Journal of the Korean Society of Dyers and Finishers
Vol. 18, No. 5, pp. 42 ~47(2006. 10)

〈Research Paper〉

Kinetic modeling analysis for the decolorization of dyes using a mixed adsorbent

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(Received September 4, 2006/Accepted October 18, 2006)

Abstract— A mixed adsorbent prepared by pyrolysing a mixture of carbon and flyash in 1:1 ratio was tested for its decoloration ability for three different classes of dyes namely, Astrazone Blue FRR(Basic Blue 69), Teflon Blue ANL(Acid Blue 125) and Verofix Red(Reactive Red 3GL). Kinetic analyses were carried out at the optimum conditions obtained by the author in the previous studies. The data was fitted with three kinetic model equations. The results showed that the dye uptake mechanism followed the second-order rate expression.

Keywords: *Decolorization, Mixed adsorbent, Kinetics analysis*

1. Introduction

Worldwide over 10,000 different dyes and pigments are used in dyeing and printing industries. The total world colorant production is estimated to be 800,000 tons per year and at least 10% of the used dyestuff enters the environment through wastes[1].

The release of these coloured waste waters in the ecosystem is a dramatic source of aesthetic pollution, eutrophication and perturbations in aquatic life[2]. So, the removal of dyes from effluents in an economic fashion remains a major problem for textile industries. Adsorption technique has been proved to be an excellent way to treat effluents, offering advantages over conventional process, especially from the environmental point of view. Weber[2] had identified many advantages of adsorption over several other conventional treatment methods. Activated carbon is being used as potential adsorbents because of its high efficiency[3].

But, the rise in the price of activated carbon results in economic difficulties. Hence, alternative adsorbents with an equivalent capability to activated carbon are a currently thrust area of research.

Owing to high cost of activated carbon, an adsorbent that is cheap and easily available would be a better alternative. In the present study, a mixed adsorbent consisting of 1:1 mixture of carbon and flyash was investigated for its efficiency to remove three classes of dyes namely Acid Blue 125, Basic Blue 69 and Reactive Red 3GL from aqueous solution and their chemical structures are shown in Fig. 1. In the previous publications by the author[4,5], the effect of pH, temperature and particle size on adsorption were studied in detail and optimum conditions were determined using Response Surface Methodology which are given in Table 1. But, the kinetic analysis

Table 1. Optimum condition of each dye as per previous study by the author[4,5]

parameter	Optimum conditions		
	Acid Blue 25	Basic Blue 69	Reactive Red 3GL
η (efficiency)	100 %	100 %	100 %
X2 (pH)	1.5	12.80	10.8
X3 (temperature, °C)	27.5	27.75	59.25
X4 (particle size, mm)	0.0565 mm	0.0555 mm	0.0525 mm

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*Corresponding author. Tel: +82-42-821-6620; Fax: +82-42-823-3736; e-mail: yason@cnu.ac.kr which is very important for better understanding and designing of adsorption processes were not performed and hence, in this paper, experimental studies related to kinetic modeling were carried out and results were clearly analyzed.

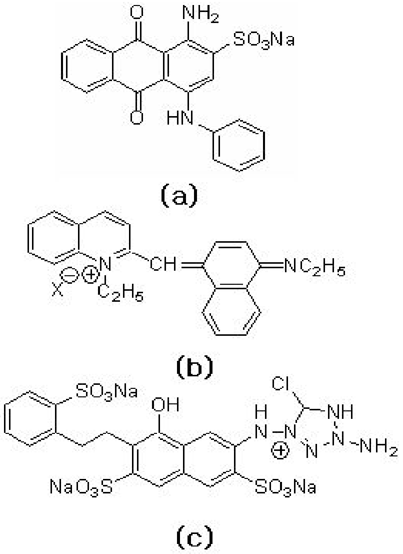

Fig. 1. Molecular Structure of (a) AB 25 (b) BB 69 (c) RR 3GL.

2. Experimental

2.1. Preparation and characterization of a mixed adsorbent

Flyash, obtained from Ennore Thermal Power Plant, Chennai, Tamilnadu, was washed with distilled water, dried under sunlight and subsequently in hot air oven at 60°C. Mixed adsorbent was prepared by mixing carbon (supplied by SD Fine chemicals) with flyash at 1:1 ratio by pyrolysing in an isothermal reactor powered by an electric furnace. High purity nitrogen was used as the purging gas. The isothermal reactor was heated to the desired temperature of 650°C at a heating rate of 15°C/min, and a holding time of 3 h. After pyrolysis, the product was activated at the same temperature for 3 h using CO_2 as oxidizing agent and subsequently used as adsorbent. Chemical analysis of the hybrid adsorbent showed that carbon was the major constituent along with small amount of silica, lime and alumina. The origin of carbon constituents could be reasoned by analyzing the process and material used for carbon manufacture. Silica and alumina content were due to the constituents present in the flyash.

2.2. Adsorption Kinetic Studies

Stock solutions of dyes(AB 25, BB 69, RR 3GL) were prepared in deionized water and diluted according to the working concentration. The required pH was adjusted by 0.1 N HCl or 0.1 N NaOH. Dye concentration was measured using UV-Vis spectrophotometer(Shimadzu UV 1600, Japan) at a wavelength corresponding to the maximum absorbance for each dye, 600 nm for AB 25 dye and 585 nm for BB 69 dye and 534 nm for RR 3GL dye. In the experiments of kinetics adsorption, dye solution added with 10 g/ ℓ of the adsorbent was placed in a 250 ㎖ Erlenmeyer flask. The flasks were kept under agitation in a rotatable orbital shaker at 150rpm. The experiments for this single adsorbate/adsorbent system were performed for various initial concentrations at the optimum conditions, given in Table 1 which was determined by both Response Surface Methodology(RSM) and Monte-Carlo optimization techniques in the previous publications by the author[4,5]. The samples were taken off at regular intervals and analyzed for dyes adsorption.

The amount of dyes adsorbed per gram of adsorbent were computed as follows,

$$q_e = \left[\frac{C_0 - C_e}{W} \right] V \qquad (1)$$

where, C_0(mg/ ℓ) represents the initial concentration of dye solution, C_e(mg/ ℓ) represents the equilibrium concentration of dye solution, V (m ℓ) represents the volume of the solution and W(g) represents the weight of the adsorbent.

3. Results and Discussion

The prediction of batch sorption kinetics gives the most important information for designing batch sorption systems. In order to design an effective and efficient model, it is always desirable to study a meticulous kinetic understanding of the process and a prior knowledge of the optimal conditions would herald a better design and modeling of the process. A thorough study of adsorption kinetics is therefore a vital importance for exploiting the potentiality of the adsorbents. Adsorption kinetics explain how fast the sorption process occurs and also the factors affecting the reaction rate. Information on the kinetics of solute uptake is required for selecting optimum operating conditions for full scale batch process. Also it is important to establish the time dependence of adsorption systems under various process conditions.

The nature of sorption process will depend on the physical or chemical characteristics of the adsorbent system and also on the system conditions.

The principle behind the adsorption kinetics involves the search for a best model that well represents the experimental data. Numerous kinetic models have been used to describe the reaction order of the system. Adsorption kinetics reveals the solute uptake rate; hence kinetic studies are important in water treatment process design. The following models can investigate the mechanism of adsorption,

- Pseudo first order model, pseudo second order model by Lagergren [6]
- Intra-particle diffusion process by Weber and Morris [2]

All the kinetic analysis was carried out only at the optimum conditions obtained by the design of experiments concepts, published by the authors [4,5].

The adsorption kinetics can also be described by pseudo first order and second order mechanism as per Lagergren [6], For the pseudo first order reaction,

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

On integration for the boundary condition t=0, t=t and q_t=0 to q_t=q_t gives in linear form,

$$\int_0^{q_e} \frac{dq_t}{q_e - q_t} = k_1 \int_0^t dt$$

$$\left[-\ln(q_e - q_t)\right]_0^{q_e} = k_1 t$$

$$-\ln(q_e - q_t) + \ln q_e = k_1 t$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

Converting into log, $2.303\log(q_e - q_t) = 2.303\log q_e - k_1 t$

Dividing the whole equation by 2.303,

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (2)$$

where, q_e(mg/g) represents the amount of dye adsorbed at equilibrium, q_t(mg/g) represents the amount of dye adsorbed at any time t, k(1/min) represents the rate constant for the first order reaction. The straight-line plot of log(q_e – q_t) Vs t results in log q_e as the intercept of the plot. If the intercept does not equal to be experimental q_e then the reaction is unlikely to be pseudo first order reaction even though the plot has high correlation co-efficient with experimental data.

Most sorption processes take place by a multistep mechanism comprising: (i) diffusion across the liquid film surrounding the solid particles(a process controlled by an external mass transfer coefficient), (ii) diffusion within the particle itself assuming a pore diffusion mechanism (intraparticle diffusion) and (iii) physical or chemical adsorption at a site [6] The transient behavior of the batch adsorption process was analyzed using Lagergren first and second order kinetic equations. The experimental data thus obtained were fitted based on equation (2) and (3) and are given in Fig. 2 and 3. The reaction constants were evaluated from slope and intercept of the curves for each dye and are given in Table 2. From the Fig. 2, it was observed thatAB 125 and BB 69, having the appreciable correlation coefficient value 0.9753 and 0.9688 showing normal fit for the first order kinetic model

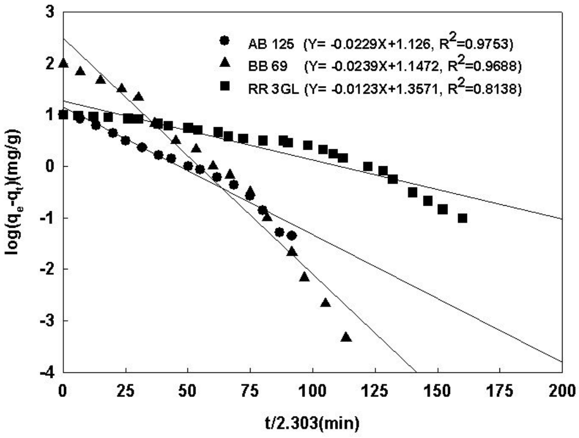

Fig. 2. Pseudo first order plot for the adsorption of three classes of dyes on mixed adsorbent at the optimum conditions.

but the RR 3GL deviates from the theory for first order reaction model and hence, this is not appropriate to use first order model for RR 3GL.

For pseudo second order reaction,

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

Integrating for the boundary condition t=0 to t=t and $q_t=0$ to $q_t=q_t$

$$\int_0^{q_e} \frac{dq_t}{(q_e - q_t)^2} = k_2 \int_0^t dt$$

In linearised form,

$$\frac{t}{q_t} = \frac{t}{q_e} - \frac{1}{k_2 q_e^2} \tag{3}$$

where q_e (mg/g) represents the equilibrium dye concentration on the adsorbent, q_t(mg/g) represents the dye adsorbent at any time t, k_2 (1/min) represents the equilibrium rate constant of the pseudo second order model. In the straight-line plots of t/q_t Vs t the slope i.e. q_e should fit with the experimental q_e for the model to be valid. The data, obtained through experimental were fitted for second order model and constants evaluated through slopes and intercepts are given in Table 2. Fig. 3 presents the linear correlation of the pseudo second order kinetics for the two dyes.

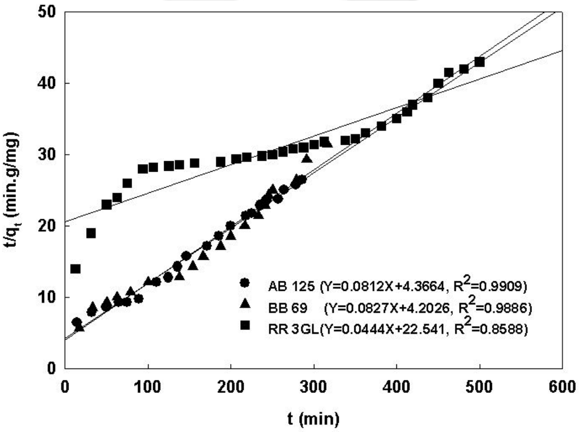

Fig. 3. Pseudo second order plot for the adsorption of three classes of dyes on mixed adsorbent at the optimum conditions.

In this study, the kinetic data show a good compliance with this pseudo second order equation and the equilibrium adsorption capacities are close to the experimental data.

The correlation coefficients for the first order kinetic model obtained at various optimum conditions are lower than the case of the second-order model for all the three dyes. Also the calculated q_e values found from the first-order kinetic model did not give reasonable values for the dyes. The correlation coefficients for the second-order kinetic model were 0.9909, 0.9886 and 0.8588 for AB 125, BB 69 and RR 3GL respectively at all the optimum conditions studied for each dye. The calculated q_e values also agreed very well with the experimental q_e values in the case of second-order kinetics. These suggest that each of the dye sorption system is not first-order reaction but the second-order model. The similar phenomena are also observed in biosorption of dye RB 2 and RY 2 on biomass7). According to the pseudo second-order model, the adsorption rate $\frac{dq_t}{dt}$ is proportional to the second-order of (q_e — q_t).

Since the mixed adsorbent in our experiments has relatively high equilibrium adsorption density q_e, the adsorption rates become very fast and the equilibrium times are short. Such short equilibrium times coupled with high adsorption capacity indicate a high degree of affinity between the dyes and the mixed adsorbent6).

Intraparticle diffusion model(Weber-Morris model) assumes that the film diffusion is negligible and intraparticle diffusion is the only rate controlling step, which is usually true for well-mixed solutions. The intraparticle diffusion model is a single-resistance model in nature and can be derived from Fick's second law under two assumptions8):

Table 2. Kinetic parameters for the adsorption of three classes of dyes on mixed adsorbent at the optimum conditions

S.No.	Dyes	Pseudo first order rate constant		Pseudo second order rate constant		Intra particle diffusion rate constant	
		k_1 (g/mg. min)	R^2	k_2 (g/mg. min)	R^2	k_i (g/mg. min$^{-0.5}$)	R^2
1	AB 25	0.0229	0.9753	0.001510	0.9909	0.5620	0.9800
2	BB 69	0.0239	0.9688	0.00162	0.9886	0.5772	0.9747
3	RR 3GL	0.01232	0.8138	0.00087	0.8588	0.5964	0.8994

(1) The intraparticle diffusivity D is constant; (2) The uptake of sorbate by the adsorbent is small relative to the total quantity of sorbate present in the solution. The mathematical expression thus obtained for the intraparticle diffusion model is[2)]

$$q_t = k_i t^{0.5} \tag{4}$$

where k_i (mg/gmin0.5) is defined as the intra-particle diffusion rate constant and is related to the intraparticle diffusivity in the following way,

$$k_i = \frac{6q_e}{R}\sqrt{\frac{D}{\pi}} \tag{5}$$

where R(cm) is the particle radius and q_e(mg/g) is the solid phase concentration at equilibrium. Equation(4) indicates that a plot of the average particle loading, q_t(mg/g), versus the square root of time, $t^{0.5}$, would yield a straight line passing through the origin if the adsorption process obeyed the intraparticle diffusion mode. The slope of the straight line equals to k_i, the intraparticle diffusion rate constant. This intercept gives an idea of boundary layer thickness i.e. the larger the intercept the greater the boundary layer effect as per Crank[9)].

From a mechanistic viewpoint, to interpret the experimental data, it is necessary to identify the steps involved during adsorption, described by external mass transfer(boundary layer diffusion) and intraparticle diffusion. According to previous studies, the intraparticle diffusion plot may compose multilinearity, representing the different stages in adsorption. Weber-Morris model was applied to the sorption of three different dyes on mixed adsorbent and the variation of q_t versus $t^{0.5}$ was given in Fig. 4. The experimental data thus obtained were fitted with the model and constant values was evaluated from slope of the curves and shown in Table 2. The linear portions of the curves do not pass through the origin indicating that the mechanism of dyes removal on mixed adsorbent is complex and both the surface adsorption as well as intraparticle diffusion contributes to the actual adsorption process. From the plots and intercept values, it was observed that intercept resulting in negative value shows the completely negligible boundary layer effect. This could be reasoned for their small particle size and structure and could enter the internal structure of the adsorbent without any boundary later effect.

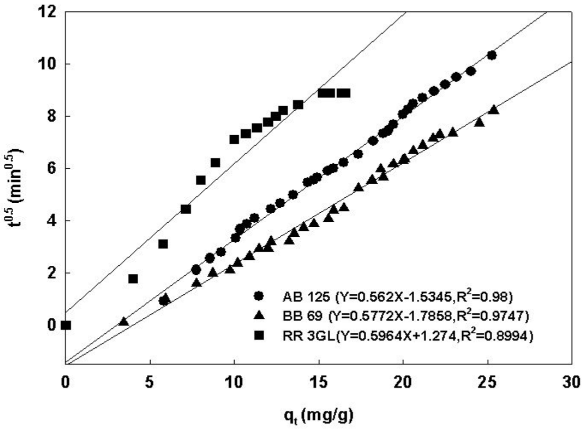

Fig. 4. Intraparticle diffusion plot for the adsorption of three classes of dyes on mixed adsorbent at the optimum conditions.

4. Conclusions

The capability of the use of mixed adsorbent for removing three classes of dyes was examined through kinetic studies. The obtained results showed that adsorbent have a high sorption capacity to remove the dyes. The suitability of the pseudo first and second order kinetic models for the sorption of dyes onto mixed adsorbent is also discussed. It was decided that the sorption kinetics of the dyes to mixed adsorbent obeyed the second order adsorption kinetics. The values q_e calculated from this kinetic model can be used to find the adsorption isotherm constants as long as q_e experimental values are difficult to determine experimentally. It may be concluded that mixed adsorbent can be used as a low-cost, natural and abundant source for the removal of reactive dyes as an alternative to more costly materials such as activated carbon.

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