

Study of Adsorption of Methyl Orange and Methyl Violet Dyes on the surface of Triethyl amine glyceryl maleate polymer

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Abstract

The adsorption processes of two dye compounds (Methyl orange (MO) and Methyl violet (MV)) in aqueous solutions on the surface of crosslinked Triethyl amine glyceryl maleate polymer were investigated at different temperature, ionic strength and pH. The results revealed that the adsorption of these compounds at (25°C) follow S-mode adsorption according to Giels classification. At fixed adsorbent, the adsorbate quantity of MV more than MO and no different pattern was noticed with regard to the adsorption depending on the ionic strength. Generally, it was noticed that the adsorption quantities is correlated with the pH values of the medium. In addition, it was found that the polymer has higher ability to adsorb the two dye compounds in comparing to zeolite (25A).

Introduction

It is well known that phenolic compounds and dyes are common pollutants in municipal and industrial effluents (1). The disposal of colored waste such as dyes into receiving waters causing a damage to the environmental as they are toxic to aquatic life. Textile industrial waste water is the main source of pollution due to the dyes contained therein (2-4).

Due to the toxicity of dyes, their removal from water is an important issue. Hence different treatment methods such as neutralization of acidic and alkaline effluents, aerobic and anaerobic biological treatment and chemical oxidation are used (5). However, adsorption process is one of the most effective methods for removal of different classes of dyes from the waste effluents. Activated carbon and carbonaceous precursors are widely used as adsorbents due to its high adsorption efficiency for the dyes (6-11).

On the other hands, many workers have investigated the feasibility of using alternative materials like clays, and polymers as adsorbents for removal of dyes and organic compounds (12-17).

Therefore, the present work undertaken to evaluate using newly synthesized cross linked polymer (polytriethyl amine glyceryl maleate) as adsorbent for some organic dyes from aqueous solution. The investigation extended to compare the efficiency of using the polymer as adsorbent with zeolite(25A).

Materials and Methods

The two dyes MO and MV were obtained from Fluka and HW respectively, with 99.9% purity for both.

Dye	Source	Purity %
Methyl Orange	Fluka	99.9
Methyl Violet	HW	99.9

The Zeolite obtained from the Iraqi company Alraia with molecular formula $(Ca_4.5Na_3(AlO_2)_{12}(SiO_2)_{13}.30H_2O)$ and W% is shown in table (2)

Constituent	W%
SiO ₂	32.52
Al ₂ O ₃	27.64
CaO	4.38
Na ₂ O	4.2
L.O.I.	20.25
Total	99.9

L.O.I.= Lost Of Ignition

Polymer Synthesis

The polymer was synthesized by condensation polymerization of mixture of tri ethanol amine and glycerol with maleic anhydride. However, full detail for polymer preparation has been explained elsewhere(18).

Methods

A stock solution 100ppm of (MO and MV) were prepared by dissolving each compound (0.05gm) in deionized water 500ml. Other standard solutions, with concentrations of (5-30 ppm), were prepared from the stock by subsequent dilution using deionized water of the stock solution.

Determination Of The Equilibrium Time

A polymer sample (0.04gm) in less than 300μ diameter (granules) was placed in a 250 ml conical flask. Then 50 ml of adsorbed of 20 ppm adsorbate was added at constant temperature and the flask was placed in water path shaker. The initial time has been recorded and after each half an hour a sample has been piped and placed in centrifuge (4000rpm) for 10 min, a supernatant has been separated by decantation and adsorption of solution has been recorded at λ_{max} for certain sample. The process has been achieved repeatedly to the equilibrium.

Adsorption isotherms

In order to determine the adsorption isotherms for each dye, six conical flasks have been used containing (0.01 gm) of the polymer. Then adsorbent (10ml) in a concentration range (5-30ppm) has been added into the flasks. After closing, the flasks were shaken with water bath shaker at 25°C according to the equilibrium time. Then, they are centrifuged for 10 minutes; UV-Vis. Spectroscopy has been used to measure the absorbance for the solutions, at the convenient wavelength for each compound. The absorbance has been used to determine the equilibrium concentration (After adsorption process) from the calibration curve.

Effect of Temperature

The effect of temperature on adsorption process has been studied at temperature (25,35, and 45°C). Hence, the adsorption isotherm for each compound has been studied in each degree..

pH effect

To accomplish this study two pH values has been suggested pH=8 and pH=6, a fully study of adsorption isotherms has been achieved.

Ionic strength

The effect of ionic strength has been performed on the two dyes, at two different ionic strength values. With fixed amount of adsorbent i.e.(0.01 gm), sodium chloride solution of concentration (0.1 and 0.2 M) has been used and the effect of this salt on adsorption has been recorded.

Results and Discussion

Adsorption Isotherms:

The adsorbed amount of dyes were calculated from the concentration in solutions before and after adsorption according the following equation:

$$Q_e = \frac{V_{sol.}(C_o - C_e)}{m} \quad \dots\dots\dots (1)$$

Where Q_e = the quantity of adsorbate in mg/g

V = the total volume of adsorbate in L

C_o = the initial concentration of solution in mg/L

C_e = the concentration at equilibrium of adsorbate in mg/L

m = weight of adsorbent in gm

The adsorption isotherms of dyes studied are presented in figure (2). It shows that the adsorption follow S_3 -mode for both dyes according to Giles classification⁽²⁰⁾.

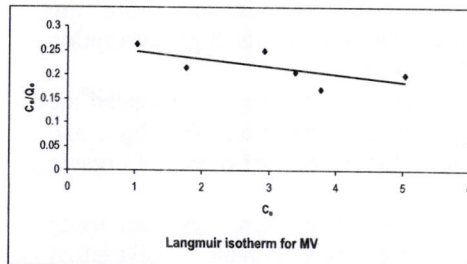
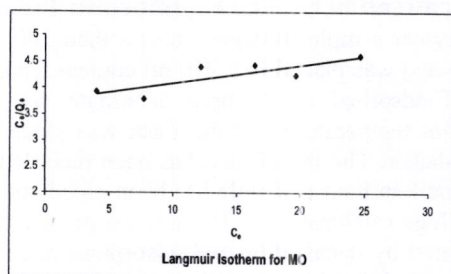


Figure (3): Langmuir Isotherms for (MO and MV)

Frendlich equation in logarithmic form can be written as follows:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad \dots\dots\dots (3)$$

Where the constant K_F , partition coefficient in equilibrium, is positively related to the extent or degree of adsorption, while the constant n provides a rough estimation of the intensity isotherms of adsorption.

In equation (3) applies, a plot of $\ln Q_e$ against $\ln C_e$ will give a straight line, of slope $1/n$ and intercept $\ln K_F$ ⁽¹¹⁾.

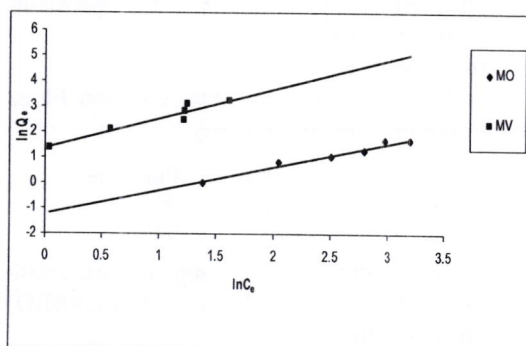


Figure (4): Frendlich Isotherms for (MO and MV)

Adsorption isotherms were obtained in terms of equation (2) and (3) by using experimental adsorption results in these equations. Values of (a , b , K_F and n) are summarized in table (3). The isotherm data were calculated from least square method and the related correlation coefficient (r value) given in the same table.

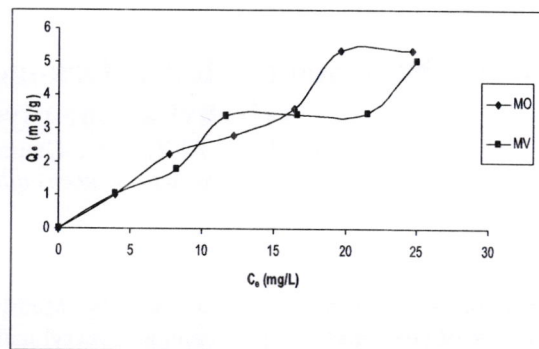


Figure (2): Adsorption Isotherms for (MO and MV)

The equilibrium adsorption isotherms are fundamentals importance in the design of adsorption system. The analysis of the isotherm data is important to develop an equation which a currently represents the results and which could be used for design purposes⁽⁹⁾. Several isotherms equations are available. Two of them have been selected in this study: Langmuir and Frendlich isotherms.

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

$$\frac{C_e}{Q_e} = \frac{1}{a} + \frac{b}{a} C_e \quad \dots\dots\dots (2)$$

Where a is the monolayer capacity of adsorbent (mol g^{-1}) and b is the adsorption constant (L mol^{-1}). According to the equation (2), a plot of C_e/Q_e versus C_e should be a straight line with a slope b/a and intercept $1/a$ when adsorption follows the Langmuir equation⁽¹⁰⁾.

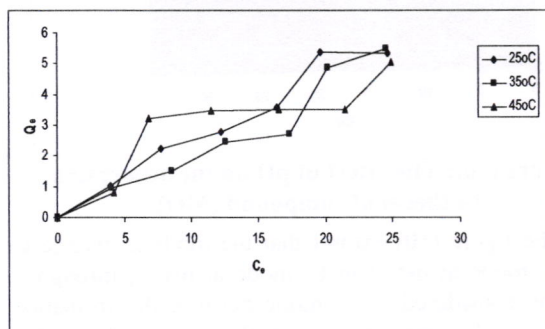
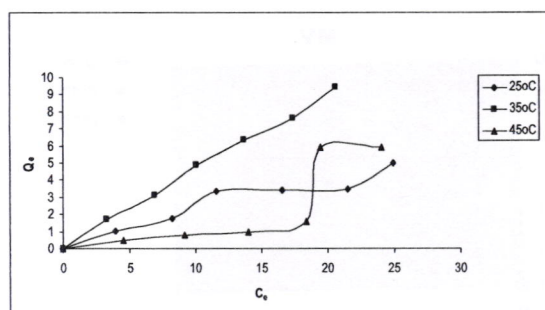
Table (3): The Freundlich and Langmuir constant.

Compound	Freundlich Constant			Langmuir Constant		
	K_F	n	R	a	b	r
MO	0.9243	1.95	0.9911	31.026	0.99996	0.694
MV	4.0609	0.87	0.96135	3.944	0.04898	0.4645

From the r values which shown in table (3) we can conclude that the adsorption data are fitted well to the Freundlich adsorption isotherm.

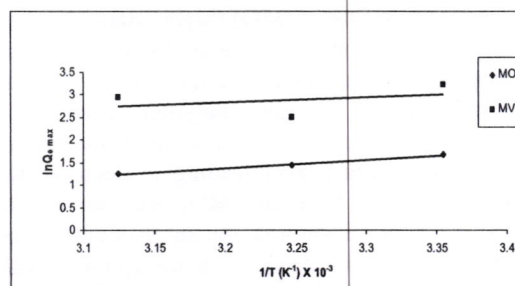
Effect of Temperature :

The adsorption isotherms at deferent temperatures are shown in figures (5) and (6). It is found that the adsorption capacity decreases with temperature increasing but with change in mode for (MO) of adsorption from S_3 -mode at 25°C to L_3 -mode at 35°C. It could be explain as the cluster of S_3 -mode are spreading by increase in temperature and to be distributed regularly on the surface area of the polymer around these sites resulting the L_3 -mode adsorption⁽⁷⁾. And when temperature is elevated to 45°C, the (MV) will be a great change in general mode of adsorption from S_3 to S_2 with large increment in adsorption quantity. This could be due to the polymer swelling leading to the increment in pores diameter on its surface and enabled (MV) to pass through the cavities of the polymer. Thus during the adsorption process, two layers have been recognized: the layer of cavities and the outer surface layer.

**Figure (5): Adsorption Isotherms of MO at (25, 35 and 45°C)****Figure (6): Adsorption Isotherms of MV at (25, 35 and 45°C)**

Thermodynamic calculation:

ΔH has been calculated for the adsorption processes, according to equation (4)⁽¹²⁾, via plotting logarithmic value of the maximum adsorption quantity at equilibrium concentration as ($\ln Q_{e \max}$) against the inverse of absolute temperature as ($1/T$). The results are shown in figure (7):

**Figure (7): Plots of $\ln Q_{e \max}$ against $1/T$ for adsorption of compound (MO and MV) on the adsorbent of the surface.**

$$\ln \frac{Q_{e \max}}{C_{e \max}} = -\frac{\Delta H}{RT} + \text{constant} \dots (4)$$

The Gibbs free energy ΔG for adsorption is associated with equilibrium constant K_{eq} according to the following equation:

$$\Delta G = -RT \ln K_{eq} \dots (5)$$

Since

$$\frac{Q_e}{C_e} = K_{eq} \dots (6)$$

So equilibrium become:

$$\Delta G = -RT \ln \frac{Q_e}{C_e} \dots (7)$$

ΔS have been calculated from Gibbs relationship:

$$\Delta G = \Delta H - T\Delta S \dots (8)$$

Table (4) illustrate the values of thermodynamic functions of compounds on the surface of polymer. From the value of ΔH for these compounds we noticed that adsorption is exothermic for compounds, since the quantity of adsorption decreases as the temperature increases. From the value of ΔG we noticed that the adsorption processes for two compounds were thermodynamically favored or adsorption process is spontaneous. From ΔS value we noticed that the order of (MV) molecules increases much highly when they transfer from solution into the surface of the polymer and arranged randomly on the surface. But for (MO) molecules it appears to be less disorder than that of (MV), when (MO) molecules transfer from solution into the surface of the polymer. The freedom for the (MO) molecules is less than that of (MV).

Table (4): thermodynamic function values for adsorption compound (MO and MV) on the surface of polymer.

Compound	ΔH KJ/mol	ΔG KJ/mol	ΔS J/mol
MO	-16.73151	-13.88765	+41
MV	-11.21943	-21.085	+33.10933

Effect of Ionic Strength :

Ionic strength affects the activity coefficients of OH^- , H_3O^+ and specifically the adsorbable dyes ions. The figure (8) exhibits that the adsorption isotherm for (MO) compound follows the S_3 -mode in a solution free salt, while in solution of 0.1 M NaCl, the mode change to L_3 -mode accompanied with slight increase in adsorption quantity. The increment in adsorption appears at high equilibrium concentration of (MO) (higher than 20 ppm), but at a lower than 20 ppm, there is no big difference in adsorption quantity. The change the mode to L_3 indicate that the adsorption on the polymer surface is homogenous, while at increases due to the formation of sodium ions on the third layer leading to decrease the electrostatic repulsion between (MO) and surface of polymer. At 0.2 M NaCl solution, the mode of adsorption change from L_3 to S_2 with decrease in adsorption reveals that the first and second adsorption layers at 0.2 M NaCl are equivalent in shape to that curves of L_1 to L_2 at 0.1 M NaCl and equivalent to S_1 and S_2 as well as solution free of salts the unoccupied sites of adsorption retain unchanged of concentrations lower than 20 ppm and have a high affinity to be saturated by adsorbing (MO) molecules at different ionic strength with a change in mode between L to S, may be due to a changed in regularity or homogeneous of these sites in different solutions of different ionic strength. In solution of 0.2M NaCl there is competition between the factors decreasing adsorption quantity (solubility) with those increasing factors (electrostatic double layer)^(13,14).

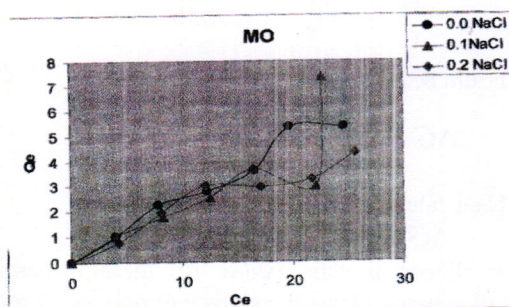


Figure (8): The effected of ionic strength on the adsorption isotherm of compound (MO).

From the figure (9) it seems that (MV) compound follows the S_3 -mode in salt free solution, but in solution of 0.1 m NaCl it is large, but to a lower extent than in salt free solution. This could be due to the increase in solubility of (MV) as the ionic strength increases, the adsorption mode change from S_3 to L_2 -mode by the presence of salt in solution indicates that the adsorption of (MV) is homogenous on the surface of polymer by adsorption of some of these salts which occurred with out swelling the polymer. This mechanism inhibits the formation of second layer inside pores and outer surface of the polymer. The decline in curve for both solutions (0.1 and 0.2 M) NaCl is nearly similar, through there is a change from L_2 to S_2 . However, that indicates the change of polymer surface from homogenous for (MV) compound to non-homogenous surface. The factor that influence on the adsorption as; electrostatic double layer, ionic strength and common ion effect are kept normal.

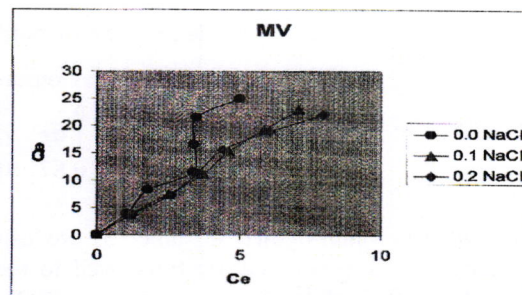


Figure (9): The effect of ionic strength on the adsorption isotherm of compound (MV).

Effect of pH:

The adsorption isotherms at various pH are shown in figures (10) and (11). It is seen that the presence of polymer in a weak acidic medium may reduce the swelling of the polymer in this medium. This leads to a decrease in surface area and plugging the pores of the polymer. These explain show why adsorption absence of absorption processes. On the other hand at pH=8 we observed an increment in adsorption quantity.

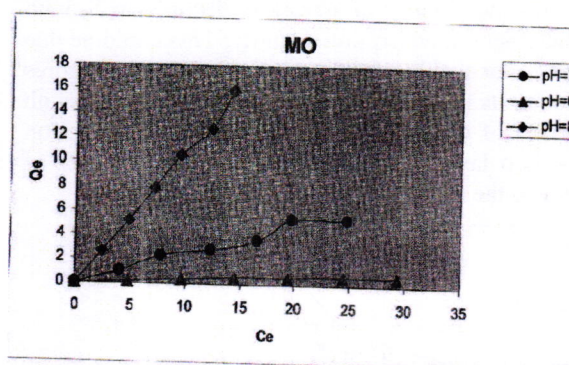


Figure (10): The effect of pH on the adsorption isotherm of compound (MO).

From the figure (10) exhibit that the mode is change to form S_3 -mode at pH=7 to L_2 -mode at pH=6, through it could be considered as L_1 -mode because the formation layer at $Q_e = 0.7$ ppm is more stable than that formed at $Q_e = 0.4$ ppm. And the figure (11) shown that the general adsorption isotherm is the S_2 -mode.

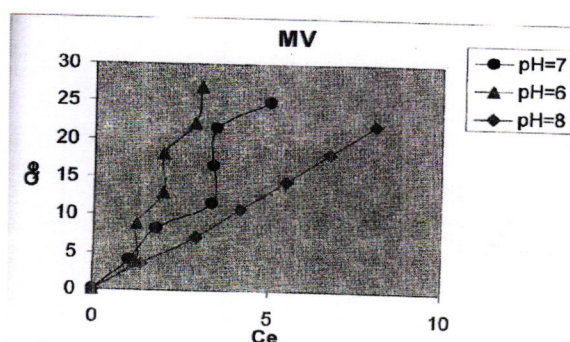


Figure (11): The effect of pH on the adsorption isotherm of compound (MV).

Comparison between adsorption on the polymer (Triethanolglycerolmalate) with that on Zeolite 5A :

The adsorption isotherm of (MO) compound on the surface of the Zeolite is followed L-mode, while it is of S-mode on the surface of polymer as shown in figure

(12). The adsorption quantity of (MO) is much higher on the molecules diffuses of pores during swelling of the polymer, the diffusion can not take place in case of Zeolite, because of the negative charge being centered in Zeolite lattice which leads to repulsion between (MO) and Zeolite much more higher than that of (MO) with the polymer.

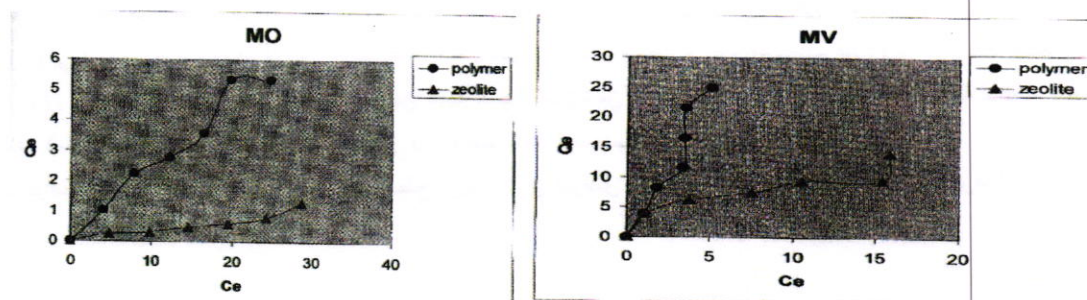


Figure (12): The adsorption isotherms on the polymer and Zeolite for (MO and MV).

Conclusions

- 1- At temperature of 25°C :
- a- the adsorption mode was S for (MO) and (MV).
- b- the adsorption quantities followed the following order MV>MO.

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دراسة امتزاز صبغتي المثل البرتقالي والمثل البنفسجي على سطح البوليمر (تراي ايثانول أمين كليسيروول ماليت)

عماد طه بكر التكريتي ، غسان سعدون داود ، نهى يحيى العتابي

قسم الكيمياء ، كلية العلوم، جامعة تكريت ، تكريت ، العراق

الملخص

تم دراسة امتزاز صبغتي المثل البرتقالي (MO) والمثل البنفسجي (MV) في المحاليل المائية وعلى سطح البوليمر (تراي ايثانول أمين كليسيروول ماليت) . وفي درجات حرارة وشدة أيونية وحامضية مختلفة . أظهرت النتائج إن امتزاز هذه الصبغات عند (25 ° م) تأخذ النمط (S) حسب تصنيف Giles . وإن كمية المادة الممتزة من (MO) اكبر من كمية المادة الممتزة من (MV) في حين إن تأثير الشدة الايونية لم يظهر اختلاف ملحوظ في كمية المادة الممتزة. كما بينت النتائج إن كمية الامتزاز ترتبط بقيم الدالة الحامضية. أوضحت دراسة مقارنة لامتزاز تلك المركبات على سطح الزيولايت إن البوليمر ذو قابلية أعلى لامتزاز المركبات قيد الدراسة .