REMOVAL OF A BINARY DYE MIXTURE OF CONGO RED AND MALACHITE GREEN FROM AQUEOUS SOLUTIONS USING A BENTONITE ADSORBENT

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Abstract—An important application of clay is as a solid adsorbent for industrial dyes. The aim of the present work was to carry out an experimental−theoretical study of the adsorption of dye mixtures, namely malachite green (MG) and Congo red (CR), by bentonite. Adsorption studies were conducted after evaluation of the impact of several parameters, including pH, adsorbate dose, and contact time, on the removal of MG and CR. The pH of the dye solution is strongly affected by the chemistry of both the dye molecules and of the adsorbent in an aqueous solution. Where both dye molecules exist in solution, the optimum pH was found to be 8.2 in order to achieve the maximum adsorption of both MG and CR. Preliminary studies showed that 60 min of contact time is sufficient to reach adsorption equilibrium. The adsorption studies were carried out using 1.0 g samples of bentonite. The amount of dye adsorbed was found by application of classical least squares to the synthetic dye mixtures. Data from equilibrium adsorption on bentonite were analyzed by Freundlich, Langmuir, Redlich-Peterson, and Temkin isotherm equations using regression analysis for non-linear forms of those equations. For binary-mixture analysis, isotherm parameters were determined from single-component adsorption studies and the theoretical amount of dye adsorbed was calculated using an extended Langmuir isotherm. Non-linear error analysis showed that the Temkin and Redlich-Peterson isotherms gave the best fits to the equilibrium data for adsorptive removal of MG and CR by bentonite.

Key Words—Adsorbent, CLS, Congo Red, Extended Langmuir, Malachite Green.

INTRODUCTION

Increasing international demand for textiles has lead to increasing demands for raw materials, including dyes. As more dye is used, huge amounts of related, polluted sewage is discharged into rivers. If those pollutants are not removed from the water, they affect the ecological system (Georgiou *et al.*, 2002; Tsui *et al.*, 2003). The greatest environmental concern with dyes is their absorption in water and reflection of sunlight, which interferes with the growth of bacteria, limiting it to levels which are insufficient to biologically degrade impurities in the water (Annadurai *et al.*, 2002). The removal of colored reagents from aqueous effluents is, therefore, of significant environmental, technical, and commercial importance. Many chemical and physical methods of dye-removal have been used and adsorption techniques have gained considerable importance in recent years because of their proven efficiency. Many tests have been carried out to assess the performance of various adsorbents for the removal of dyestuffs created by the textile industry.

Adsorption of single-component dye systems has been studied extensively. Many industrial effluents contain a mixture of more than one component requiring multi-component theoretical equilibrium models. Most of the aforementioned studies were carried out using single-component adsorption, though several experimental results were reported on binary and ternary dye mixtures adsorbed on different adsorbents (McKay and Al-Duri, 1989; Porter *et al.*, 1999; McKay and Al-Duri, 1991; Choy *et al.*, 2000, 2004). Compared with single-component systems, multi-component isotherms require much more, tedious, experimentation. For most multi-component adsorption models, the parameters of single-component equations are used to predict adsorption in multi-component systems. McKay and Al-Duri (1989) claimed that this approach is inadequate. In the present study, all of the calculated isotherm parameters were derived from single-component dye systems and used for binary dye mixture calculations.

The adsorption process for multi-component dye systems requires complex graphical solutions. In the case of adsorption, the amounts of dye remaining in water are determined in several ways. The method used most to calculate the amount of dye in solution is a spectrophotometric method at a single wavelength. For quantitative calculations, single-point calibrations usually introduce errors, so for better results more comprehensive methods have to be deployed. For multi-component analysis, chemometric methods are best, namely partial least squares (PLS), principal component analysis (PCR), classical least squares (CLS), and inverse least squares (ILS).

Equilibrium studies for the removal of two different dyes, MG and CR, singly, and in the form of a binary

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mixture, from aqueous solution, by adsorption onto bentonite, are presented here. The amounts of dyes adsorbed onto bentonite were calculated using the CLS chemomteric technique. In the binary system presented, isotherm constants for the Langmuir (1918), Freundlich (1906), Redlich and Peterson (1959), and Temkin and Pyzhev (1940) isotherms were determined for non-linear forms of the equations.

MATERIALS AND METHODS

The dye-removal potential of a bentonite adsorbent, from textile effluents, was investigated. Two different dye components namely MG and CR were used and no interaction was observed when their solutions were prepared in a 1:1 volume ratio at various concentrations.

Adsorbent

Commercial-grade bentonite, obtained from Pendik Tumaylar Ticaret, Istanbul, Turkey, was used to remove the dye components from prepared dye solutions. The chemical composition of the bentonite is listed in Table 1. The bentonite was sieved to give different particle-size fractions using ASTM standard sieves, and the 53−75 μm particle size was used in the experiments. The cation exchange capacity (CEC) of bentonite is 1.35 meq/g (by the proton exchange method, Ozacar and Sengil, 2005). The bentonite was used without pretreatment in the adsorption experiments.

Adsorbates and adsorption procedure

The anionic dye, CR (C.I. = 22120, chemical formula $C_{32}H_{22}N_6Na_2O_6S_2$, FW = 696.7 g/mol, λ_{max} = 500 nm), and cationic dye, MG (C.I. Classification Number 42000, Malachite Green oxalate, chemical formula $C_{23}H_{25}N_2Cl$, FW = 364.91 g/mol and λ_{max} = 614 nm), were supplied by the Sağlam Boya Company, Istanbul, Turkey. Both dyes are commercial grade and were used without further purification. For single-dye systems, the experiments were carried out at various concentrations (71.8, 108.0, 144.0, 179.0, 215.0, 251.0, 287.0, 323.0, and 359.0 μmol/L in the case of CR, and 137.0, 206.0, 274.0, 343.0, 411.0, 480.0, 548.0, 617.0, and 685.0 μmol/L in the case of MG) using 1.0 g of the bentonite adsorbent at a temperature of 25ºC for 60 min to attain equilibrium conditions. Binary systems were prepared by mixing equal volumes of each dye in solution. The mole ratio of GR to MG was constant at 0.52 for all of the dye-mixture solutions.

Preparations

A series of solutions with predetermined initial dye concentrations was prepared and mixed with predetermined amounts of bentonite (1.0 g/L). The solutions were agitated at a constant temperature of 20ºC and left for 3 h to equilibrate. Preliminary studies indicated that 60 min was sufficient to reach the equilibrium point so each adsorption study was carried out over 60 min.

For the CLS calculations, a calibration set was prepared containing 71.7−359.0 μM of CR and 137.0−685.0 μM of MG in 20 varied compositions. A validation set containing 10 synthetic mixtures of CR and MG solutions was prepared from the stock solutions. Those calibration and validation study tables are not presented here.

Analysis

In order to measure the remaining dye concentration, the solutions were analyzed by UV-Vis spectrophotometry (Shimadzu UV-Vis 160A) by measuring the full absorption spectrum of mixtures in the range of 350−700 nm. Dye concentrations were calculated using the CLS method. For a binary dye mixture, a series of dye mixtures was prepared for CLS calibration.

The theory of the CLS algorithm has been described in detail elsewhere (Kramer, 1998; Beebe and Kowalski, 1987; Adams, 1995). CLS is also known as the K-matrix calibration, which consists of the application of multiple linear regression to the Beer-Lambert Law. The method is carried out in two steps. In the first step, an empirical mathematical model was built, representing the relationship between the absorbance (*A*) and concentration (*C*) data generated from a set of standard samples (calibration set). The second step is the prediction step in which the calibration model is used to determine the concentration of the components (validation set) from their spectral data. The accuracy and precision of predictive ability of the model can be defined as the root mean square error of prediction (RMSEP). The mathematical expression is given as,

$$\text{RMSEP} = \sqrt{\frac{\sum_{i=1}^{N}(C_i^{\text{added}} - C_i^{\text{found}})^2}{n}} \quad (1)$$

where, C_i^{added} = the added concentration of the dye, and C_i^{found} = predicted concentration of the dye.

The CLS calibration technique, based on a linear CLS algorithm, involves the calculation of *K*, the calibration

Table 1. The chemical composition (wt.%) of bentonite.

Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	Loss on ignition
16.3	63.2	3.0	2.1	2.4	1.3	2.0	9.7

coefficient, using the absorbance data from the calibration set. The linear CLS algorithm has the following steps:

$$A = KC \qquad (2)$$

Solving the equation creates a CLS estimate of the pure component responses:

$$K = AC^T \, [CC^T]^{-1} \qquad (3)$$

where T represents transpose of C matrix and $^{-1}$ the inverse of the matrix calculation. Finding K allows prediction of the unknown amount of each component dye in each sample. From the first equation, we can write a similar equation for the unknown samples:

$$A_{uk} = KC_{uk} \qquad (4)$$

where A_{uk} is the unknown sample absorbance and C_{uk} is the concentration of unknown samples which will be found.

$$C_{uk} = [K^T K]^{-1} K^T A_{uk} \qquad (5)$$

THEORETICAL BACKGROUND

The Langmuir isotherm

Langmuir (1918) proposed a theory to describe the adsorption of gas molecules onto metal surfaces. A basic assumption was that sorption takes place at specific homogeneous sites within the adsorbent. Once a dye molecule occupies a site, no further adsorption can take place at that site. In the following equation, K_L and a_L are the Langmuir isotherm constants:

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \qquad (6)$$

where C_e is the initial concentration (mol/L) of acid dyes in the solution and q_e is the amount of acid dye adsorbed by the adsorbent per unit of mass.

The Langmuir equation is applicable to homogeneous adsorption, where the sorption of each molecule has equal adsorption activation energy. The equation follows Henry's Law thermodynamically at low concentrations. As C_e reduces, $a_L C_e$ is less than unity and $q_e = K_L C_e$, which is analogous to Henry's Law.

The Freundlich isotherm

The Freundlich expression is an exponential equation and therefore assumes that as the adsorbate concentration increases, the amount of adsorbate on the adsorbent increases:

$$q_e = K_F C_e^{b_F} \qquad (7)$$

where K_F (L/g) and b_F are the Freundlich constants. This expression is characterized by the heterogeneity factor, b_F, and so the Freundlich isotherm may be used to describe heterogeneous systems (Moon and Lee, 1983;

Al-Duri and McKay, 1988; McKay, 1980). In theory, an infinite amount of adsorption can occur when using this expression (Freundlich, 1906).

The Freundlich equation agrees well with the Langmuir equation over moderate concentration ranges but, unlike the Langmuir expression, it does not reduce to the linear isotherm (Henry's law) at low surface coverage. Both theories suffer from the disadvantage that equilibrium data over a wide concentration range cannot be fitted with a single set of constants (McKay, 1980).

The Temkin isotherm

Temkin and Pyzhev (1940) considered the effects of indirect adsorbate:adsorbate interactions on adsorption isotherms, noting that the heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate:adsorbate interactions. The Temkin isotherm has been used in the following form:

$$q_e = \frac{RT}{b}(\ln A C_e) \qquad (8)$$

where R is the universal gas constant, T is temperature (K), A is the Temkin isotherm constant, and b is the Temkin isotherm energy constant (J/mol).

The Redlich-Peterson isotherm

The Redlich-Peterson isotherm approximates to Henry's law at low adsorbate concentrations, and at high concentrations it behaves like the Freundlich isotherm. The isotherm formula is given as (Redlich and Peterson, 1959):

$$q_e = \frac{K_R C_e}{(1 + a_R C_e^{\beta})} \qquad (9)$$

where K_R (L/g) and a_R (L/mol) are Redlich-Peterson isotherm constants and β is the heterogeneity factor which is between 0 and 1. If it deviates from unity, the system is said to be more heterogeneous.

Extended Langmuir model

Butler and Ockrent (1930) were the first to develop the Langmuir model for competitive adsorption. The extent of adsorption, $q_{e,i}$ of the ith solute from an n-solute mixture is given as:

$$q_{e,i} = \frac{K_{L,i} C_{e,i}}{1 + \sum\limits_{j=1}^{n} a_{L,i} C_{e,i}} \qquad (10)$$

For a two-solute mixture of substances, for example, equation 10 written for solutes A and B becomes:

$$q_{e,A} = \frac{K_{L,A} C_{e,A}}{1 + a_{L,A} C_{e,A} + a_{L,B} C_{e,B}} \qquad (11)$$

$$q_{e,B} = \frac{K_{L,B} C_{e,B}}{1 + a_{L,A} C_{e,A} + a_{L,B} C_{e,B}} \qquad (12)$$

where $K_{L,A}$, $K_{L,B}$, $a_{L,A}$, and $a_{L,B}$ are Langmuir constants determined from adsorption measurements in solutions each containing a single solute, and $C_{e,A}$ and $C_{e,B}$ are equilibrium concentrations of the two solutes in the mixture.

Binary-system sorption is different from single-system sorption. Binary-component systems generally involve adsorbate-adsorbate interaction and competition that changes sorbent affinity due to an adjustment of the equilibrium in the system (Choy *et al.*, 2000). Interaction between the adsorbate particles was first proposed by Schay *et al.* (1957) who suggested an interaction factor, η, for multi-component systems. McKay and Al-Duri (1989) used this parameter to correlate experimental with theoretical results by incorporating it into the Langmuir equation as in equations 13 and 14. The interaction term, η, was estimated using the values predicted by equation and experimental data. The

$$q_{e,A} = \frac{K_{L,A}(C_{e,A}/\eta_A)}{1 + a_{L,A}(C_{e,A}/\eta_A) + a_{L,B}(C_{e,B}/\eta_B)} \qquad (13)$$

$$q_{e,B} = \frac{K_{L,B}(C_{e,B}/\eta_A)}{1 + a_{L,A}(C_{e,A}/\eta_A) + a_{L,B}(C_{e,B}/\eta_B)} \qquad (14)$$

calculations were carried out using *Matlab* 7.0 **(**Math-Works Inc, USA**)** and a MS-Excel™ spreadsheet.

In order to evaluate the results obtained, several error functions were selected and, for each isotherm, error amounts were calculated for non-linear forms. The selected error functions are summarized in Table 2 (Porter *et al.* 1999; Marquardt, 1963; Kapoor and Yang, 1989). As each of the error criteria is likely to produce a different amount of error, an overall optimum error is difficult to identify directly. Hence, in order to

try to make a meaningful comparison between the parameter sets, a procedure of normalizing and combining the error results was adopted producing a 'sum of the normalized errors' (SNE) (Allen *et al.*, 2004) for each parameter set for each isotherm. For each type of error calculation, the largest error value was determined and all the same type of error values obtained by different isotherms were divided by this number and this procedure was repeated for each error function.

RESULTS AND DISCUSSION

Bentonite has been studied and all its chemical properties have been summarized (Ozacar and Sengil, 2006). SiO_2 and Al_2O_3 are its major constituents with other oxides present in trace amounts, so one of the major oxides present in the adsorbent, or a combination of them, is expected to be responsible for the adsorption of dye. Bentonite comprises a three-sheet structure with two tetrahedral silicate sheets enveloping an octahedral aluminate sheet. This three-sheet structure has an overall neutral charge, but the individual layer bears an excess negative charge on its lattice due to isomorphic substitution of trivalent Al for tetravalent Si in the tetrahedral sheets and/or divalent Mg for trivalent aluminum in the octahedral sheet, which is neutralized by exchangeable Ca^{2+} ions (Ramakrishna and Viraraghavan, 1997). The excess negative charge allows the adsorption of positively charged dyes onto bentonite via cation exchange. The amount of dye that can be removed from a solution by an adsorbent depends on process variables used in batch systems such as particle size, initial dye concentration, contact time, cation exchange capacity (CEC), *etc*. In the present study, these values were $53-75$ µm, $50-300$ mg/L, 60 min, and 1.35 meq/g, respectively. The adsorption capacity increases with a decrease in the particle size, due to the increase in surface area. The amount of the dye adsorbed increases with an increase in the initial concentration of dye solution if the amount of

Table 2. The error functions used for non-linear systems.

Sum of the squares of the errors	SSE	$\sum_{i=1}^{p} (q_{e,calc} - q_{e,meas})_i^2$	
Composite fractional error function	HYBRID	$\sum_{i=1}^{p} \left[\frac{(q_{e,calc} - q_{e,meas})_i^2}{q_{e,meas}} \right]_i$	(Marquardt, 1963)
Derivative of Marquardt's percent standard deviation	MPSD	$\sum_{i=1}^{p} \left[\frac{q_{e,calc} - q_{e,meas}}{q_{e,meas}} \right]_i^2$	(Kapoor and Yang, 1989)
Average relative error	ARE	$\sum_{i=1}^{p} \left[\frac{q_{e,calc} - q_{e,meas}}{q_{e,meas}} \right]_i$	(Allen and McKay, 2004)
Sum of the absolute errors	EABS	$\sum_{i=1}^{p} |q_{e,calc} - q_{e,meas}|_i$	

adsorbent is unchanged. This is due to the increase in the driving force of the concentration gradient with the greater initial dye concentration (Ozacar and Sengil, 2005). Contact time is another important variable in adsorption processes. The adsorption capacity and the removal efficiency of dyes by an adsorbent increase for greater contact times. At some point in time, this value reaches a constant value where no more dye is removed from the solution. Figure 1 shows the absorption spectra of pure dyes, of a mixture of dyes, and of a dye mixture after adsorption onto bentonite. No shift in absorption maxima was observed for either dye at pH 8.2. pH is an important parameter in the spectrophotometric determination of MG and CR. At pH <2, MG shows a yellow color and at pH >13.2 it becomes colorless. The molecular form of CR changes markedly in the pH range of 2−4 and the color of CR changes from dark blue at pH 2−4 to red at pH 12. However, the red color is different from the original red in the pH range 10−12. In the present study, therefore, the solution pH was kept at 8.2 to obtain optimum adsorption of both dyes and to avoid any miscalculations due to absorption-measurement differences.

Although not presented here, the effect of pH on the dye adsorption was studied while the dye molar concentration, shaking time, and amount of bentonite were fixed at 359.0 µmol/L for CR and 691.0 µmol/L for MG, 15 min, and 1.0 g/L, respectively, for a single system and where the amount of dye was 179.5 µmol/L for CR and 345.5 µmol/L for MG for a binary system. The chemical structures of the two dyes are shown in Figure 2. The Malachite Green is a cationic dye, as

denoted by the presence of the positive N ion in its structure, and it should be attracted by an anionic adsorbent. Congo Red is an anionic dye, so it should be repelled by an anionic adsorbent. The positive charge on the cationic dye ensures that it is attracted by an anionic adsorbent. The adsorption of these charged dye groups onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent, which is influenced by the solution pH.

In the presence of water, the potential of the bentonite surface is determined by the activity of H^+ and OH^- ions, which react with and modify the bentonite surface, which affects the type of dye adsorbed. At low pH, the SiOH will be in the form of $SiOH_2^+$ which attracts the anionic dyes, and at high pH it will be in the form of SiO^- which is important for cationic dyes (Tahir and Rauf, 2006). The present adsorption measurement was done at pH 8.2. As revealed in Figure 1, the malachite green was adsorbed mostly onto the bentonite in the mixture of both dyes at the studied pH.

The remaining dye content of the solutions was determined by the CLS method. The accuracy and precision of that method was tested by calculating the RMSEP value of each dye: 0.4746 for CR and 0.4158 for MG. Most of the adsorption of dye onto bentonite occurred during the first 5 min; thereafter the amount adsorbed decreased.

The equilibrium adsorption isotherms for CR and MG adsorption onto bentonite (Figures 3 and 4, respectively) were obtained by plotting the solid-phase vs. liquid-
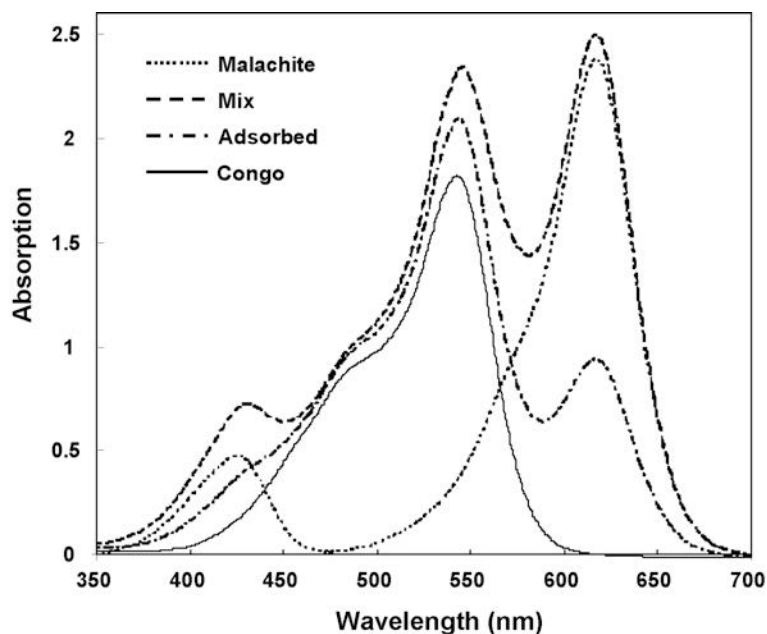

Figure 1. Absorption spectra of malachite green (MG) (32.8 mmol/L), Congo red (CR) (17.2 mmol/L), mixture of both dyes (at the same concentrations), and mixture of the dyes after the adsorption process. Conditions: bentonite particle size range of 53−75 µm, dose = 1 g/L, temperature = 298 K, and pH = 8.2.
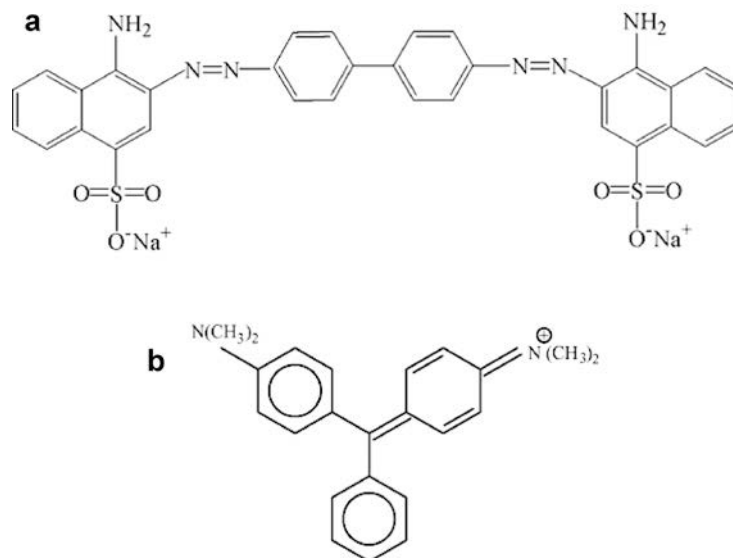
Figure 2. The chemical structures of (a) Congo red (CR) and (b) malachite green (MG).

phase concentrations (q_e *vs.* C_e) of the dye, from which certain constants were obtained that express the affinity and surface properties of the adsorbent. To optimize the design of an adsorption system to remove dyes from effluents, the most appropriate correlation for the equilibrium curve must be established. Hence, the correlation of equilibrium data using either a theoretical or empirical equation was essential for the adsorption interpretation and prediction of the extent of adsorption. The equilibrium experimental data for adsorbed MG data on bentonite were, therefore, analyzed using the Langmuir, Freundlich, Temkin, and Redlich-Peterson isotherms. After calculating the isotherm parameters for each dye from single-component systems, these parameters were used in an extended Langmuir equation to calculate the theoretical amounts of dye.

The Langmuir isotherm

The assumption made in the Langmuir adsorption theory is that no interaction occurs between the dye molecules. Once a dye molecule occupies a site on bentonite, no further adsorption occurs on it, revealing why a saturation value is reached after adsorption of a certain amount of dye onto bentonite. For non-linear calculations, *Matlab* 7.0 was used to calculate the parameters K_L and a_L (presented in Table 3), which are Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L (Namasivayam and Ranganthan, 1993), which is defined by

$$R_L = \frac{1}{(1 + a_L C_0)} \qquad (15)$$

where C_0 is the initial concentration of the dye. The value of R_L lies in the range $0.0349-0.0071$ for CR and $0.0122-0.0025$ for MG dyes. They are in the range of $0-1$ which indicates favorable adsorption on bentonite for all studied concentrations.

The Freundlich isotherm

The Freundlich isotherm constants determined by non-linear regression of experimental values (Table 3) indicate that this model may give a reasonable approximation to the optimum parameter set. The b_F values in the Freundlich equation were calculated as 0.1729 and 0.1421 indicating favorable adsorption for the CR and MG dyes, respectively.

The Temkin isotherm

The experimental adsorption data for MG and CR fit closely with the non-linear form of the Temkin isotherm (Figures 3 and 4; Table 3).

Redlich-Peterson isotherm

The Redlich-Peterson isotherm has three parameters and the form of the equation includes features of both the Langmuir and Freundlich isotherms. These parameters were determined by minimizing the error between the experimental data and the calculation of values of q_e by the Redlich-Peterson equation. All of the calculated data using the non-linear form of the Redlich-Peterson isotherm plots for adsorption of the CR and MG dyes onto bentonite (Figures 3 and 4; Table 3) showed that this model describes well the adsorption of dyes onto bentonite over the concentration ranges studied (see Table 3 for the isotherm constants a_R, K_R, and β, and the non-linear correlation coefficient). The isotherm parameter β (Table 3) was close to unity, indicating that it

Table 3. Non-linear isotherm parameters and calculated error values for single-component systems.

Isotherm	Parameter	Congo Red	Malachite Green
Langmuir	a_L	384.8	593.5
	K_L	79.41	265.9
	R2	0.9676	0.9713
	SSE	0.0020	0.0116
	HYBRID	0.0250	0.0841
	MPSD	0.0005	0.0006
	ARE	0.0012	0.0027
	EABS	0.1020	0.2755
	SNE	0.7645	0.5737
Redlich-Peterson	K_R	85.69	953.8
	a_R	336.2	1611.0
	β	0.9264	0.8831
	R2	0.9826	0.9990
	SSE	0.0018	0.0003
	HYBRID	0.0024	0.0019
	MPSD	4.48E−05	1.01E−05
	ARE	0.0005	0.0004
	EABS	0.0471	0.0408
	SNE	0.2970	0.0655
TempkinTemkin	B	96690	41530
	A	58930	23300
	R2	0.9944	0.9941
	SSE	0.0024	0.0014
	HYBRID	0.0019	0.0037
	MPSD	1.92E−05	1.53E−05
	ARE	0.0003	0.0004
	EABS	0.0404	0.0492
	SNE	0.2579	0.0828
Freundlich	b_F	0.1729	0.1421
	K_F	0.3127	0.6249
	R^2	0.9851	0.9909
	SSE	0.0008	0.0015
	HYBRID	0.0079	0.0417
	MPSD	0.0001	0.0007
	ARE	0.0008	0.0020
	EABS	0.0674	0.1330
	SNE	0.4452	0.2780

tends toward a Langmuir isotherm. The results showed that the non-linear equation method is a suitable approach for using this three-parameter isotherm.

In the case of the Temkin and Freundlich isotherms, non-linear fitting provided satisfactory results; even though the linear forms of the isotherms sometimes provided better fitting, use of the non-linear form was better because it gave a uniform error distribution for the whole range of experimental data.

Non-linear system error analysis

Because each of the error functions produces a different set of isotherm parameters, an overall optimum parameter set is difficult to identify directly. By comparing the results of the values of all five error functions (Table 3), best-fit results for CR and MG adsorption on bentonite were determined. The Redlich-Peterson and Temkin isotherms gave the best fits for the isotherm data for the adsorption of both dyes onto the bentonite. Determination of the isotherm parameters for the two dyes using the approach of linear regression appears to give acceptable fits to the experimental data with respective regression coefficients (R^2 values) close to unity, as shown in Table 3.

The error calculations of the isotherms gave a better understanding of the experimental results. In order to try to make a meaningful comparison between the parameter sets, a procedure of normalizing and combining the error results as reported by Ho *et al.* (2002) was adopted to produce the sum of the normalized errors (SNE) for each parameter set and each isotherm. The SNE values (Table 3) of the calculations improved the fitting of the different isotherms to the experimental results. The parameter set with the smallest SNE was considered to be optimal for that isotherm. Interpretation of the error values implies that the non-linear Temkin isotherm for
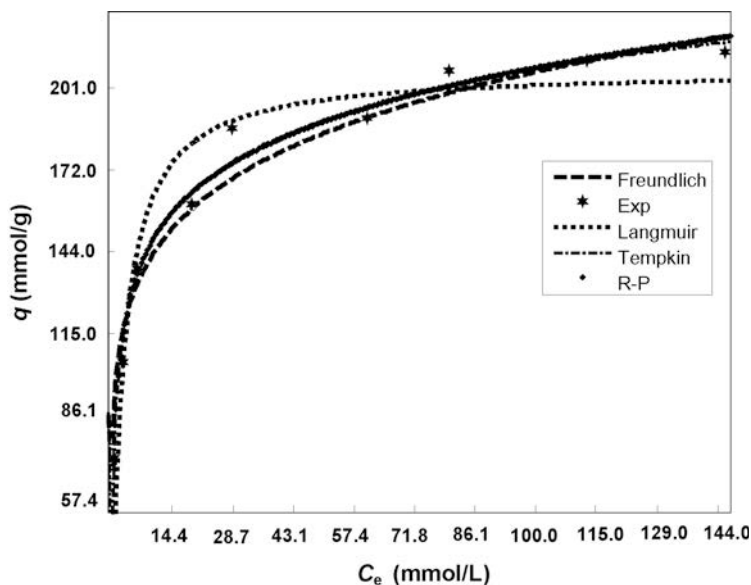
Figure 3. Non-linear equilibrium adsorption isotherms for the adsorption of reactive Congo red (CR) from a single system onto bentonite. Conditions: bentonite particle size range of 53−75 μm , dose = 1 g/L, temperature = 298 K, and pH = 8.2. R-P: Redlich-Peterson.

CR and the Redlich-Peterson isotherm for MG provided accurate depictions of the adsorption of both dyes onto bentonite.

BINARY EQUILIBRIUM ISOTHERMS

Extended Langmuir model

In order to examine the correlation between the type of single-component isotherm and the binary system itself, an extended Langmuir isotherm was analyzed in the same way as the single-component data presented in Table 3. Butler and Ockrent (1930) were the first to develop the Langmuir model for competitive adsorption. This model assumed an homogeneous surface with respect to the energy of adsorption, that adsorbed species did not interact, and that all adsorption sites were equally available to all adsorbed species. Binary-equilibrium isotherms have been determined for the sorption of CR and MG onto bentonite as part of a binary system. The binary dye mixtures were investigated using
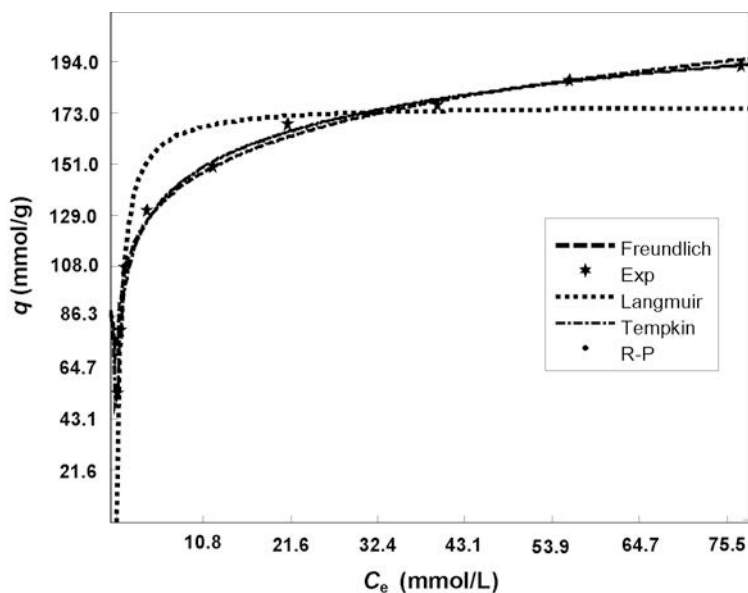

Figure 4. Non-linear equilibrium adsorption isotherms for the adsorption of reactive malachite green (MG) from a single system onto bentonite. Conditions: particle size range of 53−75 μm; dose = 1 g/L, temperature = 298 K, and pH = 8.2. R-P: Redlich-Peterson.
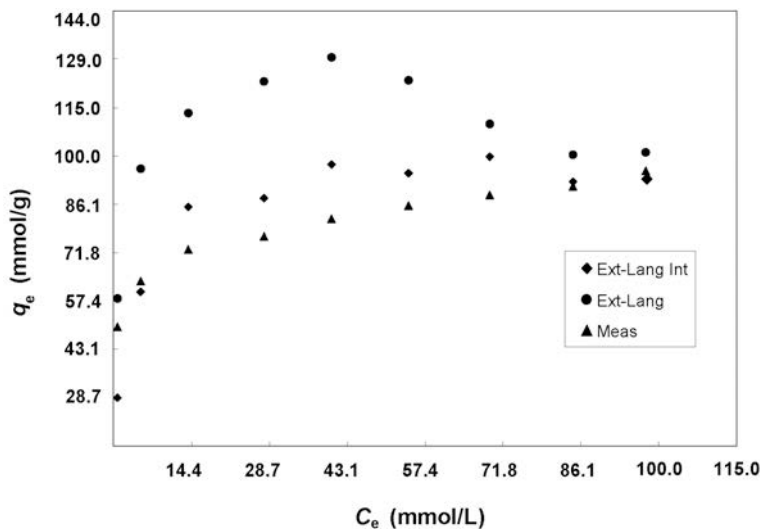
Figure 5.Non-linear extended Langmuir (Ext-Lang) isotherm of Congo red (CR) without (●), with (◆) interaction parameter, and experimental results (▲).

the extended Langmuir isotherm, with and without an interaction factor. Other extended isotherms were not investigated in the present study.

Non-linear Langmuir isotherm parameters from the single-component adsorption study were used to investigate the correlation between calculated and experimental data in binary solutions. Results (Figures 5 and 6) revealed that the correlation between the experimental data and the calculated data for both CR and MG was poor. For the non-linear parameters, equation 10 over-predicted the adsorption capacity of bentonite for CR and MG. Similar results have been reported in the literature (McKay and Al-Duri, 1989; Choy *et al.*, 2000, 2004; Allen *et al.*, 2004). This means that the assump-

tions of the Langmuir model are likely invalid for this system.

Extended Langmuir model with an interaction factor, η

In the multi-component adsorption process, adsorbate-adsorbate interaction has to be taken into account. In multi-component adsorption systems, interaction and competition generally changes the adsorbent affinity due to equilibrium readjustment in the system. An interaction term, η, constant and specific to each dye, should be added to the extended Langmuir equations 13 and 14. The computed interaction parameters are 4.9543 and 4.5456 for CR and MG, respectively. The non-linear Langmuir parameters from the single solute systems of
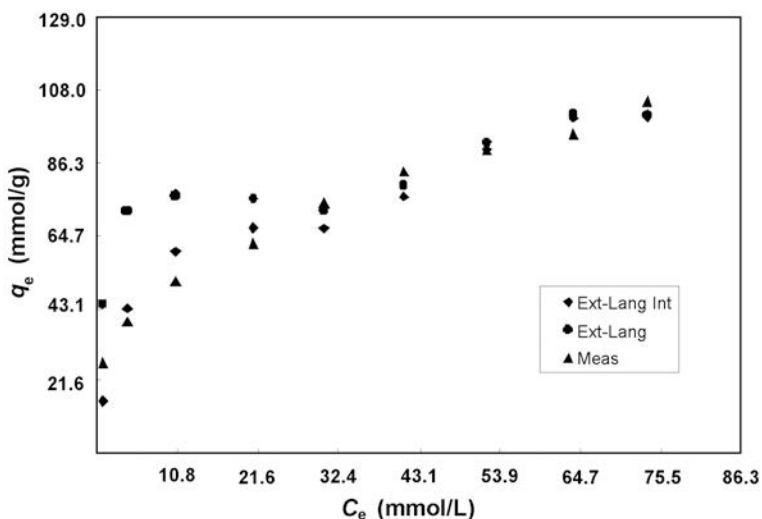

Figure 6. Non-linear extended Langmuir (Ext-Lang) isotherm of malachite green (MG) without (●), with (◆) interaction parameter, and experimental results (▲).

each species were used in these predictions. The comparison of predicted and experimental data for CR and MG in binary solution (Figures 5 and 6) indicates that the correlation plots produced a significant improvement when compared to the results predicted by the extended Langmuir equation. The agreement between the experimental data and modeled calculated data using equations 13 and 14 is good when compared to the simple extended Langmuir model.

The results obtained showed that the presence of additional competing adsorbate decreased the level of adsorption. The adsorption of CR or MG changes in the presence of another dye in the same solution. As the extended Langmuir model shows that without an interaction parameter, the expected adsorption should be large for CR and small for MG, which is unrealistic. As observed in Figure 1, more adsorption of MG occurred when the competing species was in the same solution. This may be attributed to the difference in molecular weight, molecular size, and chemical characteristics (cationic or anionic) of the dyes and adsorbent. Hence, MG as a cationic dye is attracted more than its anionic competitor, CR, onto the anionic bentonite. The result implies that either an interactive process existed and the adsorbents were competing for the same adsorption sites or the models without an interaction term failed to characterize the binary sorption systems properly.

CONCLUSIONS

The present study investigated and determined the ability of existing predictive and correlative models to calculate equilibrium sorption data of CR and MG in single and bisolute systems by conducting single and multicomponent adsorption batch experiments in their aqueous solutions. Bentonite clay was selected as a cheap and readily available adsorbent for the removal of subjected dyes in single and binary systems. The nonlinear forms of the Freundlich, Langmuir, Redlich-Peterson, and Temkin isotherms were studied to obtain the best fitting to the experimental data. Five different error measures were evaluated in single solute systems for experimental data derived from the analytical method. From the calculated SNE values, the Redlich-Peterson and Temkin isotherms performed better than the other two isotherms. For the studied binary system, single component parameters of Langmuir were used to correlate the theoretical results with the experimental results. The obtained theoretical results from the extended Langmuir equations did not show correlation with the experimental results, but introduction of an interaction parameter (η) into this equation improved the correlation of both results and provided a very close fit to the experimental data of each component. Thus, the basic assumptions of the extended Langmuir model, namely constant energy of adsorption, no interaction

among adsorbates, and equal independent competition between species, was invalid in this application.

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NOMENCLATURE

PLS	partial least squares	T	temperature (K)
PCR	principal component analysis	B	heat of adsorption (J/mol)
CLS	classical least squares	A	equilibrium binding constant (L/g)
ILS	inverse least squares	K_R	Redlich-Peterson isotherm constant (L/g)
X^T	transpose of X matrix (X = any unknown)	a_R	Redlich-Peterson isotherm constant $(L/mg)^{1/\hat{a}}$
X^{-1}	Inverse of X matrix (X = any unknown)	C_t	liquid-phase concentration at time t (mol/L)
A	absorption	i	i^{th} component in a multisolute system
K	coefficient matrix	R_L	equilibrium parameter
C	concentration	C_0	initial concentration of dye (mol/L)
A_{uk}	unknown absorption	SSE	sum of the squares of the error
C_{uk}	unknown concentration (mol/L)	$a_{L,A}$, $a_{L,B}$	Langmuir constants for components A and B (L/mol)
K_L	Langmuir isotherm constant (L/mol)	$K_{L,A}$, $K_{L,B}$	Langmuir constants for components A and B (L/mol)
a_L	Langmuir isotherm constant (L/mol)	$C_{e,A}$, $C_{e,B}$	A and B equilibrium concentrations (mol/L)
q_e	equilibrium solid-phase concentration (mol/g)		
Q_0	Langmuir monolayer adsorption capacity (mol/g)		
k_F	Freundlich isotherm constant $(mol/g)(L/mol)^{b_F}$		
C_e	equilibrium liquid-phase concentration (mol/L)		
b_F	Freundlich isotherm constant		
R	ideal gas constant (J/mol K)		
R^2	square of correlation constant		

Greek letters

λ_{max}	maximum absorption wavelength (nm)
β	Redlich heterogeneity factor
η	extended Langmuir interaction parameter