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THERMODYNAMICS OF ADSORPTION OF ERIOCHROME BLACK-T DYE FROM AQUEOUS MEDIA ON EACH MODIFIED KAOLIN CLAY AND TALC

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ABSTRACT

Modified kaolin clay and talc have been employed as adsorbents for the removal of industrially important dye namely erichrame black-T from aqueous solution. The effect of solution pH, initial dye concentration, temperature and adsorption time on dye removal were studied using UV-visible spectroscopy technique at λ_{max} = 541 mm. The equilibrium time was found to be 30 minutes on each surface. The best results were achieved at pH = 9 and T = 318 K on modified kaolin clay surface and at pH = 7 and T = 288 K on talc surface. It was noted that adsorption of the dye on modified kaolin clay increases with an increase in temperature while its adsorption on talc decrease with an increase in temperature. The result showed that the equilibrium datas were fitted by both of the Freundlich and Langmuir isotherm. Values of parameters for these isotherm equations were calculated. Isotherms have also been used to obtain the thermodynamic parameters such as free energy, enthalpy and entropy of adsorption. The adsorption of EBT (Eriochrome Black-T) is endothermic on modified kaolin clay and exothermic on talc.

Key words: Thermodynamics, Adsorption, Eriochrome black-T, Kaolin clay, Talc.

INTRODUCTION

Wastewater from textile industries creates a great problem of pollution due to the dyes contained therein[1]. Many dyes reaching the water source are difficult to decompose and cause many problems due to their carcinogenicity[2,3]. Due to low biodegradability of dyes, conventional biological treatment process is not very effective in treating dye wastewater. Adsorption processes have been investigated as an efficient and effective method to remove dyes from wastewater. The most widely used adsorbent for industrial applications is activated carbon[4-6]. Due to its higher cost and considering the large quantity of wastewater normally produced by the textile industries, research has recently been focused towards alternative adsorbents, namely low cost adsorbents including natural clay[7], woodchips[8], cotton and natural cellules[9]. Eriochrome back-T dye has been studied using activated charcoal, and rice bran and its coal as adsorbents[10]. The aim of this study was to determine the adsorption capacity of modified kaolin clay and talc in aqueous solution varying with process factors include initial dye concentration, contact time, pH, temperature and adsorbent dose.

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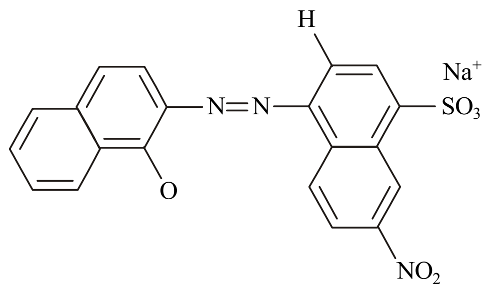
EXPERIMENTAL

Material and apparatus

Adsorbate: Eriochrome Black-T (EBT) was used as adsorbate supplied by fluka (Fig. 1). Adsorbents: kaolinite was obtained from general Company for Geological survey and mining, Doghla, Iraq, poly vinyl alcohol was supplied by AG, CH – 9476 Fluka. Commercial talc was supplied from locally market. pH-solution: pH values (3-11) were prepared using (0.01 M) of buffer solution (ammonium hydroxide and acetic acid). Apparatus: All absorbance measurements' were Carried out on Shimadzu UV-VIS 1700 digital double beam recording spectrophotometer using 1 cm glass Cells, Japan. A digital pH meter, 720 WTW 82362 Denmark was used.



[1-(1-hydroxy-2-naphthol azo) 6-nitro-2-naphthol4-sulphonic acid sodium salt]

Fig. 1: Structured of EBT

Thermic treatment of the clay

Kaolinite sample (50 mm) was washed with an excess amount of distilled water. Then it was heated in an oven at temperature 50 to 100°C for 24 hrs and at 100°C for 7 hrs. It was then grounded and sieved by 50 mms sieve[11].

Modified clay manufacturing

Poly vinyl alcohol solution was mixed with (100 mL) of distilled water and refluxed at 90°C for 30 minutes. It was treated with HCl solution of pH = 5. Then it was mixed with clay and heated to 200°C for two hours in an oven, grounded then sieved by 50 mm sieve', the mass ratio of clay/polymer was (0.5%)[12,13].

Adsorption studies

Solutions of different concentrations of erichrome black-T (EBT) dye (3-18 ppm) were prepared by serial dilution. The absorbance values of these solutions were measured at λ_{max} = 541 nm and plotted against the concentration values. The calibration curve in the concentration range that falls in the region of applicability of Beer-Lamberts' law way employed.

Effect of shaking time

To find the equilibrium time, experiments were performed using a (30 mL) aqueous solutions of the dye (9.0 ppm) and was shaken together with (0.05 g) of each adsorbent for different time ranging from 10 to 60 mins. The absorbance of the supernant was measured by the spectrophotometer at the λ_{max} of the dye. The adsorption of the dye increased with increasing shaking time and then attains constant value when equilibrium was established. The equilibrium time was found to be 30 mins, which was used for all further adsorption studies.

The weight of the adsorbent

Solutions of the dye (30 mL) of known initial concentrations (9.0 ppm) and different amounts of each adsorbent (0.05-0.5 g) were added in the flasks. The absorbance values of these solutions were measured at λ_{max} = 541 nm after 30 mins (equilibrium time). The best weight for modified kaolin clay was found to be (0.5 g) and for talc (0.1 g).

Calculation the quantity adsorbed

The quantity of the dye adsorbed on each surface was calculated according to the following Eq. (1)[14].

$$Qe \text{ or } x/m = V\,(Co\text{-}Ce)/M \qquad \ldots(1)$$

x/m: The quantity adsorbed

M: Weight of the adsorbent (g)

Co: Initial Concentration (mg/L)

Ce: Equilibrium Concentration (mg/L)

V: Volume of solution (L)

RESULTS AND DISCUSSION

Adsorption isotherms

Analysis of equilibrium isotherm data is important to develop an equation which, accurately represents the result and which could be used for design purposes. Out of possible several isotherms equations, two have been applied for this study, the Langmair and Freandlich isotherms. The Freundlich isotherm has been widely adopted to characterize the adsorption capacity of organic pollutions using different adsorbents by fitting the adsorption data.

The Freundich isotherm has the general form such as –

$$Qe = Kf\ Ce\ 1/n \qquad \ldots(2)$$

$$Qe = (Co\text{-}Ce)/M = Kf\ Ce\ 1/n \qquad \ldots(3)$$

Where Qe, is the adsorption capacity (mg g^{-1}), Ce and Co are the initial and equilibrium concentration (mg L^{-1}), respectively, M is the adsorbent dose (g), Kf and 1/n are the adsorption capacity and intensity of adsorption, respectively. The value of Kf and 1/n can be determined from the intercept and slope, respectively of the logarithmic plot in Eq. (4).

$$\text{Log } Qe = \log Kf + 1/n \log Ce \qquad \ldots(4)$$

In order to facilities the estimation of the adsorption capacities at various conditions, the Langmuir adsorption isotherm, a typical model for monolayer adsorption was applied. The linearized Langmuir model can be written as –

$$Qe = a\ Ce/1 + bCe \qquad \ldots(5)$$

Where, Qe is the amount of dye adsorbed at equilibrium (mg. g^{-1}), Ce is the equilibrium concentration of dye, the amount of dye adsorbed Qe (x\m) (mg.g^{-1}) is platted against the equilibrium concentrations (ppm) on each surface at 288, 298, 308 and 318 K to obtain the adsorption isotherms (Fig. 1 and 2). The adsorption isotherm of the dye on each surface is of the type S.

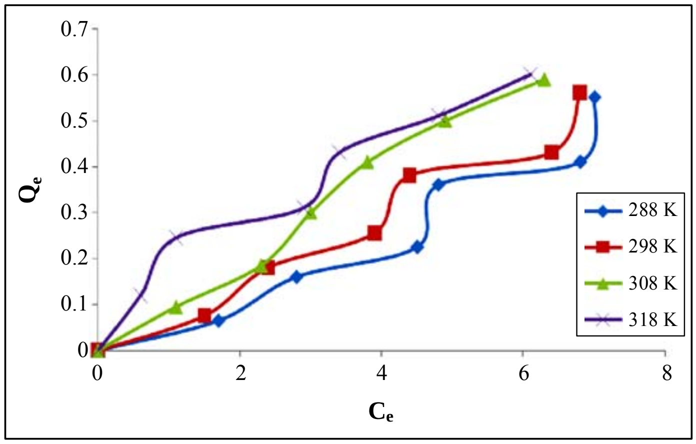


Fig. 1: Effect of temperature on the adsorption capacity of eriochrome black-T dye with modified Kaolin Clay at pH = 7

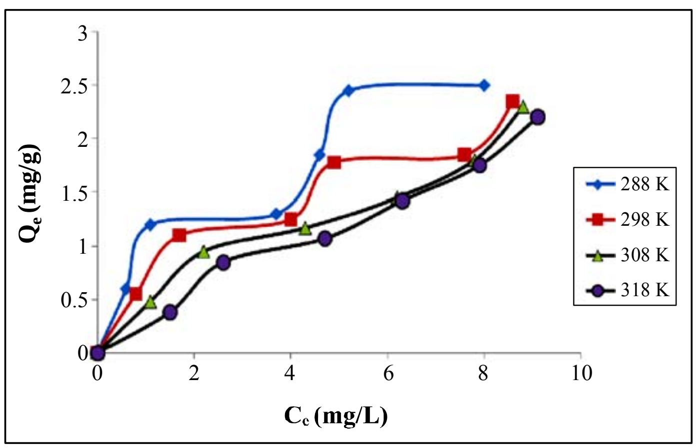


Fig. 2: Effect of temperature on the adsorption capacity of eriochrome black-T dye with talc at pH = 7

Using Freundlich and Langmuir isotherms (Eq. 2 and 5) the experimental equilibrium adsorption data were analyzed.

The constant (a) represent practical limiting adsorption capacity when the surface is fully covered with a monolayer of adsorbate, the constant (b) is the equilibrium adsorption constant, which related to the affinity of the binding sites. (Table 1) from the liner from of Eq. (2).

$$Ce/Qe = 1/ab + Ce/a \qquad \ldots(6)$$

The Langmuir adsorption parameters were determined. Figures 3 and 4 show that the experimental results are applicable on Freundlich and Langmuir equations.

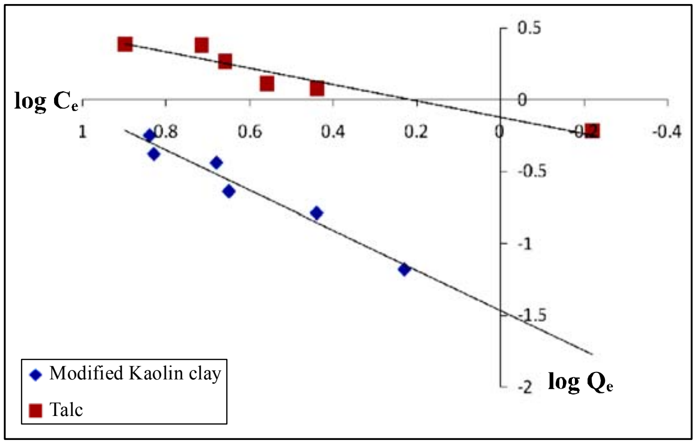


Fig. 3: Freundlich adsorption isotherm of eriochrome black-T dye with modifed kaolin clay and talc at pH(7)

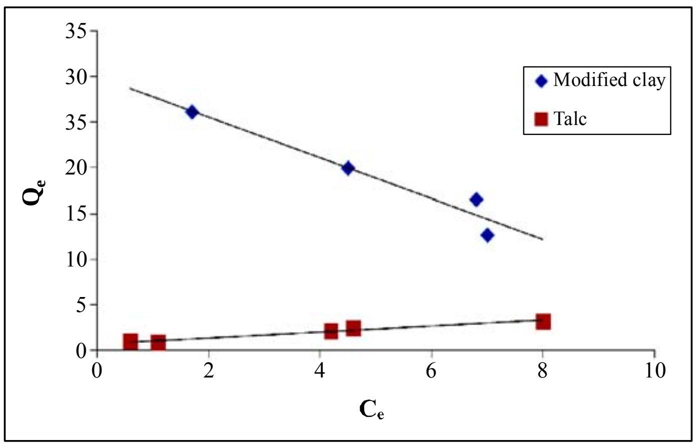


Fig. 4: Langmuir adsorption isotherm of modified Kaolin Clay at pH 7

Binding parameters of the adsorption of the dye on each surface which are calculated from intercepts and slopes of these plots are represented in Table 1 together with the correlation coefficients R2 as a goodness of fit criterion. Figure 1 shows that adsorption of the dye on modified kaolin clay increased with increasing temperature, indicating endothermic process; while the adsorption of the dye on talc decreased with increasing exothermic process.

Table 1: Freundlich and Langmuir constants for the adsorption of Eriochrome Black-T on using modified Kaolin clay and talc

Adsorbent	Eriochrome Black-T					
	Freundlich constants			Langmuir constants		
	R2F	N	KF	R2L	a	B
Modified Kaolin clay	0.956	0.718	0.034	0.94	0.033	-12.98
Talc	0.927	1.75	0.75	0.969	1.33	2.32

The eriochrome black-T dye is consisting of two portions polar and non-polar (Fig. 1). The sulphonic group is susceptible to electrostatic interactions with the adsorbent surface, whereas non polar portion play an important role in hydrophobic interactions (Vander Waals bonds)[15]. The removal of the dye by modified clay is due to the increasing of exchange sites produced by the acidleaching or a collapsed kaolinite framework[13]. Talc, a hydroxyl magnesium silicate $Mg_3\ Si_4O(OH)_2$, is another inexpensive mineral of pyrophyllite family[16]. Its structure comprises of magnesium-oxygen-hydroxyl tri-octahedralbrucitelayer, sand-witched between two sheets of silicon-oxygen tetrahedral layers. The adjacent layers are held together by weak van der waals forces and hence give rise to soapy feeling in the talc[17]. The removal of the dye by the talc surface may be attributed to hydrogen bonding as well as Chemical interaction of the dye and the surface metal hydroxide groups of talc. It was found that talk surface is more effective than modified kaolin in removing the dye (Fig. 5).

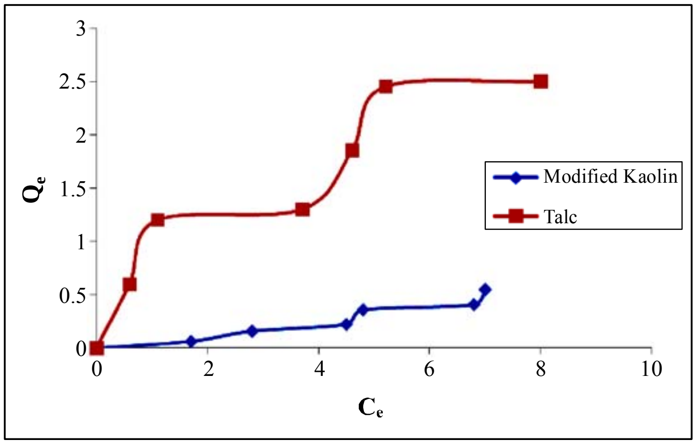


Fig. 5: Adsrption isotherm of eriochromeblack-T dye by modified Kaolin clay and talc at pH 7

Thermodynamic study

The removal of eriochrome black-T using modified kaolin clay and talc has been studied at 288 to 318 K.

Thermodynamic parameters, i.e. free energy (ΔG) enthalpy (ΔH) and entropy (ΔS) changes were calculated using Eqs. (7-9):

$$\Delta G = - RT \ln k \quad \ldots(7)$$

$$\text{Log } Xm = \Delta H \backslash 2.303\ RT + \text{Constant} \quad \ldots(8)$$

$$\Delta S = \Delta H - \Delta G \backslash T \quad \ldots(9)$$

Where R is the gas law constant and T is the absolute temperature. ΔH for each adsorbent was Calculated from the slope of linear dependence of Log Xm on 1\T (Fig. 6). The values of parameters are represented in Table 2.

Table 2: Thermodynamic values of Eriochrome Black-T in aqueous solution using residual of modified Kaolin clay and talc as an adsorbents

Adsorbent	ΔH ($KJ.mol^{-1}$)	ΔG ($KJ.\ mol^{-1}$)	ΔS ($J.mol^{-1}.k^{-1}$)	Cos.
Modified Kaolin clay	2.64	0.43	7.69	0.2
Talc	-3.34	-1.72	-6.54	-0.2

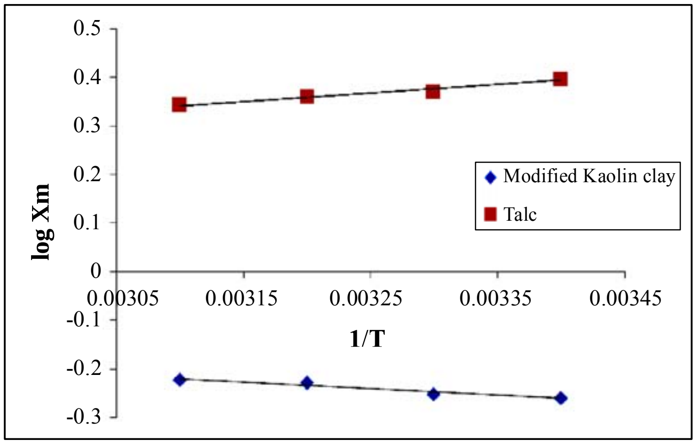


Fig. 6: Relationship between the Log Xm and 1/T of dye with modified Kaolin clay and talc as an adsorbent

The adsorption of EBT on modified Kaolin clay is non-spontaneous process (positive ΔG), endothermic (positive ΔH) and an increase non orderliness of the system (positive ΔS). While the negative values of the parameters ΔG, ΔH and ΔS of the adsorption of EBT on talc show that the process is spontaneous, exothermic and an increase in the orderliness of the system[18,19]. The exothermic in nature of the adsorption process may be due to atendecy for the dye molecules to esape from the solid phase of talc to the liquid phase of dye with an increase in temperature of the solution[20].

Effect of pH

The adsorption Capacity of the dye on each surface over a broad range of pH at room temperature is shown in Fig. 7. On modified kaolin clay, the highest adsorption capacity is at pH 9 (0.32 g/gm) then decreases with increasing bassist and acidity. On talc the highest adsorption capacity is at pH 7 (1.09 g/gm) then decrease with increasing acidity and bassist. At high pH the sulphonic acid group is completely deprotonated which make the dye molecule more soluble in water, So the adsorption decreased with increasing pH. At low pH the columbic interactions between the adsorbent and the dye is weak. or it may be related to the presence of excess H^+ ions competing with the dye cation in aqueous solution for adsorption. It is also possible that the surface properties of the clay and talc are depended on pH of the solution.

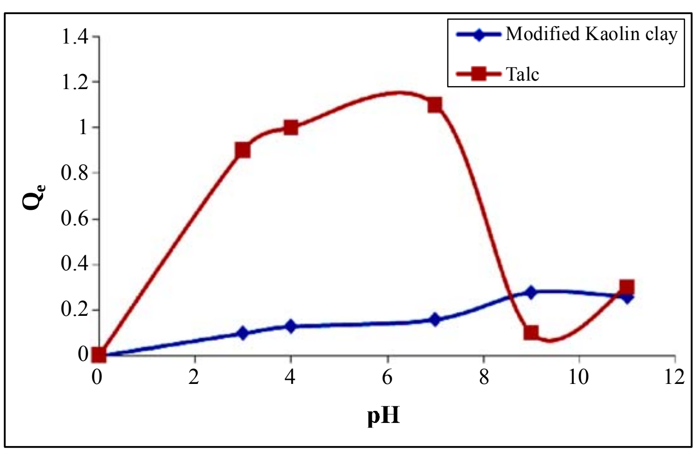


Fig. 7: Removal of the colour from aqueous solution of Eriochrome black-T with different pH of solutions

CONCLUSION

Talc surface is more effective in removing of erichrome black-T than modified kaolin. The adsorption of the dye at talc surface is spontaneous and exothermic as evidenced by negative values of the changes in free energy (ΔG) and enthalpy (ΔH), while the adsorption at modified kaolin clay is non-spontaneous and endothermic as indicated by the positive values of the changes in free energy and enthalpy.

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