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Multicomponent Equilibrium Studies for the Adsorption of Basic Dyes from Solution on Lignite

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Abstract. The ability of lignite or brown coal to adsorb basic dyes in single and multicomponent systems is analysed using IAST. The single component isotherms were correlated well using the Langmuir (L) and Freundlich (F) isotherms and the same isotherms, as L-L, F-F, L-F and F-L were used to model the binary dye-lignite isotherms. A sensitivity analysis was carried out on the Langmuir constants in the IAST.

Keywords: isotherm, adsorption, lignite, basic dyes, multicomponent

1. Introduction

Adsorption has gained prominence in recent years as a method of removing pollutants from water. Over 107 kg dyes are discharged in wastewaters from textile plants, dyehouses and food manufacturing facilities each year. Activated carbon (McKay and Al-Duri, 1988; Lin and Liu, 2000; Hui et al., 2003) has been shown to have a high adsorption capacity for dyes, especially basic dyes. However, activated carbon are relatively expensive, consequently, there has been extensive research to assess the capability and capacity of other cheaper adsorbents (McKay and Poots, 1986; Allen et al., 1998; Mohan et al., 2002; Gupta et al., 2003). However, only single component basic dye adsorption studies have been reported for lignite (Mohan et al., 2002; Duggan and Allen, 1997). In the present study the adsorption of three single component basic dye on lignite systems has been studied. The isotherms have been correlated using the Langmuir and Freundlich equations and then the three bicomponent systems have been predicted using L-L, F-F, L-F and F-L for each bicomponent system.

2. Materials and Methods

Lignite. The lignite sample was obtained from one of the significant lignite deposits in Northern Ireland. Macroscopically, lignite is dark brown or black in colour when moist, turning light brown when dry. The mechanical strength of lignite is generally poor; consolidation increasing as coalification proceeds. Its density lies in the range 1.00–1.35 g·cm^{-3}. Lignites are amorphous and fibrous or woody in texture, the asmined material possessing numerous water filled pores and capillaries. This feature means that the lignites

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Table 1. Molecular dimensions of the adsorbates.

Dye	Molar volume (cm^3·mol)	Molecular diameter (nm)	Maximum wavelength λ_{max} (nm)
Basic Red 22	337.6	1.13	538
Basic Blue 3	438.6	1.15	641
Basic Yellow 21	419.3	1.24	417

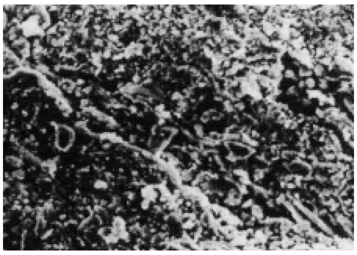

Figure 1. SEM photograph of lignite.

have high moisture contents (30–70%). Pore diameters vary and include micropores. As a consequence of their highly porous nature lignites possess high surface areas (100–200 $m^2 \cdot g^{-1}$). Figure 1 is a SEM photograph of lignite.

Dyes. The basic dyes fall within the class of Polymethine Dyes. As such they are cationic polymethines—because ionization in solution they possess an overall positive charge. The relative molecular size of each of the basic dye is shown in Table 1. The structures of each of the dyes, along with their commercial name and manufacturer are given in Fig. 2.

3. Experimental

Adsorption Studies. Adsorptions for this research were carried at 18 ± 2°C using a bottle point procedure. A constant mass of lignite (0.05 g), of particle size 500–710 μm, was weighed into each of twelve, 60 ml dark glass powder jars. A 1000 mg·dm^{-3} stock solution of each dye was prepared and diluted accordingly to obtain twelve concentrations within the range 50–1000 mg·dm^{-3}. 50 ml aliquots of dye solution, of specified concentrations, were then added to each of the preweighed sorbent samples. The glass jars were sealed using parafilm and screw top lids and kept in a state of constant agitation using a constant temperature shaking water bath until equilibrium was reached. A Perkin-Elmer, model 550S double beam spectrophotometer was used to determine the dye concentration in aqueous solution. Finally, the results were used to obtain lignite loading q by material balance: (1) $C = C_e$ then $q = q_e$; (2) $C = C_o$ then $q = q_o$. The equilibrium study mass balances are defined by:

$$(C_o - C_e)V = (q_e - q_o)M \tag{1}$$

4. Theory

The Ideal Adsorbed Solution Theory (IAST) was applied to dilute liquid adsorption systems by Radke and Prausnitz (1972) because it requires only single component isotherm parameters to predict the sorption equilibrium for the multi-component system. The IAST uses several equations to calculate the mole fraction of adsorbed phase concentrations. The use of these equations is shown and discussed. From the mass balance for each non-volatile component i (Eq. (2)) and the overall mass balance (Eq. (1)), the IAST dictates that the spreading pressure should be constant for each component, $\pi_1 = \pi_2 = \pi_3 \cdots = \pi_n$, in a given system:

$$\sum_{i=1}^{n} s_i = 1 \tag{2}$$

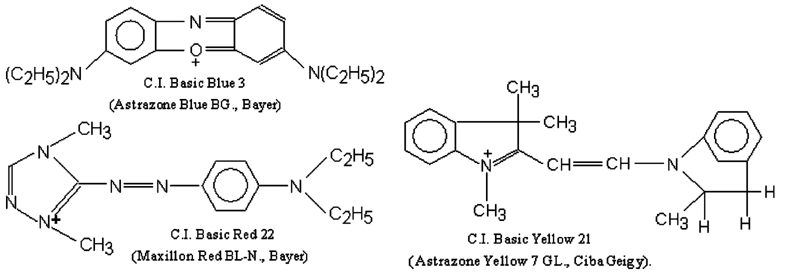

Figure 2. Structure of the Three Basic Dyes.

In the present study, the Langmuir and Freundlich are used to calculate the spreading pressure. The spreading pressure, π, and reduced spreading pressure, Π, can be evaluated from Eqs. (4) and (7):

For Langmuir Isotherm:

$$q^o_{e,i} = \frac{K_{L,i}C^o_{e,i}}{1+a_{L,i}C^o_{e,i}} \tag{3}$$

$$\Pi_i = \frac{\pi_i S_A}{R_g T} = \int_0^{C^o_e} \frac{q^o_{e,i}}{C^o_{e,i}} dC^o_{e,i} = \frac{K_{L,i}}{a_{L,i}} \ln\left(1+a_{L,i}C^o_{e,i}\right) \tag{4}$$

Rrearranging Eqs. (4) and (5) allows each to be used to obtain the equivalent pure component fluid and adsorbed-phased concentrations at the specified spreading pressure:

$$C^0_{e,i} = \frac{\exp(\Pi_i(a_{L,i}/K_{L,i}))-1}{a_{L,i}} \quad \text{and}$$

$$q^0_{e,i} = \frac{K_{L,i}}{a_{L,i}}[1-\exp(-\Pi_i(a_{L,i}/K_{L,i}))] \tag{5}$$

Similarly, for Freundlich Isotherm

$$q^o_{e,i} = a_{F,i}C^{o^{b_{F,i}}}_{e,i} \tag{6}$$

$$\Pi_i = \frac{\pi_i S_A}{R_g T} = \int_0^{C^o_e} \frac{q^o_{e,i}}{C^o_{e,i}} dC^o_{e,i} = \int_0^{q^o_e} \frac{d\ln C^o_{e,i}\left(q^o_{e,i}\right)}{d\ln q^o_{e,i}} dq^o_{e,i} = \frac{q^o_{e,i}}{b_{F,i}} \tag{7}$$

$$q^o_{e,i} = \Pi_i b_{F,i} \quad \text{and} \quad C^o_{e,i} = \left(\frac{q^o_{e,j}}{a_{F,i}}\right)^{1/b_{F,j}} \tag{8}$$

Since the IAST dictates that the spreading pressure should be constant for each component in a given system, for a binary system: $\Pi_1 = \Pi_2$, the program will be optimized the $C^o_{e,1}$ value until the spreading pressures of component 1 and 2 are equal. Hence, the value of $C_{e,1}$ and $C_{e,2}$ can be calculated by Eq. (9).

$$C_{e,i} = C^o_{e,i} \cdot s_i \tag{9}$$

5. Results

Single Component Isotherms. The analysis of the single component isotherms for the adsorption of BB3, BR22 and BY21 onto lignite are shown with the experimental results in Fig. 3. The Langmuir and Freundlich parameters according to Eqs. (3) and (6) are presented in Table 2. The maximum sorption capacities, $q_{\max}$, are 1.966, 1.514 and 0.939 mmole·g^{-1} for BB3, BR22 and BY respectively. From the figures, the both Langmuir and Freundlich equations provide good fitting for three basic dye/lignite systems. It is difficult to confirm which equation provides the best correlation of the data from these figures. Therefore, the SSE values of each equation were used to compare the difference between experimental and theoretical data of the equilibrium solid-phase concentration, q_e (see Eq. (10)). It was found that the Freundlich isotherm gives much lower SSE values in BB22 and BY21 systems compared to the Langmuir isotherm and but not in the BB3 system. It implies that the Freundlich isotherm provides better correlation of BR22 and BY21 equilibrium data while the Langmuir isotherm provides better correlation of BB3 equilibrium data.

$$SSE = \sum_{i=1}^{p} (q_{e,\text{cal}} - q_{e,\text{exp}})^2_i \tag{10}$$

Table 2. Langmuir and Freundlich single component constant.

	Langmuir				Freundlich		
	K_L	a_L	$q_{\max}$	SSE	a_F	b_F	SSE
BB3	31.27	15.90	1.966	*0.157*	2.183	0.332	*0.210*
BR22	11.76	7.77	1.514	*0.180*	1.328	0.293	*0.011*
BY21	59.22	63.08	0.939	*0.050*	1.210	0.256	*0.002*

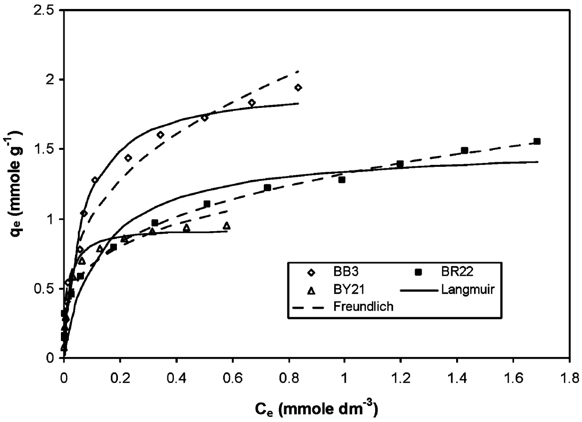

Figure 3. Langmuir and Freundlich isotherm plots for three basic dyes on lignite in single component system.

Binary Component Isotherm Systems. The isotherm data for the binary system are predicted from the single-component dye sorption data alone. The IAST as defined in Section 4 was initially arranged in combinations of isotherms (L-L, F-F, L-F & F-L), a detailed analysis has been carried out to investigate the influence of combinations of isotherm on the results of IAS model simulations in this paper. Figures 4(a) and (b) show the plots for the binary systems BB3+BR22 and BB3+BY21 using IAST-F-F model. Visually the IAST with F-F isotherm combinations provides reasonable good prediction for both BB3+BR22 and BB3+BY21 systems. For the BB22+BY21 system, the correlation between the predicted data and experimental data are good for BY21 dye but not for BB22, the IAST-FF model under predicts the equilibrium concentration of BR22 dye. The predicted results by the IAST model using LL and FL combinations isotherm for three binary systems are shown in Figs. 4(c) and (d). The theoretical and experimental isothems from four IAST models

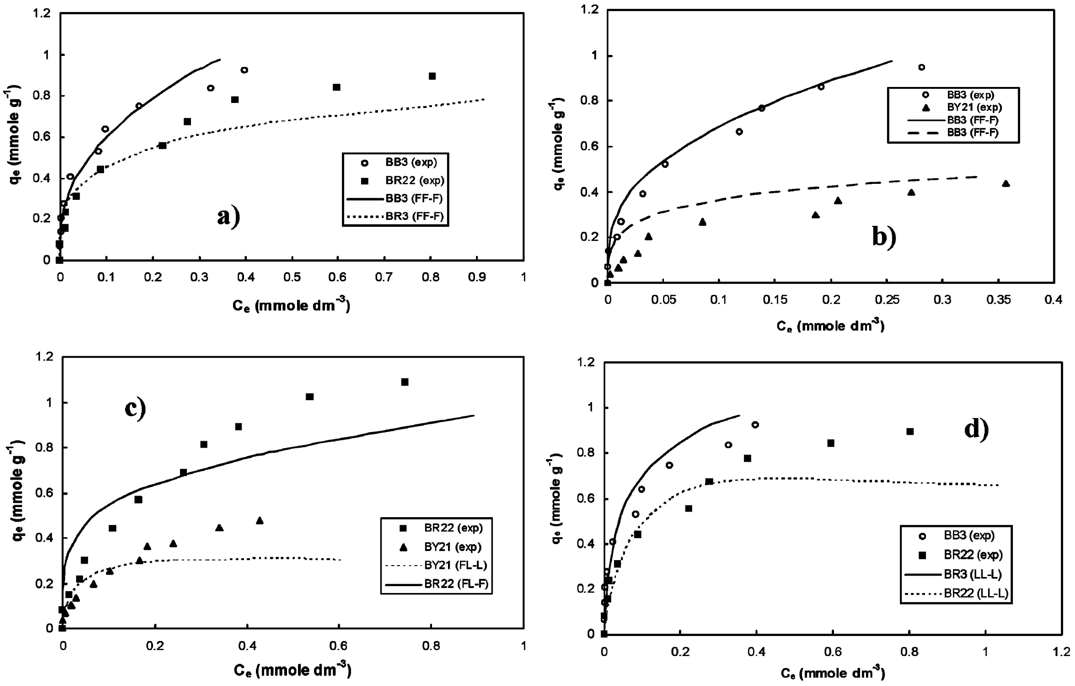

Figure 4. IAST analysis on BR22 plus BY21 binary mixtures using Freundlich(BR22)-Freundlich(BY21) isotherm.

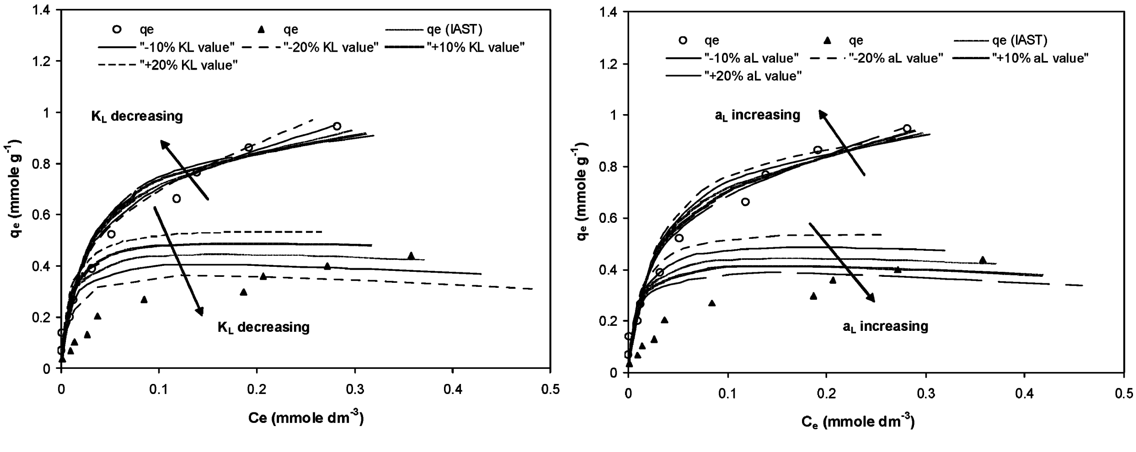

Figure 5. Sensitivity analysis for the IAST-LL predictions.

Table 3. IAST model evaluation using SSE error function.

	SSE values			
	IAST-LL	IAST-FF	IAST-LF	IAST-FL
BB3+BR22	0.4986	0.2304	*0.0813*	2.1714
BB3+BY21	0.0622	*0.0275*	0.1176	0.0501
BR22+BY21	0.6380	*0.1924*	1.0393	0.2494

Table 4. Comparison of IAST predictions and sensitivity analyses by SSE in BB3+BY21 binary system.

	SSE values				
	−20% K_L	−10% K_L	K_L	+10% K_L	+20% K_L
BB3	0.003	0.002	0.003	0.006	0.008
BY21	0.056	0.042	0.059	0.096	0.144
	−20% a_L	−10% a_L	a_L	+10% a_L	+20% a_L
BB3	0.006	0.005	0.003	0.002	0.001
BY21	0.144	0.092	0.059	0.045	0.046

were compared using SSEs and the results are shown in Table 3. Most of the cases, the results obtained from IAST-LL, IAST-LF and IAST-FL are worse than IAST-FF.

A sensitivity analysis was carried out using the IAST by changing the Langmuir, K_L and a_L, parameters of BY21 by percentage increments of ±10% and ±20%, to asses how sensitive the predicted isotherm curves of BB3+BY21 binary system were to changes in these parameters. The theoretical and experimental isotherms were compared using SSEs and the results are shown in Table 4 and Fig. 5. The predicted results of BY21 in BB3+BY21 system by the IAST-LL model are highly dependent on the values of $K_{\mathrm{L,BY21}}$ and $a_{\mathrm{L,BY21}}$ parameters while no significant change was found on the predicted results of BB3 in BB3+BY21 system.

Mechanism. Lignite has a strong affinity for basic dyes. The lignite-cationic dye sorption process is facilitated by the presence of the humic acid groups in the lignite. The adsorption process is a function of the dye structure and the lignite structure. Different ions will experience different physical and electrical attractive and repulsive forces according to their structure, molecular size and functional groups. The process is a combination of ionic attraction/repulsion, hydrogen bonding, ion-dipole forces, covalent bonds and van der waals forces. The differential sorption capacity of coal based sorbents like lignite will in part be due to the grade of the coal. The relationship between the extent of the coalification and the inherent ion exchange capacity may reduce as the coal ages. During the coalificaiton process there is a marked increase in the hydroxyl and carboxyl group content of the coal which may facilitate the increase in the ion exchange and sorption characteristics of the adsorbent.

Acknowledgments

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