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〈Research Paper〉

Equilibrium investigation for dyes removal using a mixed adsorbent

K. Ravikumar and Young A Son*

BK21 FTIT, Dept. of Organic Materials and Textile Engineering, Chungnam National University, Daejeon, South Korea

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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(C.I. Basic Blue 69), Teflon Blue ANL(C.I. Acid Blue 125) and Verofix Red(Reactive Red 3GL). Equilibrium investigations were carried out at the optimum conditions obtained in the previous studies. The equilibrium data fitted reasonably well to both the Freundlich and Langmuir adsorption models. However the Langmuir model was more appropriate to describe the adsorption behavior of the dyes to the hybrid absorbent system compared with the Freundlich model. The mixed adsorbent can be an low-cost alternative to activated carbons.

Keywords : *Dyes removal, Mixed adsorbent, Equilibrium investigation, Decoloration*

1. Introduction

Wastewater from textile industries is a problem in large parts of the world. The degradation products of textile dyes are often carcinogenic. Furthermore, the light absorption of textile dyes can create problems to photosynthesis of aquatic plants and algae 1). Due to the variability of the organic dyes and the resultant waste solution it is inadequate to treat the colored wastewater using traditional biochemical treatment process and coagulation treatment process. Ozone and hypochlorite oxidations are effective decolorization methods, but they are not desirable because of the high cost of the equipments, operating costs and the secondary pollution arising from the residual chlorine2).

Weber had identified many advantages of adsorption over several other conventional treatment methods. Activated carbon adsorption process for the removal of dyes is an accepted practice, but the cost of treatment is high 3). But, the rise in the price of activated carbon results in economic difficulties. Hence, alternative adsorbents with an equivalent potential of activated carbon are a currently thrusting 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

Table 1. Optimum conditions of three classes of dye as per previous study by the autho r4,5)

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 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 equilibrium analysis which is very important for better understanding and designing of adsorption processes were not performed and hence, in this paper both the experimental studies were carried out and results were clearly analyzed.

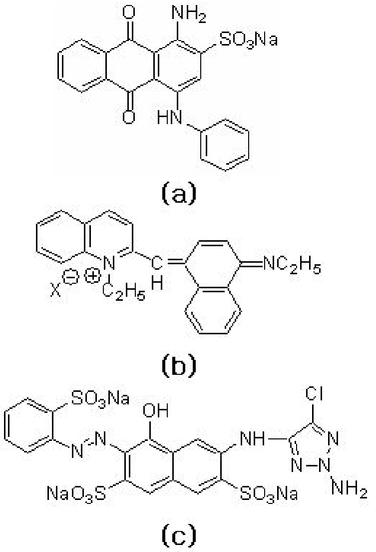

Fig. 1. Molecular structures of (a) AB 25 (b) BB 69 (c) RR 3GL.

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 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 and 534 nm for RR 3GL dye. In the experiments of equilibrium adsorption isotherm, dye solution added with 10g/ℓ of the adsorbent was placed in a 250㎖ Erlenmeyer flask. The flasks were kept under agitation in a rotatable orbital shaker at 150rpm until equilibrium was attained. After equilibrium was attained, dye concentration of the solution was analyzed by an UV-Vis spectrophotometer. 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 authors[4,5].

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

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

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

3. Results and Discussion

Adsorptive removal of three different classes of dyes, namely Astrazone Blue FRR(BB 69), Teflon Blue ANL(AB 125) and Verofix Red(RR 3GL), was carried out on a novel adsorbent, prepared by pyrolysing a mixture of carbon and flyash in 1:1 ratio. The analysis and design of adsorption requires the equilibrium study for better understanding of the process. Sorption equilibrium study provides the fundamental physiochemical data for evaluating the applicability of sorption process as a unit operation[6] and hence equilibrium study was carried out as given in the experimental section and data obtained were analyzed with model equations as given below.

3.1. Adsorption Equilibrium Modeling

The equilibrium adsorption isotherm is fundamental in describing the interaction behaviour between solute and adsorbent and is important in the design of an adsorption system. This model is valid for monolayer adsorption on a surface containing a finite number of identical sites. The widely used Langmuir isotherm[7] has found successful application in many real sorption process and is expressed as,

$$q_e = \frac{bq_m C_e}{1 + bC_e} \tag{2}$$

where, q_m(mg/g) represents the concentration of the adsorbed species on the surface when one complete monomolecular layer of coverage is achieved, C_e(mg/ ℓ) represents the solute concentration in the solution at equilibrium, q_e (mg/g) represents the concentration of solute adsorbed per unit weight of adsorbent, b(ℓ/g) represents the Langmuir constant related to the affinity of binding sites. Assumptions in Langmuir Isotherm: (a) adsorption occurs at definite located sites on the surface. (b) each site can bind only one molecule of the adsorbing species, (c) energy of adsorption is same for all sites, (d) there are no forces of interaction between adjacently adsorbed molecules.

The values of Langmuir constant, q_m mono layer capacity of the adsorbent are 344.82 mg/g, 357.14 mg/g and 333.33 mg/g for AB 25, BB69 and RR 3GL(Table 2) respectively. The results show the promising efficiency of the mixed adsorbent. Using these Langmuir constants and mass balance equation, theoretical amount of the dyes adsorbed per gram of mixed adsorbent were determined and compared with experimental data. The Langmuir plot for the adsorption of three classes of dyes on mixed adsorbent at the optimum conditions is shown in Fig. 2.

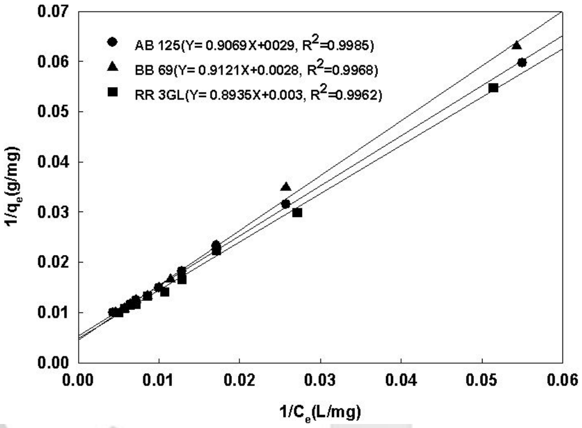

Fig. 2. Langmuir plot for the adsorption of three classes of dyes on a mixed adsorbent at the optimum conditions.

The effect of isotherm shape has been considered by Weber *et al* (1974) with a view to predicting whether an adsorption system is 'favourable 'or' unfavourable'. According to Hall *et al*[8] the essential characteristics of a Langmuir isotherm is expressed in terms of equilibrium parameter (r), which is also termed a dimensionless constant separation factor:

$$r = \frac{1}{1 + bC_{emax}} \tag{3}$$

where, C_{emax} is the maximum fluid phase concentration, mg/ ℓ, is the constant related to the energy of adsorption, ℓ/mg. The separation factor 'r' was calculated for all the dyes using the above equation and the results were found to be very encouragable. The values for all the dyes were in between 0 to 1 i.e., 0.555787, 0.565786 and 0.543699 for AB 25, BB69 and RR 3GL(Table 2)

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

No.	Dyes	Langmuir Constants		Freundlich Constants		Separation factor 'r'
		q_m (mg/g)	b (ℓ/mg)	1/n	k	
1	AB 25	344.82	0.003197	0.7799	2.1938	0.555787
2	BB 69	357.14	0.0030698	0.7819	2.18625	0.565786
3	RR 3GL	333.33	0.003357	0.7664	2.3431	0.543699

respectively that show the good adsorption property of the adsorbent and the favourable condition of the process. It was observed that mixed adsorbent exhibited better performance for the adsorption of the dyes studied in this work. These results showed that one of the most important adsorption mechanisms involves the interaction between the delocalized π electrons on the adsorbent surface and the free electrons of the dye molecule. A similar result was observed by Pereira *et al*[9].

The famous Freundlich isotherm[10] is used for heterogeneous surface energies in which the energy term qm in the Langmuir isotherm varies as a function of the surface coverage q, strictly due to variations in the heat of adsorption. The Freundlich equation has the general form,

$$q_e = kC_e^{1/n} \tag{4}$$

$$\log q_e = \log k + 1/n \log C_e \text{ in log form} \tag{5}$$

where, k (mg/g) is roughly an indicator of the degree or extent of adsorption and 1/n adsorption intensity. Freundlich isotherm equation implies that the energy distribution for the adsorption site is of essentially an exponential type rather than of the uniform type assumed in the Langmuir development. The magnitude of the exponent 1/n is an indication of the favourability of adsorption. The values in the range 0 < 1/n < 1 represents favourable adsorption conditions according to Treybal[11]. Almost, in all cases 1 < n < 10 corresponds to beneficial adsorption. The same equilibrium experimental data was fitted with Freundlich isotherm equation and constants values were evaluated. Freundlich plot for the adsorption of three classes of dyes on mixed adsorbent at the optimum conditions is shown in Fig. 3. The 1/n was found to be 0.7799, 0.7819 and 0.7664 for AB 25, BB 69 and RR 3GL(Table 2) respectively and the results verified a beneficial adsorption of the mixed adsorbent. The Langmuir mono layer capacity of the mixed adsorbent obtained for basic, acid and reactive dyes were compared with activated carbon. The monolayer capacites of activated carbon obtained for acid dyes[12], basic dyes[13] and reactive dyes[14] are 183.8 mg/g, 303.15 mg/g and 58.823 mg/g respectively which are very less compare to the mixed adsorbent.

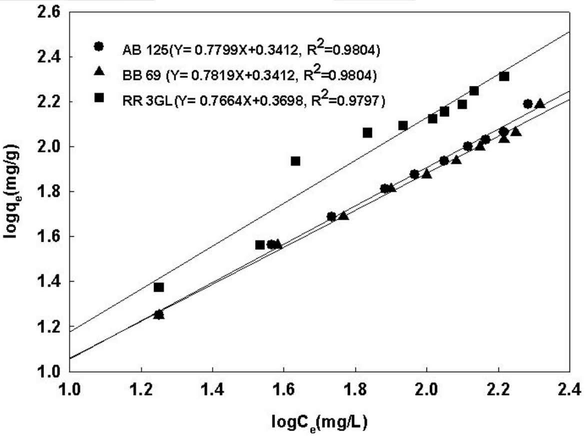

Fig. 3. Freundlich plot for the adsorption of three classes of dyes on a mixed adsorbent at the optimum conditions.

4. Conclusions

The capability of the use of mixed adsorbent for removing three classes of dyes was examined, through equilibrium investigation. The obtained results showed that the adsorbent have a high sorption capacity to remove the dyes. The Freundlich and Langmuir adsorption models are used for the mathematical description of the sorption equilibrium of the dyes. Adsorption equilibrium data fitted very well to both the models. It may be concluded that mixed adsorbent can be used as a low-cost, natural and abundant source for the removal of textile dyes as an alternative to more costly materials such as activated carbons.

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