

REMOVAL OF ACID YELLOW 49 FROM AQUEOUS SOLUTION BY ADSORPTION

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SUMMARY

In this study, the removal of an acid dye, acid yellow 49, used in the textile industry with sepiolite was investigated as a function of ionic strength, pH and temperature. Adsorption process was attained to the equilibrium within 1 h. The adsorbed amount of acid yellow 49 increased with increasing ionic strength and temperature, but decreased with increasing pH. The experimental data were analysed by Langmuir and Freundlich isotherms, and it was found that the isotherm data were reasonably correlated by Freundlich isotherm. Furthermore, for the removal of acid yellow 49, a batch reactor was designed. The results indicated that sepiolite could be employed as an alternative to commercial adsorbents in wastewater treatment for the removal of colour and dyes.

KEYWORDS:

Adsorption, sepiolite, adsorption isotherm, batch design, dye.

INTRODUCTION

The adsorption of dyes onto clays has had in the past the unique application of being a rather simple way to determine important properties of clays, like the superficial area and the cation exchange capacity (CEC) [1]. Some specific effluents from industrial production processes may be difficult to purify by traditional wastewater treatment technology, as a result of the complexity of some of their components. Wastewater from textile industries creates a great problem of pollution due to the dyes contained therein [2]. The disposal of coloured wastes such as dyes into receiving waters causes damage to the environment as they are toxic to aquatic life. As it is difficult to remove the dyes from effluents, different adsorbent have been used for this purpose.

Activated carbon is the most widely used adsorbent for the removal of color from textile effluents, because it has a high capacity for organic matter, but its use is lim-

ited due to its high cost [3, 4]. Recently, new adsorbents such as chitosan [5], alunite [6], cotton [7], orange peel [8], sludge particles [9], palm fruit bunch [10], shale oil ash [11] have been investigated for the removal of toxic materials from water. Furthermore, perlite as an adsorbent has been used for the removal of dyes and heavy metal ions from aqueous solutions [2, 12, 13]. Natural clay minerals such as sepiolite, on the other hand, may be a very good alternative to these materials.

Sepiolite has attracted remarkable attention by its sorptive, rheological and catalytic properties. Therefore the use of sepiolitic clays has been increasing [14]. A number of investigators studied sorptive properties of various cationic organic reagents with sepiolite [15-17], but fewer researchers studied the adsorption of anionic reagent with sepiolite. Sepiolite is a clay mineral with a unit cell formula $\text{Si}_{12}\text{O}_{30}\text{Mg}_8(\text{OH},\text{F})_4(\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}$, and it consists, as can be seen in Figure 1, in the alternation of blocks and tunnels that grow up in the fibre direction (c-axis) [18]. Each block is constructed by two tetrahedral silica sheets enclosing a central magnesia sheet. In some aspects sepiolite is similar to other 2:1 trioctahedral silicates, such as talc. The molecule formula is $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$, but it has discontinuities and inversions of the silica sheets that give rise to structural tunnels [16]. In the inner blocks, all corners of silica tetrahedra are connected to adjacent blocks, but in outer blocks some of the corners are Si atoms bound to hydroxyls (Si-OH). These silanol groups at the "external surface" of the silicate, are usually accessible to organic species, acting as neutral adsorption sites (denoted as N) [19]. In addition to that, some isomorphic substitutions in the tetrahedral sheet of the lattice of the mineral, such as Al^{3+} instead of Si^{4+} , form negatively charged adsorption sites. Such sites are occupied by exchangeable cations that compensate for the electrical charge. These characteristics of sepiolite make it a powerful sorbent [20] for neutral organic molecules and organic cations.

In this work we present the experimental results for adsorption of acid yellow 49 on sepiolite. The main aim of the current study has been to visualize the pattern of

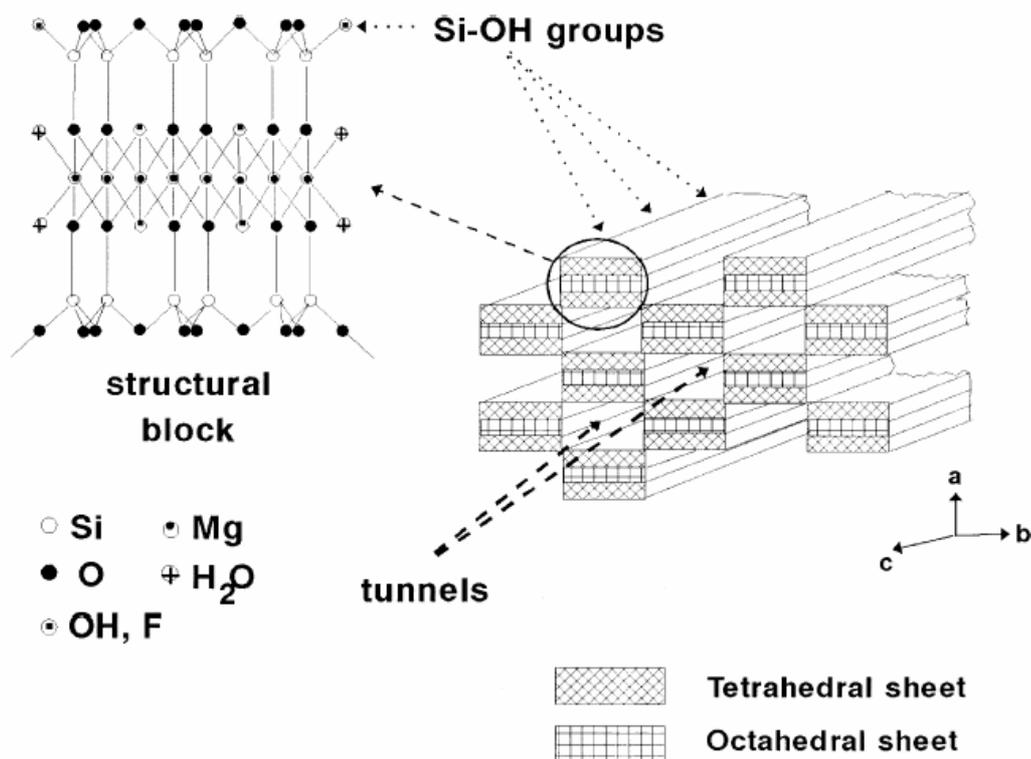


FIGURE 1
Schematic representation of the sepiolite structure.

adsorption of this anionic dye on sepiolite to various situations such as ionic strength, pH and temperature. The results obtained have been applied to a batch design for the removal of acid yellow 49 from aqueous media by sepiolite.

MATERIALS AND METHODS

Materials

The sepiolite sample was obtained from Aktaş Lületaşı Co. (Eskişehir, Turkey). The chemical composition of the sepiolite found in Eskişehir, Turkey is given in Table 1. Acid yellow 49 was obtained from Setaş Textile Co. (Bursa, Turkey). The structural form of dye is given in Figure 2. Sepiolite sample was treated before using in the experiments as follows [21]: the suspension containing 10 g L⁻¹ sepiolite was mechanically stirred for 24 h, after waiting for about two minutes the supernatant suspension was filtered through filter paper ($\Phi=12.5$ cm). The solid sample was dried at 105 °C for 24 h, ground then sieved by 75 μ m sieve. The particles under 75 μ m are used in further experiments. The cation exchange capacities (CEC) of the various sepiolite samples were determined by ammonium acetate method and densities by the picnometer method. The specific surface areas of the calcinated samples at

various temperatures (105-700 °C) were measured by BET N₂ adsorption by Micromeritics FlowSorb II-2300 equipment. The results are summarised in Table 2.

TABLE 1
Chemical composition of sepiolite.

Component	Weight %
SiO ₂	53.47
MgO	23.55
Al ₂ O ₃	0.19
Fe ₂ O ₃	0.16
CaO	0.71
NiO	0.43
Loss on ignition (LoI, %)	21.49

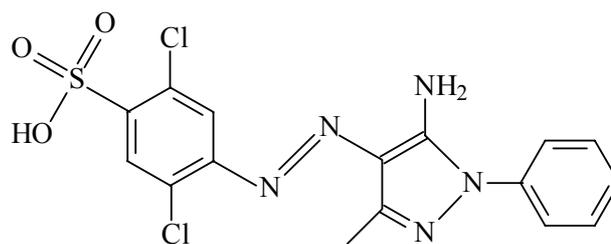


FIGURE 2
The structure of acid yellow 49.

TABLE 2
Physicochemical properties of the calcinated sepiolite samples.

Calcination temperature (°C)	CEC (meg 100g ⁻¹)	Density (g mL ⁻¹)	Specific surface area (m ² g ⁻¹)
105	25.00	2.46	341.9
200	24.66	2.70	357.1
300	25.66	2.56	320.9
500	27.16	2.47	294.8
700	25.33	2.33	250.2

Method

Adsorption experiments were carried out by shaking 0.5 g sepiolite samples with 50 mL aqueous solution of acid yellow 49 of desired concentration at various ionic strengths (0.1-0.5 M NaCl solutions in water), pHs (3-11), temperatures (25-55°C) for 1 h (the required time for acid yellow 49 to reach the equilibrium concentrations). A thermostated shaker bath was used to keep the temperature constant. The initial concentration of dye solutes, C_0 , were in the range of 1×10^{-4} - 30×10^{-4} mol L⁻¹. All adsorption experiments were performed at 25°C and pH 6.0 except those in which the effects of temperature and pH of the solution were investigated. The pH of the solution was adjusted with NaOH or HCl solution by using a Orion 920A pH meter equipped with a combined electrode. At the end of the adsorption period, the solution was centrifuged for 15 min at 3000 rpm and then the concentration of the residual acid yellow 49, C_e , was determined with the aid of Cary -1E-UV Visible Spectrophotometer (Varian). The adsorbed amounts of acid yellow 49 were calculated from the concentrations in solutions before and after adsorption according to the equation (1):

$$Q_e = (C_0 - C_e) \frac{V}{W} \quad (1)$$

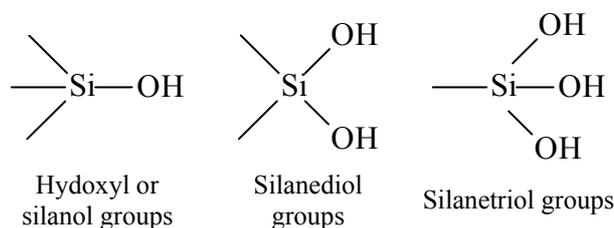
where C_0 and C_e are the initial and equilibrium liquid-phase concentrations of dye solution (mol L⁻¹), respectively; Q_e is equilibrium dye concentration on adsorbent (mol g⁻¹), V is the volume of dye solution (L), and W is the mass of sepiolite sample used (g).

Zeta Potential

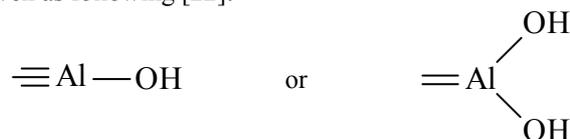
Zeta potential of sepiolite sample was measured $20 \pm 2^\circ\text{C}$ using a Zeta Meter 3.0 equipped with a microprocessor unit. The unit automatically calculates the electrophoretic mobility of the particles and converts it to zeta potential in terms of Smoluchowski equation. A 0.5 g amount of sepiolite was conditioned in 100 mL of bidistilled water for 24 h. The suspension was kept still for 5 min to let the larger particles settle. Each data point is an average of approximately 20 measurements. The pH of the suspension was adjusted using dilute NaOH and HCl. All solutions were prepared using bidistilled water.

RESULT AND DISCUSSION

The surface hydroxyl groups of the adsorbent have a main effect on the adsorption of acid yellow 49 onto the sepiolite. Therefore it would be useful to review the surface hydroxyl groups. The silicon atoms at the surface tend to maintain their tetrahedral coordination with oxygen. They complete their coordination at room temperature by attachment to monovalent hydroxyl groups, forming silanol groups. Theoretically, it is possible to use a pattern in which one silicon atom bears two or three hydroxyl groups, yielding silanediol and silanetriol groups, respectively. It is stated as improbable that silanetriol groups exist at the silica surface. The types of silanol groups are shown below [22]:



The hydrous oxide surface groups in alumina are given as following [22]:

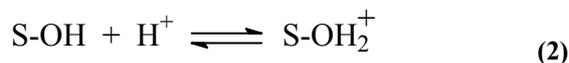


Effect of Ionic Strength

Ionic strength affects the activity coefficients of OH⁻, H₃O⁺ and specifically the adsorbable dye ions. As can be seen in Figure 3, the increasing ionic strength in the solution causes an increase in the adsorption of acid yellow 49 onto sepiolite at the pH 6. This indicates that the positive charge of the surface of sepiolite, which has pH_{pzc} at pH 6.6 (Figure 4), increase with increasing ionic strength, resulting in increasing the adsorption capacity. It is found that the adsorption capacity of perlite, which has the negative charge of the surface, in the range of pH 3-11 [23] decreases with increasing ionic strength, resulting in reducing the adsorption capacity.

Effect of pH

The adsorption isotherms at various pHs (3, 5, 7, 9 and 11) are shown in Figure 5. It is seen that the adsorbed amount of acid yellow 49 on sepiolite has decreased with increasing pH values. Figure 5 has shown that the sepiolite has point of zero charge about pH 6.6. Thus, the surface is positive at low pH where reaction (2) predominates, and is negative at higher pH when reaction (3) takes over.



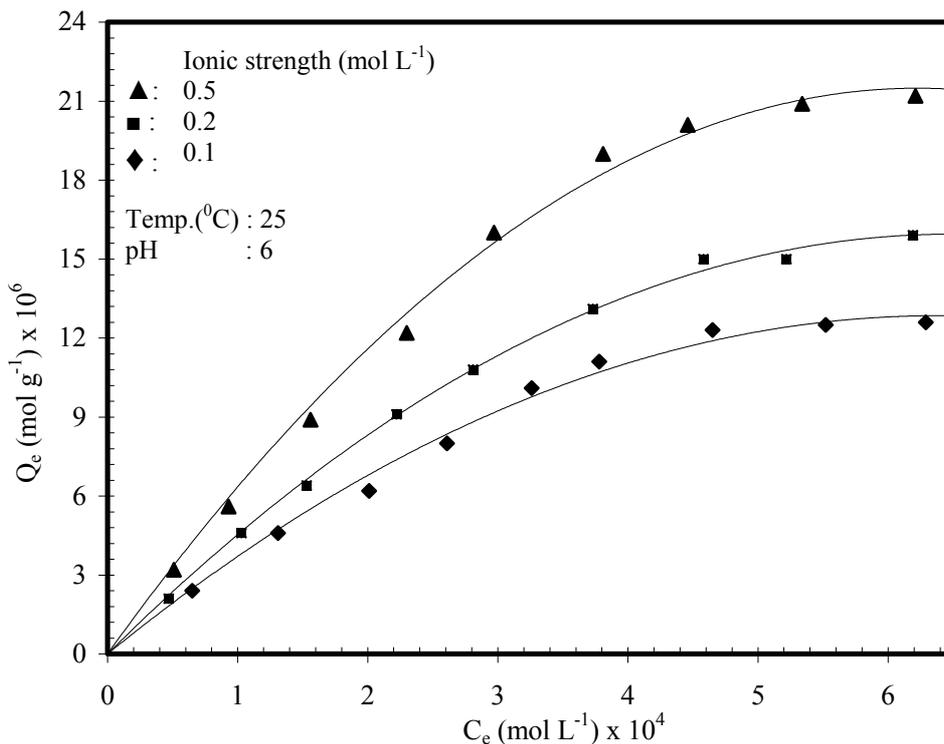


FIGURE 3
The effect of ionic strength on the adsorption of acid yellow 49 on sepiolite.

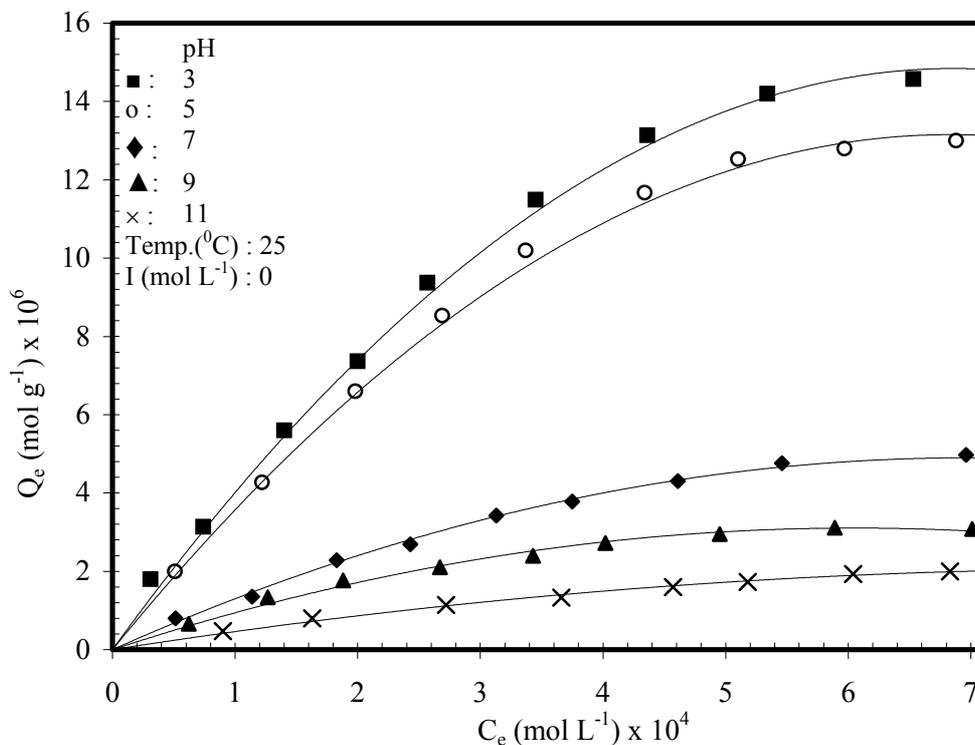


FIGURE 4
The effect of pH on the adsorption of acid yellow 49 on sepiolite.

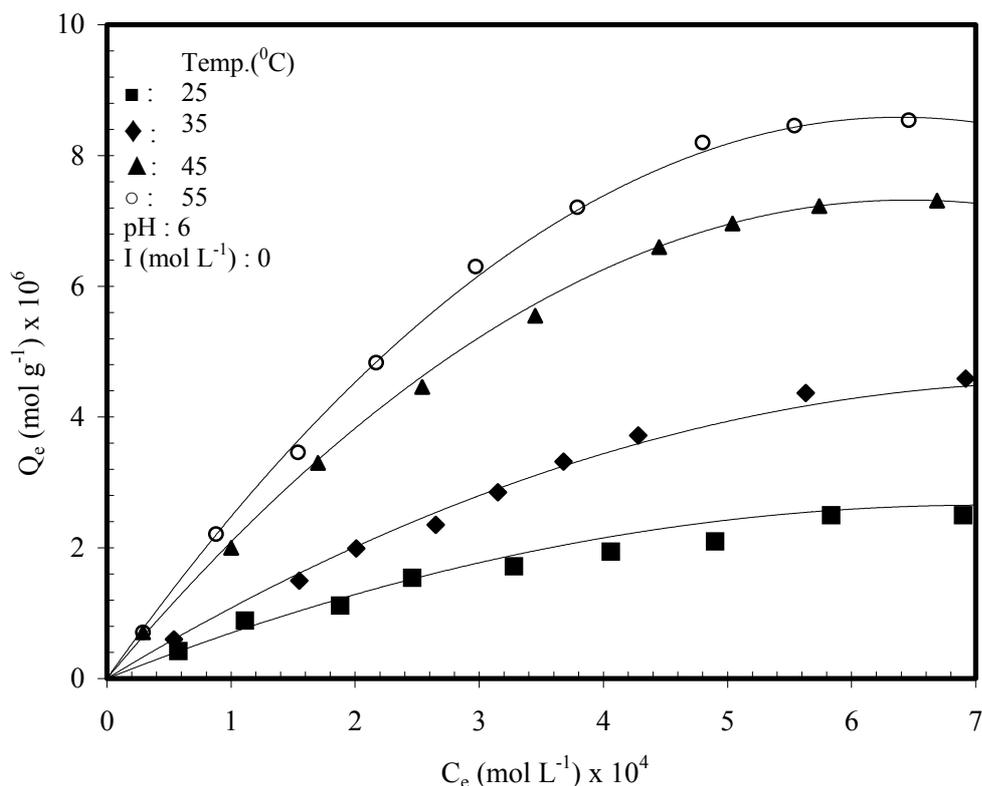
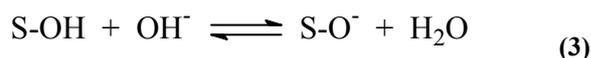
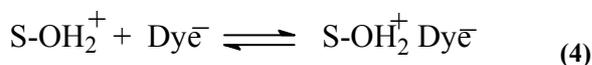


FIGURE 5
The effect of temperature on the adsorption of acid yellow 49 on sepiolite.



As the pH of the dye solutions becomes lower than pH 6.6, the association of dye anions with more positively charged sepiolite surface, because of increasing S-OH_2^+ groups, can more easily take place:



Effect of Temperature

The adsorption isotherms at different temperatures are shown in Figure 6. It is found that the adsorption capacity of acid yellow 49 increases with increasing temperatures. This may be a result of increase in the mobility of the large dye ions with increasing temperature. An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface. Furthermore, increasing temperature may produce a swelling effect within the internal structure of the sepiolite enabling large dyes to penetrate further. This indicates that the adsorption process becomes more favourable with increasing temperature [24].

Isosteric Enthalpy

The isosteric enthalpy of adsorption process was calculated according to the van't Hoff equilibrium equation and is given as follows [25]:

$$\ln C_e = \frac{\Delta H}{R} \cdot \frac{1}{T} + \ln K_v \quad (5)$$

where ΔH is the isosteric enthalpy of the adsorption process, T is temperature (K), R is gas constant ($\text{J mol}^{-1} \text{K}^{-1}$) and K_v is a constant. The isosteric enthalpy can be conveniently figured out based on the isostere, the plot of $\ln C_e$ which is related to the same equilibrium adsorption quantity at different temperatures, vs $1/T$. When we plot $\ln C_e$ vs $1/T$, we get a straight line and the isosteric enthalpy could be calculated from the slope of the line. The isosteres corresponding to different equilibrium adsorption quantities for acid yellow 49 adsorption on sepiolite are shown in Figure 7. The linear regression correlative coefficients of the isosteres and the corresponding isosteric enthalpy are presented in Table 3. The results suggest that Equation (5) fitted the experimental data very well. It can be seen from Table 3 that the isosteric enthalpy has changed in the range of 35.05-35.68 kJ mol^{-1} .

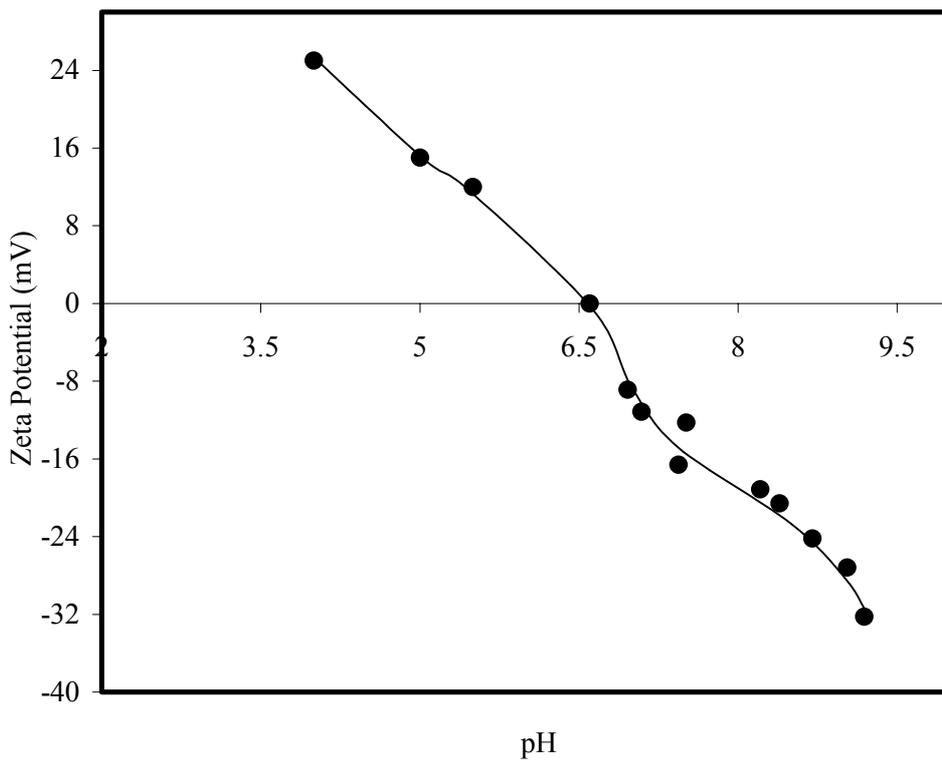


FIGURE 6
The effect of pH on the zeta potential of sepiolite.

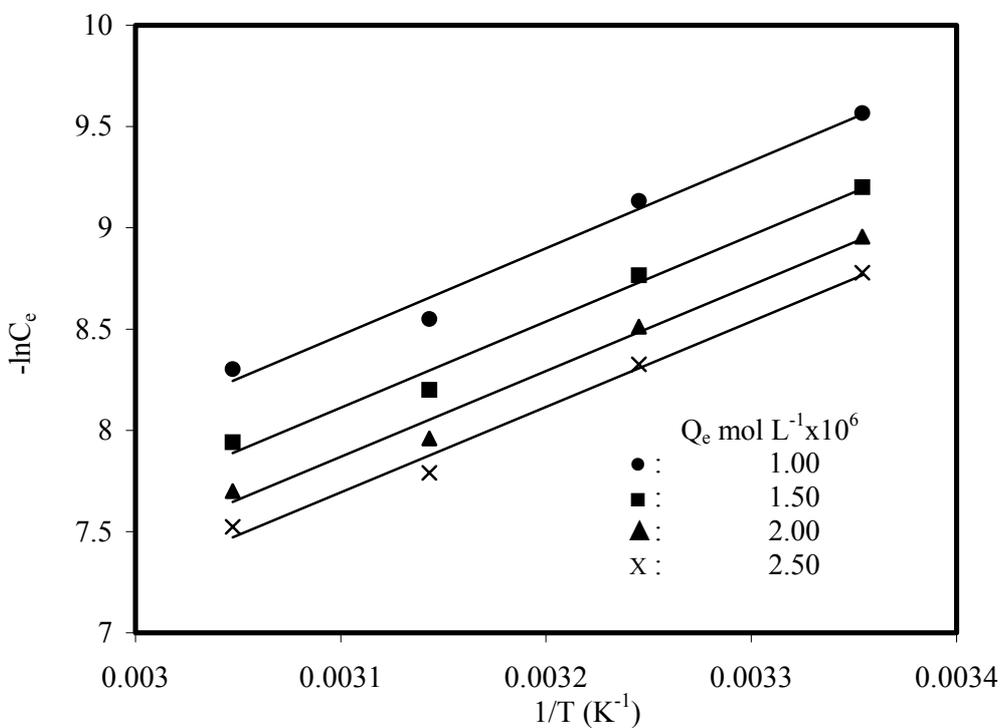


FIGURE 7
Plot of -lnC_e versus 1/T for adsorption of acid yellow 49 on sepiolite.

The isosteric enthalpy has shown that the adsorption of acid yellow 49 on sepiolite is an endothermic process. Because the isosteric enthalpy does not change significantly, it can be said that the adsorption process is uniform. The heat of physical adsorption, which involves only relatively weak intermolecular forces such as van der Waals and electrostatic interactions, is low compared to that of chemisorption, which involves essentially the formation of a chemical bond between the sorbate and molecule and the surface of the adsorbent. The upper limit for physical adsorption may be higher than 80 kJ mol⁻¹ for adsorption on adsorbents. The heat of chemisorption ranges from over 400 kJ mol⁻¹ to less than 80 kJ mol⁻¹ [26]. The results above show that the interaction between surface and adsorbate molecules is a physical interaction.

TABLE 3
Adsorption enthalpy of acid yellow 49 at different Q_e values.

Q_e (mol g ⁻¹) x 10 ⁶	R ²	ΔH (kJ mol ⁻¹)
1.0	0.984	35.68
1.5	0.986	35.41
2.0	0.987	35.21
2.5	0.989	35.05

Isotherm Analysis

The purpose of the adsorption isotherms is to relate the adsorbate concentration in the bulk and the adsorbed amount at the interface [27]. The analysis of the isotherm data is important to develop an equation which accurately represents the results and which could be used for design purposes [28]. Several isotherm equations are available. Two of them have been selected in this study: Langmuir and Freundlich isotherms.

The linear form of the Langmuir equation can be written in the following form:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K} + \frac{C_e}{Q_m} \quad (6)$$

where Q_m is the monolayer capacity of the adsorbent (mol g⁻¹) and K is the adsorption constant (L mol⁻¹). According to the Equation (6), a plot of C_e/Q_e versus C_e should be a straight line with a slope $1/Q_m$ and intercept $1/Q_m K$ when adsorption follows the Langmuir equation [26].

Freundlich equation in logarithmic form can be written as follows:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (7)$$

If Equation (7) applies, a plot of $\ln Q_e$ against $\ln C_e$ will give a straight line, of slope $1/n$ and intercept $\ln K_F$ [24].

Adsorption isotherms were obtained in terms of Equations (6) and (7) by using experimental adsorption results in these equations. Values for Q_m , K , n and K_F are summarised in Table 4. The isotherm data were calculated from the least square method and the related correlation coefficients (r values) are given in the same tables. As seen from the Table 4, the Freundlich equation represents the adsorption process very well; the r values were almost all higher than 0.99, indicating a very good mathematical fit.

The removal efficiencies, P , defined as:

$$P = \frac{C_0 - C_e}{C_0} \cdot 100 \quad (8)$$

are given in Table 4. As can be seen from the table, the removal efficiency ranged from 88.4–13.7% at 25 °C, 92.4–15.19% up to at 55 °C.

TABLE 4
Isotherm constants for different ionic strengths, pHs, temperatures and the values of the removal efficiency.

Temp.(°C)	pH	Ionic strength (mol L ⁻¹)	Langmuir isotherm			Freundlich isotherm			% P
			Q_m (mol g ⁻¹) x 10 ⁶	K (L mol ⁻¹) x 10 ⁻³	r	n	$K_F \times 10^3$	r	
25	6	-	2.6	2.5	0.934	1.412	1.9	0.992	88.5-13.7
35	6	-	4.5	3.8	0.926	1.252	3.4	0.995	89.3-13.1
45	6	-	7.3	3.9	0.922	1.112	4.0	0.998	94.2-15.5
55	6	-	8.6	4.7	0.978	1.230	1.3	0.996	92.4-15.2
25	3	-	14.8	3.7	0.956	1.284	5.6	0.996	93.8-18.4
25	5	-	13.1	3.5	0.951	1.188	8.4	0.997	89.8-14.1
25	7	-	4.9	3.2	0.949	1.282	1.8	0.993	89.7-13.0
25	9	-	3.1	4.6	0.979	1.733	0.2	0.995	87.6-12.4
25	11	-	2.0	3.0	0.987	1.529	0.2	0.997	82.1-6.4
25	6	0.1	12.8	3.4	0.922	1.180	8.7	0.996	87.0-21.4
25	6	0.2	15.9	3.3	0.941	1.155	12.4	0.994	90.6-22.6
25	6	0.5	21.5	3.6	0.921	1.154	17.2	0.997	89.8-22.4

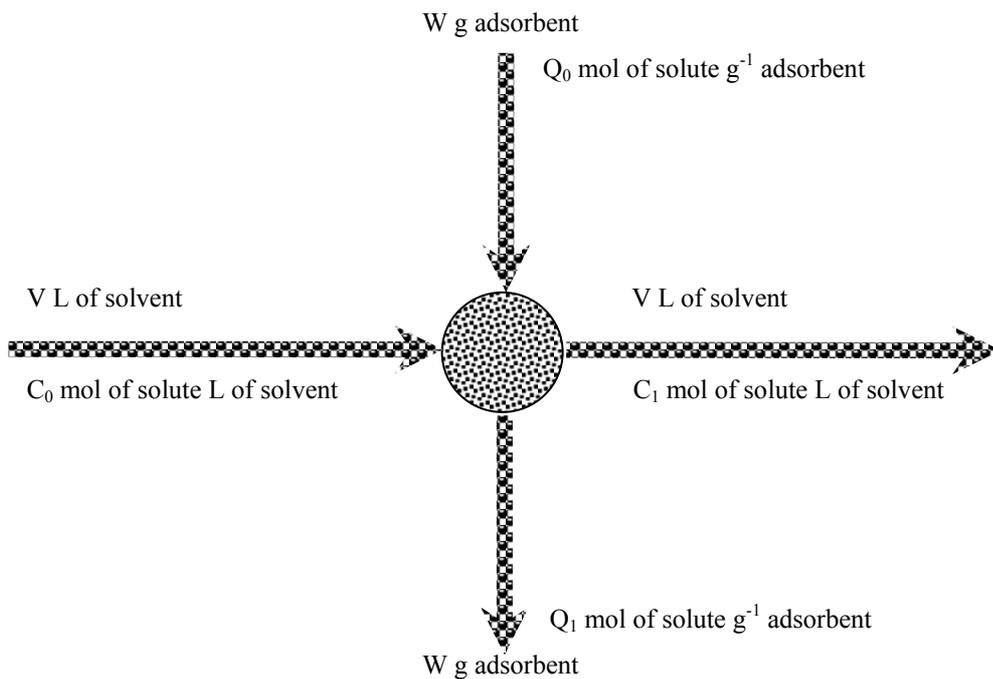


FIGURE 8
Single stage batch adsorber.

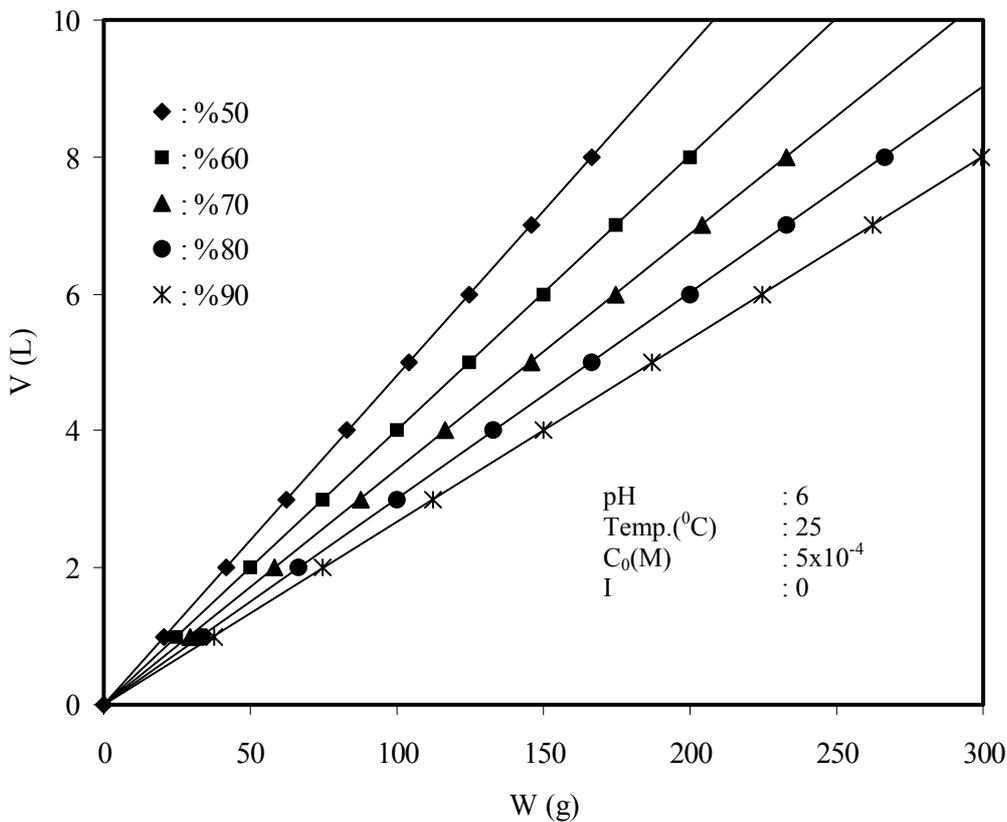


FIGURE 9
Volume of effluent (V) treated against adsorbents mass (W) for different percentage color removal of sepiolite.

Designing Batch Adsorption from Isotherm Data

Adsorption isotherms can be used to predict the design of single stage batch adsorption systems [28]. A schematic diagram is shown in Figure 8 where the effluent contains V L of water and an initial acid yellow 49 concentration C_0 , which is to be reduced to C_1 in the adsorption process. In the treatment stage W g sepiolite (dye free) is added and the dye concentration on the solid changes from $Q_0=0$ (initially) to Q_1 . The mass balance that equates the dye removed from the liquid effluent to that accumulated by the solid is

$$V(C_0 - C_1) = W(Q_1 - Q_0) = WQ_1 \quad (9)$$

For the adsorption of acid yellow 49 on sepiolite the Freundlich isotherm has given the best fit to experimental data. Consequently, equation can be best substituted for Q_1 in the rearranged form of Equation (7) giving adsorbent/solution ratios for this particular system

$$\frac{W}{V} = \frac{C_0 - C_1}{Q_e} = \frac{C_0 - C_1}{K_F C_e^{1/n}} \quad (10)$$

Figure 9 shows a series of plots derived from Equation (10) for the adsorption of acid yellow 49 on sepiolite. An initial dye concentration of 5.0×10^{-4} mol L⁻¹ at 25^o C and pH 6 is assumed and figure shows the amount of effluent which can be treated to reduce the acid yellow 49 content by 50, 60, 70, 80 and 90% using various masses of adsorbent.

CONCLUSIONS

Sepiolite as an adsorbent has a considerable potential for removing anionic dyes in commercial systems because of its higher surface area. As can be also understood from the present work, the studies about the adsorbent properties of sepiolite have been quite limited, so it was considered to be important to investigate whether or not sepiolite could be used for the removal of anionic dyes from industrial wastewater. The adsorbed amount of acid yellow 49 decreased with increasing pH, and increased with increasing temperature and ionic strength. The experimental data correlated reasonably well with the Freundlich adsorption isotherm and the isotherm parameters (K_F and n) were calculated. The sepiolite sample has a point of zero charge about pH 6.6. Thus, it can be said that the sepiolite sample exhibits positive zeta potential in the pH range 3-6.6 and negative zeta potential in the pH range 6.6-11. The order of heat of adsorption corresponds to a physical reaction. It is concluded that the acid yellow 49 is physically adsorbed onto sepiolite.

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