylic acid in solution was determined by measuring the absorbance at 295 nm, by means of a UV-vis spectrophotometer (Jasco model 7800, Japan).

5. Fixed Bed Adsorption Experiments

Dynamic column experiments were carried out in up flow columns of 0.12 m×0.01 m in dimension equipped with a peristaltic pump (SP311-Welp) and packed up to 0.10 m with the IRA-93 Resin as the adsorbent. These columns were fed with the corresponding aqueous solution of salicylic acid with the concentration of 600 ppm with the pump. The solutions prepared from pure samples were passed through the column until the breakthrough happened. The concentrations of the salicylic acid in the outlet were verified at 295 nm employing an UV-vis spectrophotometer Jasco (model 7800, Japan). The temperature of the feed was maintained at 25 °C. Fixed bed adsorption was studied at four different feed flow rates of 5.5 to 10 ml/min with the intervals of 1.5.

RESULTS AND DISCUSSION

1. Isotherms and Batch Adsorption Studies

The amount of salicylic acid or phenol adsorbed onto the adsorbent, q_e (mg g^{-1}), was calculated by a mass balance relationship presented in Eq. (7).

$$q_e = (C_0 - C_e)\frac{V}{W} \tag{7}$$

Where C_0 (mg/l) and C_e (mg/l) are the initial and equilibrium liquid-phase concentrations, respectively. V (L) stands for the volume of the solution while, W (g) corresponds the dry weight of the resin.

The adsorption isotherms of salicylic acid with varying in the concentration of the solution at 25 °C were measured and the experimental data were fitted with two isotherm models. The Lang-

Table 2. The parameters of Freundlich and Langmuir isotherm models

Model	Equation	Parameter	At 25 °C
Freundlich	(8) $q=kc^n$	k	161.053
		n	0.41
		R^2	0.976
		Adjusted-R^2	0.968
Langmuir	(9) $q=\frac{Kq_m c}{1+Kc}$	b	386.438
		q_m	28.573
		R^2	0.994
		Adjusted-R^2	0.992

muir and Freundlich isotherm models were found to well fit the experimental data. The parameters of these models were approved by EViews software. The adsorption isotherm models, commonly found in the literature, and their parameters are listed in Table 2.

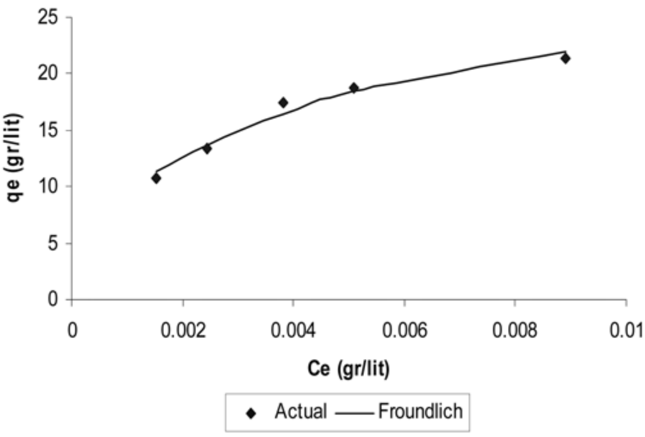

Fig. 1. Experimental adsorption equilibrium data (symbols), q_e vs. C_e, and fittings to Freundlich model (lines) for the adsorption of salicylic acid onto IRA-93 at different initial concentrations.

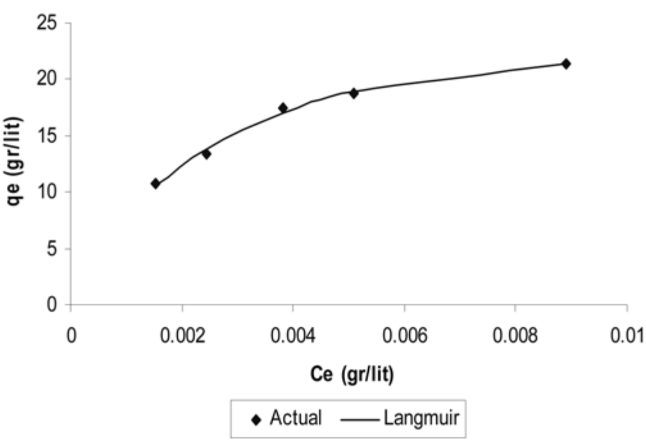

Fig. 2. Experimental adsorption equilibrium data (symbols), q_e vs. C_e, and fittings to Langmuir model (lines) for the adsorption of salicylic acid onto IRA-93 at different initial concentrations.

The experimental adsorbed concentrations as a function of liquid phase concentration corresponding to the salicylic acid adsorption onto IRA-93 fitted to Freundlich and Langmuir isotherm models are shown in Fig. 1 and Fig. 2, respectively. As is obvious, the Freundlich and Langmuir model well describes the equilibrium of salicylic acid onto the adsorbents used in this work.

Although the results obtained from the batch experiments imply that the Langmuir isotherm model reasonably fits the data at varying solution concentrations, yet, the equilibrium mobile-phase concentration in the Langmuir model cannot be expressed as a function of the stationary-phase concentration explicitly. Therefore, the Freundlich model, which also sensibly fits the isotherm data at 25 °C and natural pH with a high coefficient of determination (R^2=0.97), was employed in Eq. (5) for prediction of the breakthrough curves in the column tests.

2. Fixed Bed Adsorption

2-1. The Effect of Volumetric Feed Rate on the Ion-exchange Performance

The effect of volumetric feed rate on the ion-exchange performance was investigated in laminar flow regime at values of 5.5, 7, 8.5 and 10 ml/min. Total amount of salicylic acid taken up by the resin vs. time plot shows that ion-exchange rate increased with the increase in the feed rate as obvious in Fig. 3. The transport of the ions to be exchanged between the bulk solution and the resin occurred faster since the mass transfer coefficient improved with the growth of feed rate. However, at feed rates higher than 7 ml/min, due to the insufficient contact time of salicylic acid ions and resin,

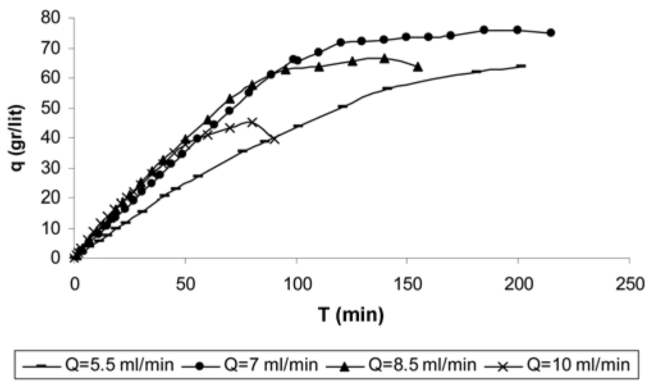

Fig. 3. Effect of feed flow rate on resin phase C=600 ppm T=25c Q (ml/min).

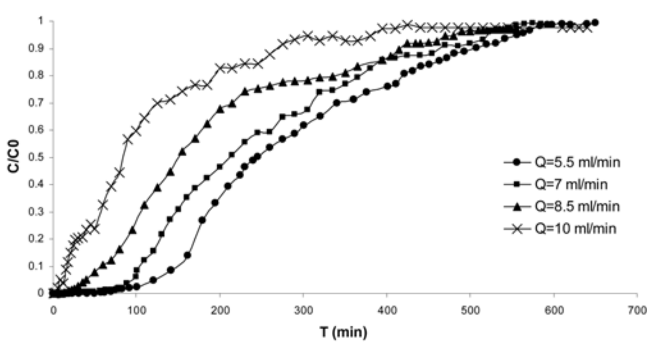

Fig. 4. Breakthrough curves of Salicylic acid adsorption on IRA-93 at different feed rates.

in order to maintain at the same amount of salicylic acid in the resin phase, a higher volume of the salicylic acid solution is needed to be passed through the column. These results reveal that 7 ml/min is favorable flow-rate for this ion-exchange process.

2-2. The Effect of Feed Rate on Breakthrough Curves

Fig. 4 represents the data obtained from adsorption on IRA-93 at different feed rates of 5.5, 7, 8.5, 10 ml/min and 600 ppm of initial solution concentration. Salicylic acid effluent concentration per initial feed concentration vs. residence time yielded to s-shaped characteristic curves.

Fig. 4 shows that when the volumetric feed flow rates were decreased from 10 to 5.5 ml/min, more favorable ion-exchange conditions were achieved. Nevertheless, under high feed rate conditions, the concentration of salicylic acid in the resin phase decreased because of the insufficient contact time of the solution and the resin. These results were in great agreement with the results reported by Salamatinia et al. [20] adsorbing heavy metals on oil palm frond in a fixed-bed up flow column. Therefore, feed flow-rate should be optimized. The effluent solution concentration reached to 5% of its feed concentration at t_B=120, 90, 40 and 14 min residence times for 5.5, 7, 8.5, 10 ml/min, correspondingly. These points are the breakpoints corresponding to each flow rate. The results indicated that flow-rates of 7-8.5 ml/min are considered the best range for the feed flow-rate to be adjusted at.

3. Mass Transfer Coefficients

The liquid phase and solid resin phase mass transfer coefficients can be expressed in terms of overall external-internal mass transfer coefficient [21,22]. The transfer coefficient from the constant-pattern wave approach (Eq. (6)) was calculated by using the Freundlich (Eq. (8)) isotherm model employing the experimental breakthrough curves as explained previously.

To properly evaluate the fix-bed adsorption process, the breakthrough curves should be determined experimentally or by mathematical models. In attendance various mass-transfer models were found for prediction of the fixed bed dynamics [23-26], among which the mathematical model based on non-linear wave propagation theory was used widely as expressed in Eqs. (4) to (6) [26]. The results calculated from K_La (min^{-1}) are listed in Table 3.

Table 3. Effect of feed flow rates on K_La (min^{-1})

Resin	Q (ml/min)	K_La (min^{-1})
IRA-93	5.5	107.67
	7	166.89
	8.5	258.42
	10	414.54

However, the increase in the volumetric feed rate led to the increase in the amount of K_La, as expected (Table 3), due to insufficient contact time the volumetric feed rate cannot increase to achieve higher mass transfer. Thus, 7 ml/min of flow rate was found to be the best volumetric feed rate.

MODELING OF MASS TRANSFER COEFFICIENT

According to Table 3, it is observed that the volumetric mass transfer coefficient has been varied in special form in respect to volumetric feed flow rate. In this section, new models for volumetric feed effect term (V.F.E.T) on volumetric mass transfer coefficient are developed. It should be noted that this type of modeling for mass transfer coefficient has not been reported previously and is considered a novel work carried out in this research paper. Therefore, according to mentioned discussion and Table 3, several models are investigated for K_La as the following equations:

$$K_La=c_1+c_2Q^n \tag{10}$$

$$K_La=c_1e^{c_2Q} \tag{11}$$

$$K_La=c_1+c_2e^{c_3Q} \tag{12}$$

Eq. (10) to Eq. (12) are analyzed and the amount of A.R.E, R^2 and other statistical functions have been calculated. Finally, based on the simplicity and error percentage, Eq. (10), was chosen as the best appropriate model. The experimental data were then fitted to all equations and the amounts of c_1, c_2, c_3 and n were determined with respect to O.L.S method by EViews software. The modeling results, including the values for c_1, c_2, c_3 and n as well as R^2 and adjusted R^2 are summarized in Table 4.

The results in Table 4 show that the amounts for the coefficient of determination (R^2>0.99) and adjusted R^2>0.99 are in an acceptable range and show good agreement with experimental data. This proves the validity of this model and reveals that it can be used to predict the mass transfer coefficient in other volumetric feed rates successfully.

CONCLUSION

By studies of salicylic acid adsorption onto IRA-93 the following results were achieved in this study. Column tests were per-

Table 4. The parameters of mass transfer coefficient models

Model	Equation	Parameter	Parameter	R^2	Adjusted-R^2
Model (1)	$K_La=c_1+c_2Q^n$	c_1	86.92823	0.999993	0.99998
		c_2	0.035211		
		n	3.968565		
Model (2)	$K_La=c_1e^{c_2Q}$	c_1	22.58254	0.995807	0.99371
		c_2	0.290001		
Model (3)	$K_La=c_1+c_2e^{c_3Q}$	c_1	53.57324	0.999923	0.99977
		c_2	7.919884		
		c_3	0.382017		

formed to plot the breakthrough curves. By employing these curves and constant wave propagation theory, the volumetric mass transfer coefficients were calculated in order to develop three new models for prediction of the mass transfer coefficient.

Two important compatible application models in adsorption phenomena, the Langmuir and Freundlich models, both were satisfactory by fitting with experimental data. The coefficient of determination of $R^2>0.97$ for both of these isotherm models confirmed the ability of these models to predict the adsorption process.

The column tests showed that by the drop in volumetric inlet the more favorable ion-exchange conditions were achieved. However, under high feed rate conditions, the concentration of salicylic acid in the resin phase decreased which could be attributed to the insufficient contact time of solution and the resin to achieve desirable adsorption. With the increase in the volumetric feed flow rates the volumetric mass transfer coefficients also showed significant growth. Nevertheless, initially the result revealed that by increasing the feed rates the amount of maximum adsorption or breakthrough point time decrease. This led to the conclusion that the system should work at optimized flow rates, which was found to be at 7 mg/*l*.

By considering several mathematical functions, an appropriate model was developed to predict the volumetric feed effect on the mass transfer coefficient. All the models could be well fitted to the experimental data with the level of significance of $R^2\geq0.99$. It should be noted that all these models were developed in this research work for the first time, and can be used to predict mass transfer coefficient at other different feed rates, as well.

REFERENCES

1. M. Otero, M. Zabkova and A. E. Rodrigues, *Sep. Purif. Technol.*, **45**, 86 (2005).
2. K. Kunin, *Pure Appl. Chem.*, **46**, 205 (1976).
3. A. Morão, A. Lopes, M. T. Pessoa de Amorim and I. C. Gonçalves, *Electrochim. Acta.*, **49**, 1587 (2004).
4. W. Kujawski, A. Warszawski, W. Ratajczak, T. Porebski, W. Capala and I. Ostrowska, *Sep. Purif. Technol.*, **40**, 123 (2004).
5. S. H. Lin, C. L. Pan and H. G. Leu, *Chem. Eng. J.*, **87**, 163 (2002).
6. S. P. Deosarkar and V. G. Pangarkar, *Sep. Purif. Technol.*, **38**, 241 (2004).
7. E. H. Crook, R. P. McDonell and J. T. McNulty, *Ind. Eng. Chem. Prod. Res. Dev.*, **14**, 113 (1975).
8. D. S. Farrier, A. L. Hines and S. E. Wang, *J. Colloid Interface Sci.*, **69**, 233 (1979).
9. G. M. Gusler, T. E. Browne and Y. Cohen, *Ind. Eng. Chem. Res.*, **32**, 2727 (1993).
10. D. Hanesian and A. J. Perna, *The sitting, process analysis and design of a manufacturing facility using hazardous material in a residential community (The manufacture of aspirin)*, Workbook, New Jersey Institute of Technology, Newark, New Jersey (1999).
11. C. G. Daughton and T. A. Ternes, *Environ. Health Perspect.*, **107**, 907 (1999).
12. E. Erikson, K. Auffarth, A.-M. Eilersen, M. Henze and A. Ledin, *Water SA.*, **29** (2003).
13. X. T. Li, B. C. Pan and F. W. Meng, *Ion. Exch. Adsorpt.*, **21**, 209 (2005).
14. D. Chatzopoulos and A. Varma, *Chem. Eng. Sci.*, **50**, 127 (1995).
15. A. Wolborska and P. Pustelnik, *Water Res.*, **30**, 2643 (1996).
16. A. J. Slaney and R. Bhamidimarri, *Water Sci. Technol.*, **38**, 227 (1998).
17. A. Wolborska, *Chem. Eng. J.*, **73**, 85 (1999).
18. J. M. Chern and Y. W. Chien, *Water Res.*, **36**, 647 (2002).
19. B. C. Pan, Y. Xiong and A. M. Li, *React. Funct. Polym.*, **53**, 63 (2002).
20. B. Salamatinia, A. H. Kamaruddin and A. Z. Abdullah, *Chem. Eng. J.*, **145**, 259 (2008).
21. S. Takac, G. Calik, M. Aytar and T. H. Ozdamar, *Biochem. Eng. J.*, **2**, 101 (1998).
22. J. J. Carberry, *Chemical and catalytic reaction engineering*, McGraw-Hill (1976).
23. D. Chatzopoulos and A. Varma, *Chem. Eng. Sci.*, **50**, 127 (1995).
24. A. Wolborska and P. Pustelnik, *Water Res.*, **30**, 2643 (1996).
25. A. J. Slaney and R. Bhamidimarri, *Water Sci. Technol.*, **38**, 227 (1998).
26. A. Wolborska, *Chem. Eng. J.*, **73**, 85 (1999).