Study the adsorption of Basic blue and neutral red dye from aqueous solution by Zeolite clay surface.

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Abstract

In this study, the removal of cationic dye basic blue and neutral red dye used in the aqueous solutions with zeolite 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 two dyes basic blue and neutral red dye increased with increasing ionic strength, but decreased with increasing temperature and pH. Adsorption of cationic dye basic blue and neutral red dye was investigated by using uv-visible technique.

The Freundlich and Dubinin- Rasdushkevich (D-R) isotherm equations were applied to the data and values of parameters of these isotherm equations were calculated.

The mean energy of adsorption E, was also calculated from the adsorption energy constant K_{eng} . It's Value determined from the D-R isotherm equation. Finally thermodynamic functions ΔG , ΔS and ΔH , were calculated by using Freundlich isotherm.

.uv-visible spectrophotometer

(D-R) (Freundlich)

Kads

 $\Delta H \Delta S \Delta G$

D-R

E

:

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⁽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 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 limited 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 ^(12, 13).

Clays are composed mainly of silica, alumina, and water; frequently with appreciable quantities of iron, alkalis, and alkali earth ⁽¹⁴⁾. Two structural units are involved in the atomic lattices of most clay minerals. One unit consists of closely packed oxygen or hydroxyls in which alumina, iron or magnesium atoms are embedded in one octahedral combination, so that they are equidistant from six oxygen's or hydroxyls. The second unit is built of silica tetrahedrons. Which are arranged to form a hexagonal network that is repeated

indefinitely to form a sheet of composition SiO_6 (OH) $_4$ ⁽¹⁴⁾. The surface oxygen in layer silicates, however, is a weak electron donor. The (Si - O) bond, of prime important, is marked by a considerable degree of polarity.

Natural clay minerals such as zeolite, on the other hand, may be a very good alternative to these materials. Zeolite has attracted remarkable attention by its sorptive, rheological and catalytic properties. Therefore the use of zeolitic clays has been increasing ⁽¹⁵⁾.

Zeolite is a clay mineral with a unit cell formula $M_{2/n}.Al_2O_3.xSiO_2.yH_2O$, where M is [Mg or Fe] and in it consists⁽¹⁶⁾.

Each block is constructed by two tetrahedral silica sheets enclosing a central magnesia sheet. In some aspects zeolite is similar to other 2:1 trioctahedral silicates. The molecule formula is $Mg_3Si_4O_{10}$ (OH) ₂, but it has discontinuities and inversions of the silica sheets that give rise to structural tunnels (17).

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) $^{(16)}$.

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 as shown in figure (1)⁽¹⁶⁾. In this work we present the experimental results for adsorption of cationic dye basic blue and neutral red dye on zeolite.



The main aim of the current study has been to visualize the pattern adsorption of these dyes on zeolite to various situations such as concentration, ionic strength, pH and temperature.

Materials and Methods Materials The Clay

Zeolite clay used in this study was obtained from the general al-raya'a company, Baghdad, Iraq, have the general structure is

 $Ca_{4.5}Na_{3}(AlO_{2})_{12}(SiO_{2}).3H_{2}O$.

The chemical analysis of zeolite is listed in Table (1).

Constituent	Wt%.
SiO ₂	32.52
Al ₂ O ₃	27.64
CaO	11.38
Na ₂ O	4.2
Loss on ignition	24.25
Total	99.99

 Table 1. The chemical analysis of zeolite [from al-raya'a company]

Zeolite clay was supplied in the powder form. It was suspended in HCl solution of pH=3 to remove carbonate and it was washed with an excess amount of distilled water to remove the soluble materials, the result was dried in the oven at 388 K for twenty-four hours then kept in airtight containers. Using the available sieve (200 mesh) the maximum particle size obtained was (75 μ m). This was used in all experiments through out this work.

The structural form of methyl basic blue and methyl neutral red dyes are given in figure 2, 3 respectively⁽¹⁸⁾.





Figure 3: Structure of Methyl Neutral Red dye

The chemical used for this work are listed in table (2) together with the purity and sources. All chemicals were used without further purification.

Chemical	Source	Conc. %
Neutral red dye	Aldrich	80
Basic methyl blue	Aldrich	85
Hydrochloric acid	BDH	35

The following instruments were used in this study:

- 1. Uv-Visible Spectrophotometer meter, Single Beam, Pye Unicam-8700.
- 2. Digital pH-Meter (Hanaa, Roman

3. Digital balance, Sartoris (BP 3015 (Germany).

4. Oven, Heracus (D-6450), Hanau, (England).

5. Shaker Bath, SB. 4, Tecam.

Method

Adsorption experiments were carried out by shaking 0.02 g zeolite samples with 20 mL aqueous solution of dyes of desired concentration at various ionic strengths (0.1, 0.3 and 0.5 M NaCl solutions in water), pHs (4, 7 and 10), temperatures (298, 308 and 318 K) for 1 h (the required time for methyl basic blue "MB" and neutral methyl red "NR" to reach the equilibrium concentrations).

A thermostated shaker bath was used to keep the temperature constant. The initial concentrations of dyes solutes, C_0 , were in the range of [2-20 ppm]. All adsorption experiments were performed at 298 K and pH 7.0 except those in

$$Q_e = (C_o - C_e) \frac{V}{W}$$
.....(1)

where C_0 and C_e are the initial and equilibrium liquid phase concentrations of dye solution (mg/L), respectively; Qe is equilibrium dye concentration on adsorbent (mg.gm⁻¹), V is the volume of dye solution (L), and W is the mass of zeolite sample used (g). All solutions were prepared using distilled water.

Result and Discussion

The surface hydroxyl groups of the adsorbent have a main effect on the adsorption of MB or NR dye onto the zeolite. Therefore it would be useful to review the surface hydroxyl groups. The 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 pH meter equipped with a combined electrode. At the end of the adsorption period, the solution was centrifuged for 5 min at 3000 rpm and then the concentration of the residual [Ce,] of MB or NR, was determined with the aid of uv- visible Spectrophotometer at a maximum absorbency λ_{max} for methyl blue 660 nm and neutral methyl red 455nm . The adsorbed amounts of two dyes were calculated from the concentrations in solutions before and after adsorption according to the equation (1)

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 ⁽¹⁹⁾:

OH



The hydrous oxide surface groups in alumina are given as following $^{(19)}$:

Adsorption Isotherms

Adsorption at equilibrium conditions were determined for methyl basic blue and neutral methyl red on

$$Q_e = (C_o - C_e) \frac{V}{W}$$
.....(1)

Plots of the Q_e (mg.g⁻¹) against equilibrium concentration $C_e(mg/L)$ for methyl basic blue and neutral methyl red onto zeolite, the data are listed in table (3) and Figure (4) which showed multilayer adsorption at relatively high zeolite adsorbent. The adsorbed quantities at equilibrium concentrations were calculated by using the following equation:

concentration concerning the heterogeneity of the surface S type of Gilles classification ⁽²⁰⁾. Also the adsorption capacity of basic methyl blue is better than neutral methyl red at different conditions.

Table (3) adsorption isotherms values of two dyes (MB and NR) on the zeolite surface at 298 K.

Co	C _e (mg/L)	Q _e (mg/gm) In C _e	ln Q _e	C _e (mg/L)	Q _e (mg/gm)	ln C	e.	ln Qe	
(mg/L)		Basic me	thyl blue	Neutral red dye						
2	0.18	1.82	-1.71	0.59	1.16	0.84	0.15	-0.	.17	
4	1.01	2.99	0	1.09	1.9	2.1	0.64	0.	74	
6	1.4	4.6	0.33	1.52	2.2	3.8	0.79	1.	33	
8	1.51	6.49	0.4	1.87	2.6	5.4	0.95	1.	1.68	
10	2.07	7.99	0.69	2.08	2.92	7.08	1.07	1.	1.95	
12	2.76	9.24	1.01	2.22	2.98	9.02	1.09	2	2.2	
14	3	11	1.09	2.39	3.87	10.13	1.35	2.	31	
16	3.32	12.68	1.2	2.54	3.91	12.09	1.36	2.	49	
18	3.41	14.59	1.25	2.68	4.4	13.6	1.48	2.	61	
20	3.7	16.3	1.308	2.79	4.72	15.28	1.55	2.	73	



Figure 4. Adsorption isotherm of MB and NR on zeolite at 298 K.

It is obvious from Figure 4 that the adsorption isotherms of dyes on clay surface is indicates that a large amount of dye is adsorbed at a lower concentration as more active sites of zeolite are available. As the concentration increases, it becomes difficult for a dye molecule to find vacant sites, and so monolayer formation occurs.

Zeolite surface is heterogeneous and this feature could be attributed by the different properties of the unsaturated adsorption sites which lead to different characters of these sites ⁽²¹⁾. The adsorption on different active sites occurs throughout different types of forces leading to the formation of clusters or packed line of the adsorbed molecules on the surface ⁽²²⁾. The results for MB and NR adsorption systems of this study are favorable. Adsorption capacity of MB dye is greater than that of NR dye.

The difference in adsorption capacities must therefore be linked to the solute acidity. The presence of amine groups and nitrogen rings increase the basicity make MB dye less acidic character and enhanced its affinity for adsorption at the adsorbent surface.

Effect of temperature on the adsorption isotherms

The effect of temperature variation on the adsorption extent of MB dye or NR dye on the zeolite surface has been studied at neutral media pH= 7. Figures 5 and 6 illustrate the general shapes of MB dye and NR dye adsorption isotherm at 298, 308 and 318 K. it can be seen that as the temperature increased, the adsorption quantity decreased.



Figure 5. Temperature dependence of the adsorption of MB dye on the Zeolite surface.



Figure 6. Temperature dependence of the adsorption of NR dye on the Zeolite surface.

The study of the temperature effect on adsorption will also help in calculation the basic thermodynamic functions Gibbs energy (Δ G), enthalpy (Δ H) and entropy (Δ S) of the adsorption process. The equilibrium constant (K_e) of the adsorption process at each temperature, is calculated from the equation

$$Ke = \frac{(Qe)}{(Ce)} * \frac{0.02 \ gm}{0.02 \ L}$$
(2)

 $\begin{array}{ccc} & Where \ Q_e \ is \ the \ amount \ adsorbate \\ in & milligram \ per & one & gram \\ adsorbent(mg/gm), \ C_e \ is \ the \ equilibrium \end{array}$

concentration of the adsorbate expressed in mg/L. The change in the Gibbs energy could be determined from the equation:

$$\Delta G^{o} = -RT \ln K_{e}$$
 (3)

Where R, is the gas constant (8.314 J K⁻¹ mole⁻¹), T is the absolute temperature in Kelvin. The enthalpy of

adsorption may be obtained from the Clausis-Clapeyron equation:

$$\ln Xm = -\Delta H/RT + Constant$$
 (4)

When Xm (mg/gm) is the maximum value of adsorption at a certain value of equilibrium concentration (Ce). Table 4 gives Xm values at different temperatures for MB and NR dyes.

Plotting ln Xm versus (1/T) should produce a straight line with a slope $-\Delta H/R$ as shown in Figures (7 and 8).

T/K	1/T*10 ⁻³	C _e =3.75 mg/L	Xm (mg/gm)	ln X _m	T/(K)	1/T*10 ⁻³	Xm (mg/gm)	C _e =4.5 mg/L	ln X _m
	Basic	e Methyl bl	lue dye			Neutra	l Methyl re	ed dye	
298	3.35	48.4	16.02	2.77	298	3.35	14.9	64.3	2.70
308	3.25	46.2	14.2	2.65	308	3.25	13.6	59.2	2.61
318	3.15	43.7	12	2.48	318	3.15	11.8	55.0	2.47

Table 4. Maximum adsorption quantity Xm values of MB dye and NR dye on theZoelite surface at different temperature.



Figure 8. Plot of ln Xm versus 1/T of NR on the Zeolite surface

The change in entropy (Δ S) was calculated from Gibbs-Helmholtz equation ⁽²³⁾:

$\Delta G = \Delta H - T \Delta S$

Table (5) gives the quantitative thermodynamic data of two dyes (MB and NR) on the adsorbent surface zeolite. Table 5 shows that a Δ H value of of two dyes (MB and NR) are negative indicating that the adsorption process is exothermic reaction. All process of adsorption consider spontaneous from the negative value of ΔG . While, ΔS have positive value for each methyl blue and neutral red dye that refer the interaction of molecules caused random of the total system.

(5)

Table 5. Thermodynamic function ΔG , ΔS and, ΔH of (MB and NR) on the adsorbent surface zeolite at 298K.

Adsorbate	$\Delta \mathbf{G} / (\mathbf{kJ mole}^{-1})$	$\Delta S/ (J mole^{-1}K^{-1})$	$\Delta \mathbf{H} / (\mathbf{kJ mole}^{-1})$
Methyl blue dye	- 3.67	45.25	- 17.16
Neutral red dye	- 2.91	32.07	- 12.47

Effect of Ionic Strength

Ionic strength affects the activity coefficients of OH^- , H_3O^+ and specifically the adsorbable dye ions. As shown in figures (9) and (10), the increasing ionic strength in the solution causes an increase

in the adsorption of two dyes (MB and NR) on zeolite surface at the neutral pH. This indicates that the positive charge of the surface of zeolite, increase with increasing ionic strength, resulting in increasing the adsorption capacity.



Figure 9. The effect of ionic strength on the adsorption of MB on zeolite surface at 298 K.



Figure 10. The effect of ionic strength on the adsorption of NR on zeolite surface at 298 K.

Effect of pH

The adsorption isotherms at various pHs (4, 7 and 10) are shown in Figures (11 and 12). It is seen that the adsorbed amount of two dyes (MB and NR) on zeolite have decreased with increasing pH values.

Figures (11 and 12) have shown that the surface of zeolite is positive at low pH where reaction (1) predominates, and is negative at higher pH when reaction (2) takes over.

$$Si - OH + H^{+} \Leftrightarrow Si - OH_{2}^{+} \dots \dots 1$$

$$Si - OH + OH^{-} \Leftrightarrow Si - O^{-} + H_{2}O \dots \dots \dots 2$$

As the pH of dyes solutions become lower than pH 7, the association of dye anions with more positively charged zeolite surface, because of increasing $S-OH_2$ groups, can more easily take place reaction (3):

$$Si - OH_2^+ + Dye^- \Leftrightarrow Si - OH_2^+ Dye^- \dots 3$$



Figure 11. The effect of pH on the adsorption of MB on zeolite surface at 298 K.



Figure 12. The effect of pH on the adsorption of NR on zeolite surface at 298 K.

Isotherm Analysis

The purpose of the adsorption isotherms is to relate the adsorbate concentration in the bulk and the adsorbed amount at the interface ⁽²⁴⁾. 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 ⁽²⁵⁾. Several isotherm equations are available. Two of them have been selected in this study: Freundlich and Dubinin- Rasdushkevich (D-R) isotherm isotherms. The widely used Freundlich isotherm has found successful application too many real sorption processes and is expressed as:

$$Q_e = K_f * C_e^{1/n}$$
(6)

Where Q_e is the adsorption capacity (mg/gm), K_f is the Freundlich constant and (1/n) of the adsorption intensity. K_f and (1/n) can be determined

from the linear plot of $\ln (Q_e)$ versus $\ln (C_e)$.

Freundlich equation in logarithmic form can be written as follows:

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

In Figures (13-18) a linear form of Freundlich isotherm are presented by plotting $\ln Q_e$ as a function of $\ln Ce$ of

two dyes (MB and NR) adsorbed on zeolite surface at different conditions.

The value of 1/n was calculated from the slope of the straight line which gives an indication for the intensity of adsorption, while the intercept with y-axis gives K_F Freundlich constant which is the measure of the adsorption capacity. Freundlich constants are listed in Table (6) of two dyes at different conditions.

pHIonicTemp (K)strength			Freundlich constant for NR dye			Freundlich constant for MB dye		
		(M)	n	K _f	\mathbf{R}^2	n	K _f	\mathbf{R}^2
298	7		2.017	0.74	0.942	1.160	3.291	0.959
308	7		0.938	1.15	0.989	1.270	2.632	0.966
318	7		2.081	0.66	0.949	1.360	2.149	0.984
298	4		2.304	0.42	0.889	1.304	2.688	0.947
298	10		2.581	0.217	0.923	1.390	2.134	0.975
298	7	0.1	2.901	0.091	0.871	2.13	0.546	0.956
298	7	0.3	2.702	0.149	0.881	1.981	0.708	0.959
298	7	0.5	2.462	0.234	0.917	1.759	1.058	0.958

 Table 6. Freundlich isotherm constants for different ionic strength, PHs, and temperatures of MB and NR dyes on the zeolite surface.



Figure 13. Linearized Freundlich plot of MB adsorption on Zeolite surface at different temperature



Figure 14. Linearized Freundlich plot of NR adsorption on Zeolite surface at different temperature







Figure 16. Linearized Freundlich plot of NR adsorption on Zeolite surface at different pHs.



Figure 17. Linearized Freundlich plot of MB adsorption on Zeolite surface at different ionic strengths.



The adsorption data were also tested for more another adsorption isotherm, the Dubinin since

more general than the Langmuir isotherm since it does not assume a homogenous surface or constant sorption potential. The D-R equation is

$$Q = \bar{X_m} \exp(-\bar{K} \varepsilon^2)$$

where \mathcal{E} (polanyi potential) = RT ln (1+1/C), Q is the amount of dye adsorbed per unit weight of Zeolite clay (mg gm⁻¹), Xm is the adsorption capacity (mg gm⁻¹), C is the equilibrium concentration of dye

Radushkevich $(D-R)^{(26)}$. This isotherm is

$$\ln Q_e = \ln \bar{X}_m - \bar{K} \varepsilon^2$$

The plots of $\ln Q_e$ against \mathcal{E}^2 are shown in Figures (19-24) at different factors that effective on adsorption process. in solution (mg L⁻¹), \overline{K} is the constant related to the adsorption energy (mol² kJ⁻²), R is the gas constant (0.008314) (kJ K⁻¹ mol⁻¹) and T is the temperature (K). The D-R isotherm can be linearized as

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temperatures.

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ionic strengths.



Most of the adsorption isotherms fitted the D-R equation with correlation coefficients R^2 >0.966, by making certain assumptions, the mean energy of adsorption, E, can be calculated from the K values ⁽²⁷⁾ using the relation $E = (2K)^{-0.5}$, values of E are presented in table 7 The calculated mean energy of adsorption, E, from the D-R isotherm, gives information about the chemical or physical properties of the sorption.

The calculated mean energy values of adsorption of two dyes by zeolite are very small and this implies that the type of adsorption is physical.

Tom			D-R iso	therm paran	neters for	D-R isothe	rm paramet	ers for MB	
1 CIII		Ionic		NR dye		dye			
р (К)	рН	strength (Molar)	X _m (mg.gm ⁻ 1)	K _m (mole ² kJ ⁻ ²)	E (kJ.mole⁻ ¹)	X _m (mg.gm ⁻¹)	K _m (mole ² kJ ⁻ ²)	E (kJ.mole⁻ ¹)	
298	7		27.77	3.55	0.375	16.38	0.82	0.78	
308	7		26.21	3.47	0.379	15.92	0.78	0.80	
318	7		25.92	3.51	0.377	15.41	0.84	0.77	
298	4		28.86	3.15	.398	16.28	0.723	0.83	
298	10		28.25	3.94	0.356	16.11	0.87	0.758	
298	7	0.1	26.5	5.66	0.297	20.00	2.455	0.751	
298	7	0.3	29.13	4.54	0.33	21.42	2.11	0.486	
298	7	0.5	34.46	3.92	0.357	22.57	1.74	0.536	

 Table 7. D-R isotherm parameters and mean energy of the adsorption for different ionic strength, PHs, temperatures of MB and NR dyes on the zeolite surface.

Conclusion

Zeolite as an adsorbent has a considerable potential for removing cationic 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 zeolite have been quite limited, so it was considered to be important to investigate. The adsorbed amount of MB and NR dyes decreased with increasing pH and temperature, and increased with increasing ionic strength.

The experimental data correlated reasonably well with the Freundlich

adsorption isotherm and the isotherm parameters (K_F and n) were calculated also D-R isotherm equation using to determine the mean energy of adsorption. The zeolite sample has a point of zero charge about pH 7. Thus, it can be said that the zeolite sample exhibits positive potential in the pH range 4-6.9 and negative potential in the pH range 7.1-10.

The order of heat of adsorption corresponds to a physical reaction and proved from two equations. It is concluded that the two dyes are physically adsorbed onto zeolite.

Nomenclature:

MB methyl blue dye NR neutral red dye C_o initial solution concentration, mg/L. Ce equilibrium solution concentration, mg/L. K_{ad} rate constant of pseudo- first order adsorption, min⁻¹.

1/n adsorption intensity.

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Q adsorption capacity mg/gm

- K_f Freundlich constant.
- E mean adsorption energy
- D-R Dubinin- Rasdushkevich equation

X_m the maximum monolayer

adsorption.

 R^2 correlation coefficient

t time, min

V volume of the solutions, L

weight of Zeolite, gm.

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