



## Comparison of optimized isotherm models for anionic dye adsorption onto Bentonite

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**Key words:** Congo red, Bentonite, pH, Surface, Isotherm, Error function

### Abstract

The commercial bentonite shows promise as a sorbent for the removal of hazardous Congo Red (CR) dye from aqueous solutions. The bentonite clay was characterized by XRD and FTIR analyses. The adsorption performance of CR on bentonite is highly influenced by the variation of pH, adsorbent dose, and initial dye concentration. More than 75% color removal was observed in the pH range 2.5-3.5. The optimum pH value for the studied CR-bentonite system was observed to be  $3.0 \pm 0.1$  with a bentonite dose of  $2 \text{ g L}^{-1}$  at  $20 \pm 2 \text{ }^\circ\text{C}$  temperature, and an initial dye concentration of  $180 \text{ mg L}^{-1}$ . The mechanism for the adsorption of anionic CR dye onto oxide surfaces of bentonite involves a surface complexation phenomenon in the adsorption process. Equilibrium data of single-component batch adsorption were modeled using the most popular two-parameter isotherms. The parameter values of each isotherm model were determined from the corresponding linear plot. The maximum Langmuir adsorption capacity was recorded to be  $Q_m = 65 \text{ mg g}^{-1}$  at the set of optimum conditions. In this study, many commonly used error functions were used to estimate the error deviation between theoretically and experimental predicted equilibrium adsorption data. The order of deviation was: Dubinin-Radushkevich (D-R) model > Langmuir model > Temkin model > Harkins-Jura model > Halsey model > Freundlich model, which indicated that the Freundlich isotherm model was the best one in describing the adsorption equilibrium of the recent study case of CR dye on bentonite. The obtained data are useful for industries to design of commercial adsorbents for color removal from aqueous solutions.

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## Introduction

Textile dyes are frequently utilized in unlimited industrial applications such as textile, printing, paint, food, and cosmetics as colouring agents (Odoemelam *et al.*, 2018). There are numerous dyes and by-products which contain hazardous effects on living organisms including humans (Kannan and Sundaram, 2001). More stability has been gained by different dyes against extreme temperatures, sunlight, and other reactive components. This resistance has been gained by complexity in the structural formation of atomic arrangements of dyes and their celluloid origin which leads them to non-biodegradable forms (Robinson *et al.*, 2002; Han and Yun, 2015).

For maintaining environmental safety standards, it is essential to eliminate the content of dyes before their interaction with wetlands or runoff water for agricultural purposes. Several methods were applied to remove textile dyes before discharge into water such as adsorption (Abdul Hameed *et al.*, 2019), photocatalysis (Jawad *et al.*, 2015), oxidation (Nidheesh *et al.*, 2018), and coagulation (Beluci *et al.*, 2019). Adsorption is a prime wastewater treatment method for dye removal due to its simplicity of design, non-generation of toxic materials, low cost, and high efficiency (Mu and Wang, 2016; Abdul Hameed *et al.*, 2019).

Activated carbon is a commonly used adsorbent for the treatment and filtration of water channels and wetlands, but a high-cost ratio and difficulty in regeneration are the drawbacks of this technique (Waranusantigul *et al.*, 2003). Some recent studies have been done to develop cheaper and effective adsorbents for the removal of various dyes from aqueous solutions. These include peat (Ho and McKay, 2003), red mud (Namasivayam and Arasi, 1997) coir pith (Namasivayam *et al.*, 2001), Neem Leaf (Bhattacharaya and Sharma, 2004), activated sludge (Basibuyuk and Forster, 2003) sawdust (Garg *et al.*, 2004), sugar cane (Ho *et al.*, 2005), rice husk (McKay *et al.*, 1986), shale oil ash (Al-Qodah, 2000) perlite (Dogan *et al.*, 2004), orange peel (Namasivayam *et al.*, 1996), sepiolite (Alkan *et al.*, 2004), vermiculite (Choi and Cho, 1996) dolomitic

sorbents (Walker *et al.*, 2003), bentonite clay (Ramkrishna and Viargavan, 1997), activated bentonite (Ozcan and Ozcan, 2004) etc.

The qualities which have increased the quality of adsorbent clays included high specific area, chemical and physical firmness, encrusted structure and high cation exchange capability (Gurses *et al.*, 2006; Acemioglu, 2004; Ghosh and Bhattacharya, 2002; Ozcan and Sengil, 2003; Globa and Nykovskaya, 1984). Of all the different types of clays that are commonly used, Bentonite considered as best quality because of the presence of montmorillonite crystals in its composition. The dioctahedral quality of montmorillonite is common due to the presence of two-thirds of octahedral sites which are bounded by trivalent cations. Octahedral sheets are also present in Dioctahedral montmorillonite which generates charges from  $Mg^{+2}$  and  $Al^{+3}$  (Mitchell, 1983; Gulsah Kirali and Lacin, 2006). Bentonite as an adsorbent for the removal of malathion (Pradas *et al.*, 1993), cationic dye (Tahir and Rauf, 2006),  $Pb^{+2}$  (Rauf and Tahir, 2001),  $Ni^{+2}$  (Rauf *et al.*, 2003), and  $UO^{+2}$  ion (Olguin *et al.*, 1997) has been reported earlier.

An anionic dye Congo Red (CR) is widely used in the plastic industries, rubber, textile, and paper industries. CR is included in the category of diazo- dyes (Finar, 1986). This dye has hazardous effects on humans due to its carcinogenic qualities. Different allergic reactions have resulted from direct exposure to the dyes. The substance is considered as toxic (Bhattacharya and Sharma, 2004). Namasivayam and Cavitha reported the removal of CR from water by activated carbon prepared from coir pith (Namasivayam and Kavitha, 2002). Purkait *et al.* studied the adsorption of CR onto activated carbon (Purkait *et al.*, 2007) Namasivayam and Arasi found the waste red mud effective in CR uptake from wastewater (Namasivayam and Arasi, 1997). Fu and Virarghavan were able to remove CR from an aqueous solution by the fungus *Aspergillus* (Fu and Viraraghavan, 2002). Bhattacharya and Sharma investigated the biosorption of CR dye by *Azadirachta indica* leaf powder (Bhattacharya and Sharma, 2004).

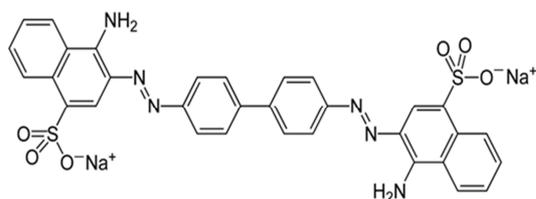
The main object of the current research work has been to determine the efficiency of removal of a hazardous dye, CR, from synthetic aqueous solutions using bentonite clay as adsorbent after optimization of the adsorption conditions such as pH, initial dye concentration and bentonite dose. Equilibrium data of single-component batch adsorption were modeled using the most popular two-parameter isotherms.

## Materials and methods

### Characterization of adsorbent

Industrial-grade bentonite was used as a sample adsorbent during the current research. Materials contain a whitish powdered-like structure containing a mesh size of 30. Drying, filtration, and washing of the sample have been done. Drying has been done by using the temperature of 150 to 170 Degree Celsius for 24 hours.

The phases of the commercial bentonite were determined by powder X-ray diffraction (XRD) analysis with a PANalytical X-ray, Philips Analytical using Cu K $\alpha$  radiation at 40 kV and 40 mA over the range (2 $\theta$ ) of 20-80 degrees at a scanning rate of 2-degree min<sup>-1</sup>. The infrared spectrum of bentonite was obtained with a Mattson 5000 FT-IR spectrometer with a pellet of powdered potassium bromide and sample. The spectra were recorded at room temperature with a resolution of 4 cm<sup>-1</sup>, with 100 scans.



**Fig. 1.** Molecular structure of Congo Red dye.

### Preparation of dye solutions

CR dye was purchased by Aldrich Chemical Company, USA. The chemical formula and molecular weight of CR are C<sub>32</sub>H<sub>22</sub>N<sub>6</sub>Na<sub>2</sub>O<sub>6</sub>S<sub>2</sub> and 696.7 g/mol, respectively. Fig. 1 demonstrates the molecular structure of CR. Double distilled water was used to

prepare a stock solution of 500 mg L<sup>-1</sup>. Different concentrations of test solutions were prepared by dissolving stock solutions with different concentrations of solution. A variety of concentrations have been used starting from 60 to 180 mg L<sup>-1</sup>. Different pH values have been altered to stabilize the solution. 0.1 M HCl or NaOH has been used to adjust particular pH levels.

### Adsorption studies

A batch system has been used to evaluate the adsorption rate of CR dye on Bentonite. A 250 mL flask has been used for the preparation of 100 mL Congo Red solution. Bentonite was added as the clay material. The components were mixed for the duration of four hours at a speed of 160rpm. At the temperature of (20  $\pm$  2 °C) adsorption stability was studied by mixing 100 ml of Congo Red dye solution in variable concentrations into the flask of 250ml. Different parameters were investigated including the effect of PH of initial solution on the adsorption rate of bentonite. The range of PH was selected from 2 to 9. The dose of bentonite was settled to 0.2-1.0 g /100ml dye solution. The rate of adsorbent was monitored on the selected concentration. A control solution was also used to detect out the adsorption rate on the inner surfaces of bottles. A control solution was used without adsorbent.

### Dye analysis

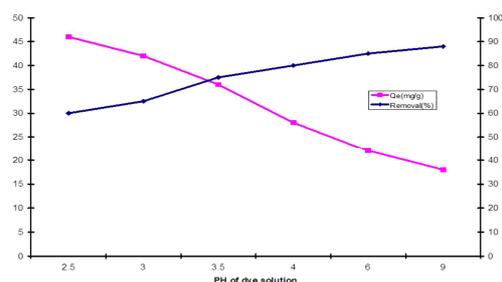
CR dye stock solution was used to prepare a variety of standard solutions with different concentrations varying between 5 to 25 mg L<sup>-1</sup>. Absorbance was calculated and a graph showing the calibration curve was formulated which resulted in the rate of adsorption at  $\lambda$  max = 499 nm. The solution was settled to equilibrium for 10 minutes after each experiment. The process of filtration has been done to filter the adsorbent. The leftover CR dye was measured by the analysis of filtrate at  $\lambda$ max = 499 nm.

### Dye uptake

The amount of dye adsorbed onto the unit weight of adsorbent Q<sub>e</sub> (mg g<sup>-1</sup>) was calculated from the mass balance equation is given below.



different bentonite dose in the range of 2-10 g L<sup>-1</sup> at 20 ± 2 °C temperature, initial pH 7.0±0.2 and initial dye concentration 180 mg L<sup>-1</sup>. The effect of bentonite clay dose is presented in Fig. 5. The adsorption removal increases with the increase in the mass of adsorbent and the uptake capacity of CR decreased from 57.6 mg g<sup>-1</sup> (64% removal) to 16.7 mg g<sup>-1</sup> (93% removal) with increasing bentonite dose from 2 to 10 g L<sup>-1</sup>. This is because at higher dosages of adsorbent due to increased surface area, more adsorption sites are available causing higher removal of CR. The decrease in uptake amounts (Q<sub>e</sub>, mg g<sup>-1</sup>) may be due to the splitting effect of flux (concentration gradient) between adsorbate and adsorbent with increasing adsorbent dose causing a decrease in the amount of dye adsorbed onto the unit weight of adsorbent (Farmer, 1974). Similar phenomena were observed for reactive dye adsorption onto the cross-linked chitosan beads (Aksu and Tezer, 2005).



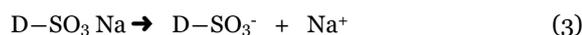
**Fig. 6.** Variation of equilibrium CR amount adsorbed (mg g<sup>-1</sup>) and CR removal (%) with initial pH

#### Effect of pH

There is an important role of pH in the adsorption rate of the adsorption dye. pH has a variety of effects on the properties of adsorbents. It influences the change in surface charges of the adsorbent. It also alters the ionization on the surface of the material and is involved in the removal of functional groups from the adsorbent surfaces. It can also alter the structural morphology of the dye (Vadivelan and Kumar, 2005). The range of pH which was selected to study the structural changes in the dye was 1.0-9.0. The time duration selected for the experimental studies was 4 hours at 20 °C. A fixed concentration of dye was used i.e., 180 mg L<sup>-1</sup>. Fig. 6 demonstrates the effects of pH on the adsorbent rate of bentonite. It has been found

that with the increase in pH, the adsorbent rate of bentonite was decreased. The optimum pH for the best functioning capacity of bentonite for CR dye was found to be 2.5 to 3.5.

CR is a dipolar molecule ( H<sub>3</sub>N<sup>+</sup> – R – SO<sub>3</sub><sup>-</sup> ) at low pH (Chiou *et al.*, 2004). In the aqueous solution, the acid dye is first dissolved and the sulfonate groups of the acid dye are dissociated and converted to anionic form as shown below.



Dye is expressed by D. The molecular structure of bentonite is complicated as it contains octahedral layers embedded in tetrahedral layers. The molecular structure facilitates the process of adsorption as bentonite because it contains three octahedral spaces which are covered with tetrahedral sheets. The reactive sites of these clay molecules are Al...OH and Si-O (Grini *et al.*, 2007). The highest level of adsorption has been found in these reactive sites. While bentonite has been mixed with aqueous solution the adsorption capacity has been controlled by ions like H<sup>+</sup> or pH. The capacity of adsorption has been determined by H<sup>+</sup> and OH<sup>-</sup> while complex ionic structures have been investigated by bonding H<sup>+</sup> and OH<sup>-</sup> (Shawabkeh and Tutunji, 2003). The bentonite emits positive charges in the lower PH values due to the formation of the aqua complex on its surfaces (Sposito, 1990).



In this equation M stands for a metal or metalloid central ion, i.e. Si or Al, and -MOH<sub>2</sub><sup>+</sup><sub>(s)</sub> is the surface aquacomplex. Acid dyes have anionic characters. Higher uptake obtained at low pH values may be due to electrostatic attractions between negatively charged dye anion and positively charged bentonite surface. As the initial pH of the solution increases (pH > p<sub>HZPC</sub>), the surface of bentonite becomes negatively charged.



A negatively charged surface site on the adsorbent does not favor the adsorption of dye anions due to the

electrostatic repulsion (Strawn and Sparks, 1999). A similar result was recorded for the adsorption of CR onto red mud (Tor and Cengeloglu, 2006) and reactive dyes onto calcined alunite (Ozacar and Sengil, 2003).

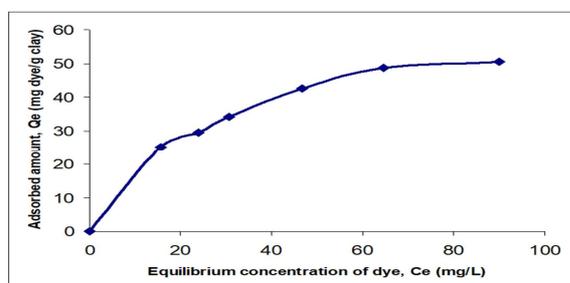


Fig. 7. Adsorption isotherm of CR on bentonite

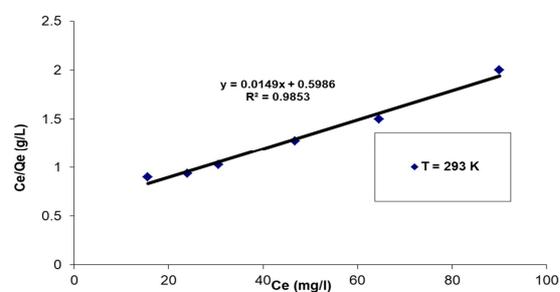


Fig. 8. Langmuir plot for the adsorption of CR on commercial bentonite

### Adsorption isotherms

Thermodynamic assumptions of adsorption isotherms and their estimated parameters provide insight into both the properties of the surface and also the mechanism of adsorption. Consequent upon this, the results obtained in our equilibrium studies were tested with six different two parameter isotherm equations (i.e. Langmuir, Freundlich, Temkin, Dubinin-Radushkevich (D-R), Harkins-Jura and Halsey isotherm equations).

### Langmuir isotherm

The interaction of intramolecular forces alters the capacity of adsorption as according to Langmuir adsorption, an increase in the distance leads to a decrease in the intramolecular forces. Langmuir adsorption is a monolayer. The theory of the isotherm equation reveals that there are some homogenous sites present on the surface of adsorbents that provide suitable adsorption area. Langmuir equation

illustrates that the homogenous adsorption surfaces available for adsorbents carry homogenous energy for their activation (Snoeyink *et al.*, 1992; Langmuir, 1918).

Fig. 7 demonstrates the isotherms for the adsorption of Congo red dye on bentonite. Higher adsorbent concentration has been found in a stable equilibrium state while studying adsorption isotherms. This was also shown in Langmuir isotherm. Monolayer formation has also been explained by Giles including the information about L-type isotherm which has been connected with the flat position of adsorbent molecules (Onyango *et al.*, 2006; Gregg and Sing, 1982). The linearized Langmuir model is represented by Eq. (6):

$$C_e/Q_e = 1/(Q_m K_L) + (1/Q_m) C_e \quad (6)$$

Where  $C_e$  is the equilibrium dye concentration ( $\text{mg L}^{-1}$ ),  $Q_e$  is the amount of dye adsorbed per unit weight of adsorbent ( $\text{mg g}^{-1}$ ),  $Q_m$  and  $K_L$  are Langmuir constants related to adsorption capacity and rate of adsorption. By plotting  $C_e/Q_e$  against  $C_e$ , it was possible to obtain the value of  $Q_m$  from the slope which was  $1/Q_m$ , and the value of  $K_L$  from the intercept which was  $1/(Q_m K_L)$ . The Langmuir plots for CR dye isothermal adsorption data were drawn (Fig. 8). It demonstrates that the Langmuir adsorptive isothermal equation fits the experimental data very well. The values of correlation coefficients were found to be  $R > 0.99$ . The calculated constants  $Q_m$  and  $K_L$  together with correlation coefficients are given in Table 1.

### Freundlich isotherm

Heterogenous surface energy systems have been explained by the Freundlich isotherm model. This model refers to the energy levels of activation sites for adsorption. It reveals that those activation sites which are highly energetic have high levels of adsorption ability and those that have low activation energy show less adsorption ability. The attachment of adsorbents to the surface area also started with high-energy sites and ended up with low-energy sites (Freundlich, 1906; Ng *et al.*, 2002). The equation is explained below.

$$\log Q_e = \log K_F + (1/n) \log C_e \quad (7)$$

where:  $C_e$  ( $\text{mg L}^{-1}$ ) and  $Q_e$  ( $\text{mg g}^{-1}$ ) are the liquid phase concentration and solid phase concentration of the adsorbate at equilibrium,  $K_F$  is the Freundlich constant related to the adsorption capacity and  $1/n$  is the Freundlich exponent (dimensionless). The plots of  $\log Q_e$  versus  $\log C_e$  (Fig. 9) enable the constants  $K_F$  and  $n$  to be determined. The Freundlich isotherm parameters and the linear regression coefficients are listed in Table 1. The highest  $K_F$  and  $n$  values were found as 8.33 and 2.42, respectively. Table 1 indicates that  $n$  is greater than unity, indicating that dye molecules are favorably adsorbed onto bentonite surfaces.

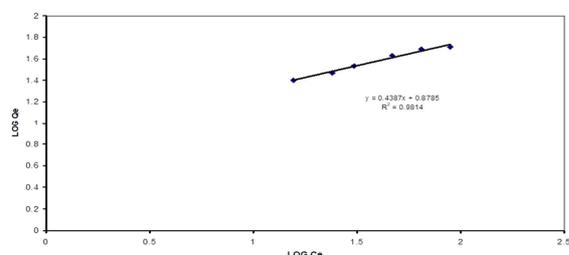


Fig. 9. Freundlich plot for the adsorption of CR on commercial bentonite

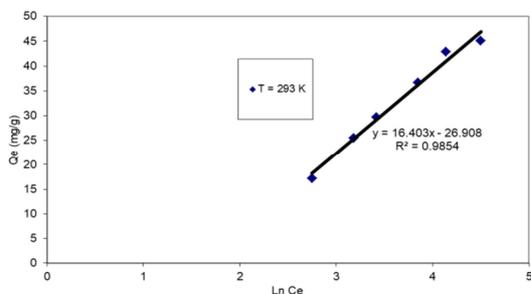


Fig. 10. Temkin plot for the adsorption of CR on commercial bentonite

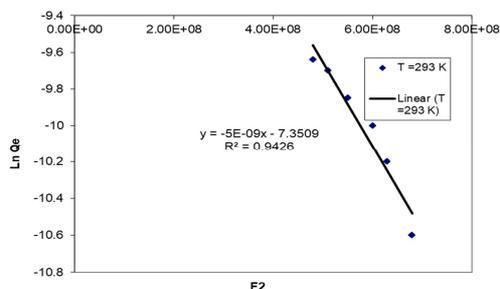


Fig. 11. Dubinin-Radushkevich plot for the adsorption of CR on commercial bentonite

Temkin isotherm

Temkin and Pyzhev (1940) studied the heat of adsorption and the adsorbent-adsorbate interactions (Temkin and Pyshev, 1940). The linearized Temkin model is given below.

$$Q_e = B_1 \ln K_T + B_1 \ln C_e \quad (8)$$

Where  $B_1 = RT/b$ ;  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and  $T$  is the absolute temperature (K). A plot of  $Q_e$  versus  $\ln C_e$  yields a straight line (Fig. 10) from which the isotherm constants  $B_1$  and  $K_T$  ( $\text{L mg}^{-1}$ ) can be determined. The values of  $B_1$  and  $K_T$  together with the correlation coefficients are listed in Table 1. The isotherms were found to be linear over The whole range of dye concentration, as evidenced by the values of correlation coefficients ( $R > 0.98$ ).

Dubinin-Radushkevich (D-R)

Different models were studied including The Langmuir, Freaundlick, and Temkins isotherms. All these models did not explain the complete mechanism of adsorption. To clarify the adsorption equilibrium data, the Dubinin-Radushkevich equation was applied. It differs from Langmuir as the requirement of a homogenous surface for adsorption is not essential in this model (Peric *et al.*, 2004; Dubinin *et al.*, 1966). The Dubinin-Radushkevich equation is expressed below.

$$\ln Q_e = \ln X_m - \beta F^2 \quad (9)$$

Where  $Q_e$  is the amount of CR dye adsorbed at equilibrium,  $\beta$  is a constant related to the adsorption energy,  $X_m$  is the theoretical saturation capacity, and  $F$  is the polanyi potential which is equal to the equation.

$$F = RT \ln (1+1/C_e) \quad (10)$$

Where  $R$  is the gas constant and  $T$  is the absolute temperature (K).

The Dubinin-Radushkevich (D-R) enables one to calculate an impotant parameter, the adsorption energy ( $E_{ads}$ ) from the value of  $\beta$  from the following equation:

$$E_{ads} = 1/\sqrt{-2\beta} \quad (11)$$

**Table 1.** Two parameter adsorption isotherm models and parameter values of the isotherms for the adsorption of CR on commercial bentonite

| Isotherm model | Linear regression equation            | Parameters   |
|----------------|---------------------------------------|--|
| Langmuir       | $C_e/Q_e = 0.0154 C_e + 0.1361$       | $Q_m = 65 \text{ mg g}^{-1}$<br>$K_L = 0.11 \text{ L mg}^{-1}$<br>$R^2 = 0.99$   |
| Freundlich     | $\log Q_e = 0.4144 \log C_e + 0.9208$ | $n = 2.41$<br>$K_F = 8.33$<br>$R^2 = 0.96$   |
| Temkin         | $Q_e = 15.88 \ln C_e - 19.336$        | $B_1 = 15.88$<br>$K_T = 0.296$<br>$R^2 = 0.98$   |
| D-R            | $\ln Q_e = -4\text{E-}9 F^2 - 7.7$    | $\beta = -4\text{E-}9$<br>$X_m = 4.5\text{E-}4 \text{ mol g}^{-1}$<br>$E_{ads} = 11.4 \text{ kJ mol}^{-1}$<br>$R^2 = 0.99$ |
| Harkins-Jura   | $1/Q_e^2 = -0.0016 \log C_e + 0.0033$ | $A = 625$<br>$B = 2.06$<br>$R^2 = 0.94$  |
| Halsey         | $\ln Q_e = 0.43 \ln C_e + 2.05$       | $n = -0.70$<br>$k = 0.28$<br>$R^2 = 0.98$  |

**Table 2.** Isotherm error deviation data related to adsorption of CR dye onto commercial Bentonite using five commonly used functions

| Isotherm     | EPRSQ   | EABS  | ARE   | HYBRID | MPSD   |
|--------------|---------|-------|-------|--------|--------|
| Langmuir     | 554.52  | 56.98 | 26.66 | 400.16 | 200.00 |
| Freundlich   | 120.68  | 23.65 | 11.19 | 80.04  | 89.44  |
| Temkin       | 181.35  | 29.58 | 14.56 | 143.65 | 119.79 |
| D-R          | 1132.06 | 59.44 | 44.81 | 753.23 | 273.86 |
| Harkins-Jura | 262.43  | 34.16 | 13.43 | 145.49 | 120.42 |
| Halsey       | 149.53  | 28.01 | 12.67 | 101.37 | 100.62 |

**Table 3.** Comparison between different sorbents for their maximum adsorption capacity of CR dye

| Adsorbent                       | Maximum adsorption capacity, $Q_m$ (mg g <sup>-1</sup> ) | Reference                          |
|---------------------------------|--|------------------------------------|
| Neem leaf powder                | 72.40  | (Bhattacharaya and Sharma, 2004)   |
| Waste Fe(III)/Cr(III) hydroxide | 44.00  | (Namasivayam <i>et al.</i> , 1994) |
| Powder activated carbon         | 16.81  | (Namasivayam and Kavitha, 2002)    |
| Orange peel                     | 14.00  | (Annadurai <i>et al.</i> , 2002)   |
| Bagasse fly ash                 | 11.88  | (Mall <i>et al.</i> , 2005)        |
| Red mud                         | 7.08   | (Tor and Cengeloglu, 2006)         |
| KJA/Ti                          | 52.00  | (Grabowska and Gryglewicz, 2007)   |
| Fly ash                         | 4.13   | (Rao and Rao, 2006)                |
| Guava Leaf Powder               | 35.72  | (Appala <i>et al.</i> , 2010)      |
| Jujuba seeds                    | 55.56  | (Reddy <i>et al.</i> , 2012)       |
| Pine bark                       | 3.92   | (Litefti <i>et al.</i> , 2019)     |
| Commercial bentonite            | 65.00  | Present study                      |

The plot of  $\ln Q_e$  versus  $F^2$  (Fig. 11) enables us to determine the parameters of the Dubinin-Radushkevich equation for the adsorption of CR dye which are shown in Table 1. The correlation coefficients are also shown. Examination of the data for the studied temperature range showed that the Dubinin-Radushkevich model was able to fit the adsorption data also very well. The correlation coefficients  $R > 0.99$  were obtained.  $\beta$  coefficient had

a negative value of  $-4\text{E-}9$ . The  $E_{ads}$  value obtained was  $11.4 \text{ kJ mol}^{-1}$ . This free energy depends on the nature of the adsorbent and adsorbate but is independent of the temperature of adsorption. If the magnitude of  $\text{kJ mol}^{-1}$  is between 8 and  $16 \text{ kJ mol}^{-1}$ , the adsorption proceeds by the ion exchange mechanism. While for values of  $E_{ads}$  less than  $8 \text{ kJ mol}^{-1}$ , the adsorption process is physical (Basar, 2006). The obtained value for  $E_{ads} = 11.4 \text{ kJ mol}^{-1}$ , shows that the interaction

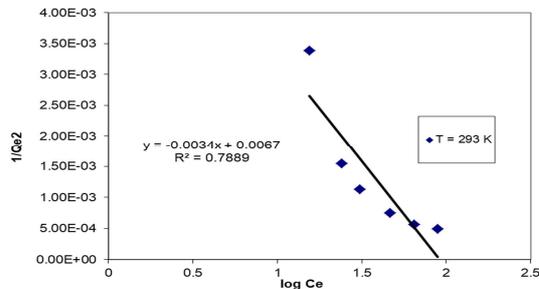
between CR molecules and bentonite clay proceeded principally by ion exchange.

*Harkins-Jura isotherm*

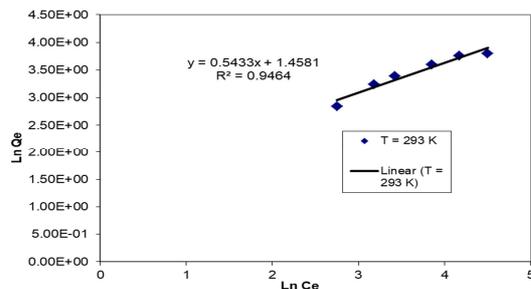
The Harkins-Jura isotherm accounts for multilayer adsorption and also for the existence of heterogeneous pore distribution in the adsorbent (Basar, 2006; Harkins and Jura, 1944). The Harkins-Jura isotherm equation can be expressed is given below.

$$1/Q_e^2 = [B/A] - [1/A] \log C_e \tag{12}$$

The Harkins-Jura isotherm parameters B and A are obtained from the plot of  $1/Q_e^2$  against  $\log C_e$  (Fig. 12) and are given in Table 1. The correlation coefficients  $R > 0.94$  were obtained.



**Fig. 12.** Harkins-Jura plot for the adsorption of CR on commercial bentonite



**Fig. 13.** Halsey plot for the adsorption of CR on commercial bentonite

*Halsey isotherm*

The Halsey adsorption isotherm is suitable for multilayer adsorption and the fitting of the experimental data to this equation attests the heterogeneous nature of adsorbent (Basar, 2006; Halsey, 1948) The Halsey isotherm equation can be given below.

$$\ln Q_e = [(1/n) \ln k - [1/n]] \ln C_e \tag{13}$$

The Halsey isotherm constants  $n$  and  $k$  are determined by plotting  $\ln Q_e$  vs.  $\ln C_e$  (Fig. 13) and are listed in Table 1. The correlation coefficients  $R > 0.98$  were obtained.

*Error analysis for isotherm studies*

In the single-component isotherm studies, the optimization procedure requires an error function to be defined to be able to evaluate the fit of the isotherm to the experimental equilibrium data.

*Commonly used error function*

*Sum of the absolute errors (EABS)*

The sum of the absolute errors method can be represented by the equation.

$$EABS = \sum | Q_{e,cal} - Q_{e,exp} | \tag{14}$$

Where  $Q_{e, cal}$  is the theoretical adsorbed solid phase concentration of CR, which has been calculated from the isotherm equations obtained by regression analysis, and  $Q_{e,exp}$  is the experimentally determined adsorbed CR concentrations at equilibrium ( $\text{mg g}^{-1}$ ).

*Sum of the squares of the errors (ERRSQ)*

This error-estimated method is written as (Basar, 2006; Allen *et al.*, 2003)

$$ERRSQ = \sum (Q_{e,cal} - Q_{e,exp})^2 \tag{15}$$

Isotherm parameters derived using this error function will provide a better fit as the magnitude of the errors and thus the squares of the errors increase the fit toward the data obtained at the high end of the concentration range.

*Average relative error deviation (ARED)*

This error function (Basar, 2006; Kumar, 2007) attempts to minimize the fractional error distribution across the entire concentration range:

$$ARED = [1/N] \sum | (Q_{e,cal} - Q_{e,exp}) / Q_{e,exp} | \tag{16}$$

Where  $N$  is the number of experimental data points ( $N=6$ ).

*Hybrid fractional error function (HYBRID)*

This error function was developed to improve the fit of the ERRSQ method at low concentrations by

dividing it by the experimental value. It also includes the number of degrees of freedom of the system- the number of data points, N, minus the number of parameters, P, of the isotherm equation – as a divisor (Kumar, 2007; Ncibi, 2008).

$$\text{HYBRID} = [1/(N-P)] \sum [(Q_{e,\text{cal}} - Q_{e,\text{exp}})^2 / Q_{e,\text{exp}}] \quad (17)$$

#### *Marquardt's percent standard deviation (MPSD)*

This error function is similar in some respects to a geometric mean error distribution modified according to the number of degrees of freedom of the system (Ncibi, 2008).

$$\text{MPSD} = 100 \sqrt{[1/(N-P)] \sum [(Q_{e,\text{cal}} - Q_{e,\text{exp}})^2 / Q_{e,\text{exp}}]} \quad (18)$$

Table 1 gives the regression equations of two-parameter adsorption isotherm models and parameter values of the isotherms for the adsorption of CR on commercial bentonite. Among the six studied isotherm models, the best-fitting one is determined based on the use of well-known functions to calculate the error deviation between the experimental and predicted equilibrium adsorption data. The results of non-linear error analysis are shown in Table 2. From this table, the comparison of error analysis showed that the order of deviation was: Dubinin-Radushkevich (D-R) model > Langmuir model > Temkin model > Harkins-Jura model > Halsey model > Freundlich model, which indicated that the Freundlich isotherm model was the best one in describing the adsorption equilibrium of the recent study case of CR dye on bentonite. These data are used in the design of commercial adsorbents and consequently the more accurate the isotherm parameters, the more accurate the design system.

#### *Data comparison*

A comparison of the maximum adsorption capacity,  $Q_m$  ( $\text{mg g}^{-1}$ ), of commercial bentonite with those of other adsorbents reported in the literature for the adsorption of CR dye is given in Table 3. The obtained uptake value in this study is higher or comparable with those values obtained for other low-cost adsorbents. Differences in dye uptake are due to the

properties of each adsorbent such as surface functional groups, surface area, and surface charge. Moreover, the degree of adsorption of dye molecules onto different materials depends on dye properties and operating conditions.

#### **Conclusion**

The adsorption performance of CR on bentonite is highly influenced by the variation of pH, adsorbent dose, and initial dye concentration. More than 75 % color removal was observed in the pH range 2.5-3.5. This was explained based on both the chemical structure and behavior of CR and bentonite in the studied conditions. The optimum pH value for the studied CR-bentonite system was found to be  $3.0 \pm 0.1$  with a bentonite dose of  $2 \text{ g L}^{-1}$  at  $20 \pm 2 \text{ }^\circ\text{C}$  temperature, and an initial dye concentration of  $180 \text{ mg L}^{-1}$ . Equilibrium data of single-component batch adsorption were modeled using the most popular two-parameter isotherm models. All the studied isotherm equations showed a good fit to the adsorption data with high linear regression correlation coefficients  $R^2 > 0.94$ . Several commonly used error functions were used to estimate the error deviation between experimental and theoretically predicted equilibrium adsorption data. The order of deviation was: Dubinin-Radushkevich (D-R) model > Langmuir model > Temkin model > Harkins-Jura model > Halsey model > Freundlich model, which indicated that the Freundlich isotherm model was the best one in describing the adsorption equilibrium of the recent study case of CR dye on bentonite. The excellent fitness of the Freundlich model was expected due to the heterogeneity of the clay surface. The Langmuir monolayer sorption capacity was found to be  $65 \text{ mg g}^{-1}$ . The commercial bentonite shows promise as a sorbent for the removal of hazardous CR dye from aqueous solutions. The obtained data are useful in the design of commercial adsorbents for color removal from aqueous solutions.

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