Study the Effects Influencing the Adsorption of Toluidine Blue O (TBO) Dye onto MnO₂ Surface

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Abstract

The research included study the adsorption of toluidine blue O (TBO) dye on the surface of MnO_2 which was used as a catalyst in several reactions especially photo reactions. Many of parameters were studied which affect the a adsorption process such as: weight of MnO_2,equilibrium time,effect of pH and the type of adsorbent. MnO_2 was used as a model adsorbent in the experiments. These experiments were done under room temperature and showed that the optimum wight of MnO_2 was (0.6 g),equilibrium time was (90 min.) while the best adsorbent was MnO_2/ZnO. Also the experiments showed that the (pH=8) was the best medium of the adsorption process while negative effects- due to acidic and basic media- were observed in the adsorption process. Adsorption isotherms and their applications were also studied such as Freundlich and Langmuir isotherms.

دراسة العوامل المؤثرة على أمتزاز صبغة تولويدين بلو O (TBO) على سطحMnO₂

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الخلاصة

تضمن البحث دراسة امتزاز صبغة تولويدين بلو O (TBO) على سطح MnO₂ والذي استخدم كعامل مساعد في بعض التفاعلات وخصوصا التفاعلات الضوئية.درست العديد من المحددات التي تؤثر على عملية الامتزاز مثل: وزن MnO₂ وزمن الاتزان وتأثير الـpH ونوع المادة المازه.وقد استخدم MnO₂ كمادة مازه نموذجية في التجارب. واجريت هذه التجارب عند درجة حرارة الغرفة وقد اظهرت بان الوزن الامثل للـMnO₂ كان (o.6g) وزمن الاتزان (.90min) بينما كان MnO₂/ZnOهو افضل مادة مازة.كذلك أظهرت النتائج بان الـpH الطبيعي (pH=8) هو افضل وسط لعملية الامتزاز في حين لوحظت تأثيرات سلبية بسبب الأوساط الحامضية والقاعدية في عملية الامتزاز.كما درست ايزوثيرمات الامتزاز وتطبيقتلنها المختلفة مثل ايزوثيرمات فرندلج ولانكماير.

1.Introduction

Adsorption technique used to achieve many of separation methods especially those which cannot be done by the known classical methods such as distillation and absorption methods [1]. The most important applications of adsorption are the purification and treatment of water especially that used in industrial processes [2].

Adsorption can be classified into two types: physical adsorption which made from the secondary attraction forces such as dipole-dipole and induced dipole which like the condensation of vapour molecules on the liquid surface from the same composition [3,4]. The second type of adsorption is chemical adsorption which containes electronic exchange between the adsorbent and adsorbate [5].

Natural dyes can be defined as coloured materials yielding from natural sources of plants or animals [6,7]. While industrial dyes are prepared using two main sources such as charcoal and petroleum [8]. Toluidine blue O (TBO) is a cationic thiazine dye of the phenothiazine family that has been shown, upon light activation, to eradicate various microbial agents in vitro [9-13]. TBO used as electron accepter probe for the pulmonary endothelium in intact lungs [14]. TBO also used to differentiate DNA from RNA by titration of fixative- treated nucleic acids against TBO in solution indicated a greater difference in conformation between DNA and RNA protein in acrolein-polyester sections than between acrolein-treated free DNA in solution [15].

Porphyromonas gingivalis is one of the major causative organisms of periodontitis and has been shown to be susceptible to toluidine blue mediated photosensitization in vitro[16]. TBO used as on adjunct in the diagnosis of epidermoid cancer of the oral eavity[17-20]. The adsorption of cationic dye TBO on to fly ash has been studied from aqueous solution, in the presence of cationic surfactant cetyl phridinium chloride (CPC) and anionic surfactant sodium dodecyl sulfate (SDS) at three different temperatures[21].

The relation between the amount of the adsorbate on acertain surface and the concentration of its at a constant temperature called adsorption isotherm [22]. Adsorption isotherm classified by many models, the main two models are Brunauer model which is classify the adsorption isotherms into five types[23]. The second is Giles model which is classify the adsorption isotherms into four types (S,L,H,C) [24].

2.Experimental

2.1.Materials and measurements

Distilled water was used as a solvent in all experiments. Zinc oxide was obtained from Merk, titanium dioxide was obtained from Degaussa, manganese dioxide was obtained from East Anglia Chemicals, aluminum oxide was obtained from BDH, copper (1) oxide was obtained from Philip Harris,Shentone and toluidine blue O (TBO) was obtained from Em Scope Laboratories Ltd. Electronic spectrum was made using Shimadzu 20 Uv- vis. 1650 Spectrophotometer, while absorption measurements were obtained with TRSP-721,Triup Intenational Corp. Spectrophotometer.

The adsorption of the dye was done using SK-300, Lab. Companion Shaker the samples were centrifuged by 80-1 Table Top Law Speed Centrifuge Truip International Corp.(120 cycle/min.) and pH$_s$ of the solutions were measured using Microprocessor pH Meter, pH-211.

2.2. Preparation of the metal oxides

All the metal oxides (MnO$_2$/ZnO,MnO$_2$/TiO$_2$,MnO$_2$/Cu$_2$O,MnO$_2$/Al$_2$O$_3$) were prepared according to the comixing method[25] .The preparation method was done using (0.06g) from each metal oxide with (0.6g) from MnO$_2$ followed by contineous stirring in water.Then these metal oxides were dried at 110 C$^{\circ}$,after this process they were calcinated at 350 C$^{\circ}$through2 hrs.

2.3. Kinetie study

It was found that the weight of the adsorbent (MnO$_2$)-lead to the equilibrium state- was (0.6g) in the use of different weights of the adsorbent (0.10- 0.70g) and in fixed concentration of the dye at room temperature.After the determination of the optimum weight of the adsorption process, a kinetic study was done to reach the equilibrium state and to the extent the time necessary for the equilibrium which had no effect on the quantity of the adsorbent because of the saturation of the adsorbent as follow:

2.3.1. Calibration curve:

Stock solution was prepared from the dye in concentration (305.83 mg.L^{-1}) through the dissolving of certain weight of the dye in water as a solvent. Then a group of solutions which have known concentrations in the range (30.58-0.31 mg.L^{-1}) were prepared and their absorbances were measured at λ_{max} = 664nm and at pH= 8. when the values of the absorbances plotted against the values of the concentrations, it was found that these concentrations obey Lambert-Beer law, while the high and low concentrations were excluded (table 1 and fig.1).

Tabel 1
Values of calibration curve of TBO.

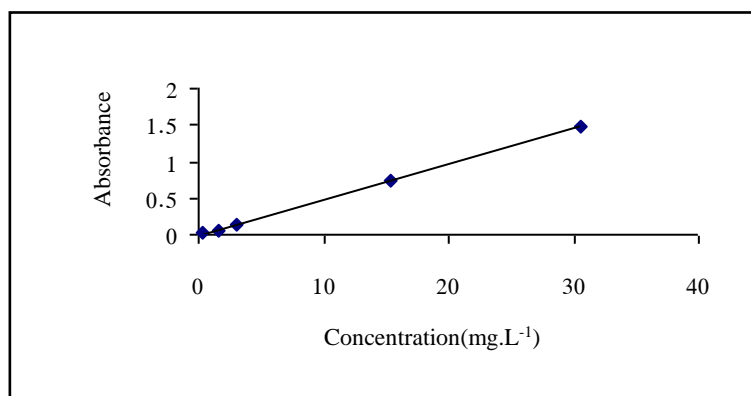| Absorbance	Concentration (mg.L^{-1})
1.484	30.58
0.744	15.29
0.146	3.06
0.055	1.59
0.017	0.31

Fig.1.Calibration curve of TBO.

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2.3.2.Eight solutions for the dye of the same concentrations (20.429 mg.L^{-1}) were put in the conical flasks (50 ml capacity). In each solution (0.6g) of MnO$_2$ was added, then the solutions were put in the shaker and their absorbances were measured at different times in the range (15-120 min). It was found that the equilibrium time of MnO$_2$ and of the reach of adsorption to the equilibrium state was (90 min).

2.4. Effect of the pH

Adsorption of the dye in different media of pH was studied and they are: (pH=6,8,10,12).

2.4.1.The adsorption at pH= 8:

The adsorption at the natural pH of the dye (pH=8) was studied using four concentrations (13.70,18.04,21.41,24.46 mg.L^{-1}).For each concentration, (0.6g) of MnO$_2$ was added with shake for (90min). Then the absorbance was taken after the adsorption in each concentration.

2.4.2.The adsorption at pH= 6,10,12:

The step no. (1) was repeated to study the adsorption at different values of pH(6,10, 12). It was found that the best value of pH in the adsorption process was at (pH= 8) which is the natural pH of the dye.

2.5. Effect of the type of the adsorbent

A number of adsorbents were used: MnO_2/TiO_2, MnO_2/Cu_2O, MnO_2/Al_2O_3 and MnO_2/ZnO to study their effects on the adsorption process using the same initial concentration of the dye with adding of (0.6g) from the adsorbent in each concentration with shake for (90min). Then the absorbance was measured and it was found that the best adsorbent was MnO_2/ZnO at pH = 8 at room temperature.

3.Results and discussion

3.1. Electronic spectrum of the dye

The dye (TBO) (fig.2) was used with out purification.A(1.59 $mg.L^{-1}$) of the dye was prepared at pH= 8 and in the room temperature by dissolving a certain weight of the dye in the distilled water as a solvent. The electronic spectrum of the dye showed a three main absorption bands: 664 nm, 524nm, 356nm. The band at (664nm) was used as aquide or reference band to measure the absorbance of the samples in all experiments (fig.3).
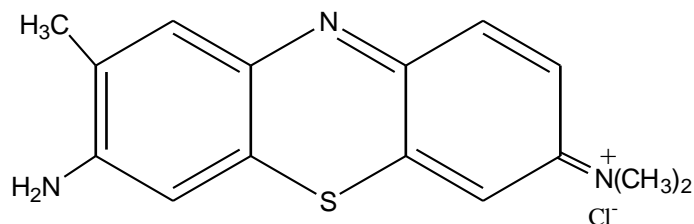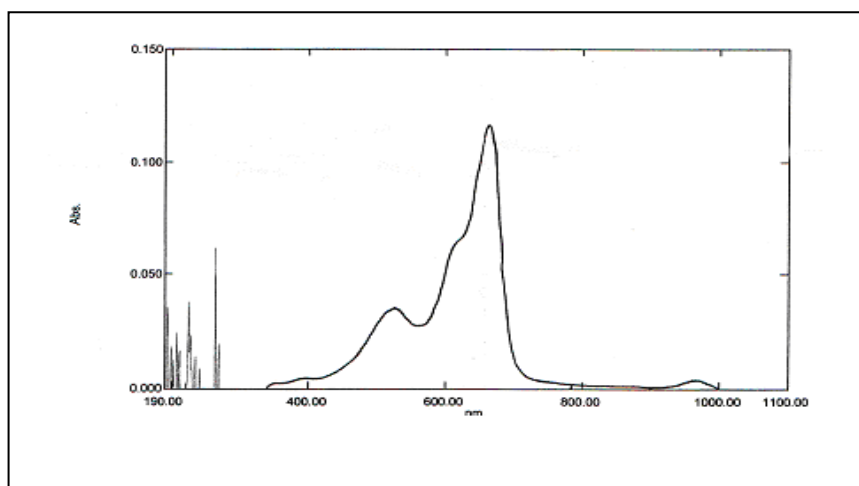
Fig.2.Structural formula of TBO.

Fig.3.Electronic spectrum of TBO.

3.2. Effect of the weight of MnO_2

The effect of the weight of the MnO_2 on the adsorption process was studied using a group of weights in the range (0.10- 0.70g) at pH =8 at room temperature. MnO_2 was used as amodel adsorbent for the later experiments. It was found that the free concentration (concentration at equilibrium state) decreased with increasing of the weight of MnO_2 until it reached to fixed concentration at (0.6g) of MnO_2 (table 2 and fig. 4). This means any increase in the weight of adsorbent had no effect, because of the perfect saturation of active centers of adsorbent by dye molecules.

Tabel 2
Effect of the weight of adsorbent.

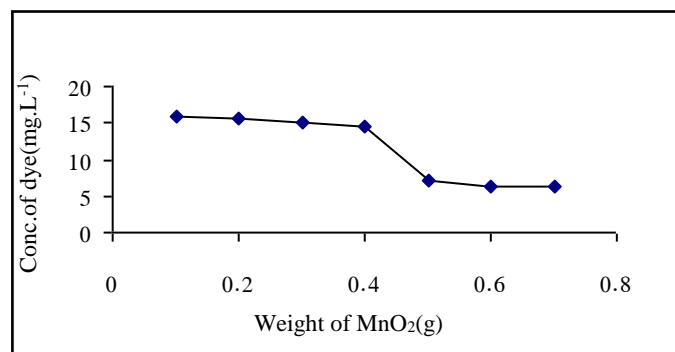| Concentration (mg.L^{-1})	Weight (g)
16.02	0.1
15.68	0.2
15.00	0.3
14.4	0.4
7.08	0.5
6.36	0.6
6.36	0.7

Fig.4.Relation between the free conc. of TBO and weight of adsorbent.

3.3.Equilibrium time

Kinetic study was done to test the required time for the dye adsorption in order to reach the equilibrium state. The study was done using different periods of the time in the range (15-120min.) with 0.6g of MnO_2 at pH =8 at room temperature. It was noticed that there was decrease in the free concentration of the dye with increase of the time of adsorption. This decrease contiues gradually till it fixed when it passed 90 min. of adsorption process. This time represented the time at which the dye reached the equilibrium state (table 3 and fig. 5).

Tabel 3
Effect of equilibrium time on free conc. of TBO.

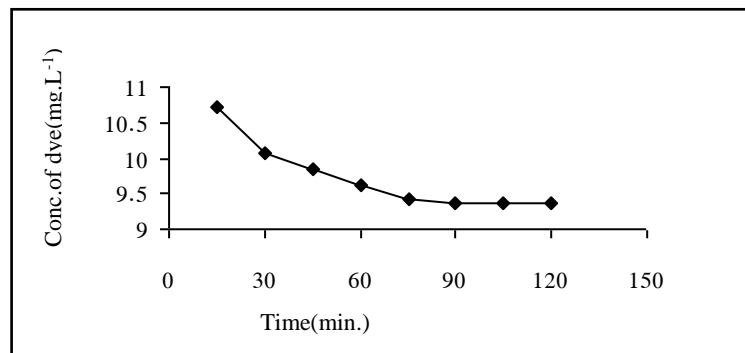| Concentration (mg.L^{-1})	Time (min.)
10.71	15
10.07	30
9.85	45
9.62	60
9.42	75
9.38	90
9.36	105
9.36	120

Fig.5.Relation between the free conc. of TBO and equilibrium time.

3.4.Effect of pH

The nature of medium had an effect on the ability of adsorption of different compounds that adsorbe in. The effect of medium was studied at different pH$_s$for the adsorption of dye. It was studied in the natural pH of the dye (pH= 8) and in (pH= 6,10,12) using 0.6g of MnO$_2$ and four initial concentrations of dye that were (13.70, 18.04, 21.41, 24.47 mg.L^{-1}) with continuous stirring of the solutions in the shaker for 90min. .

The results showed that the best pH of the adsorption of the dye was the natural pH at which the quantity of adsorbed dye possessed a highest value (atpH= 8) which equal to (0.44 mg.g^{-1}) in comparison with other pH$_s$. It was noticed that the increasing in the acidic and basic media lead to decrease of adsorbed quantity onto the surface of MnO$_2$ (table 4 and fig.6).Because in acidic media,the hydrogen bonding formed lead to removal of conjugation of double bonds in the rings of TBO molecule while in basic media an decreasing in the electronic charge density or formation the salts will form.In the two cases,an decreasing in the concentraion of TBO will produce therefore the adsorbed quantity of the dye will decreas.

Tabel 4
Values of initial conc.(C_o), free conc.(C_{eq}) and adsorbed quantity(Q_{eq}) of TBO onto surface of MnO_2 at various pHs at room temperature.

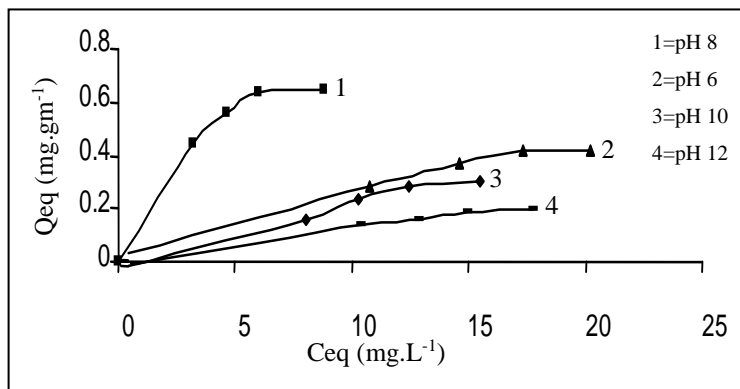| pH	$C_o(mg.L^{-1})$	$C_{eq}(mg.L^{-1})$	$Q_{eq}(mg.g^{-1})$
8	13.70	3.20	0.44
	18.04	4.62	0.56
	21.41	6.01	0.64
	24.47	8.82	0.65
6	13.70	10.30	0.25
	18.04	14.20	0.34
	21.41	16.90	0.39
	24.47	19.80	0.39
10	13.70	7.61	0.17
	18.04	9.83	0.25
	21.41	12.00	0.30
	24.47	15.10	0.32
12	13.70	9.52	0.14
	18.04	12.00	0.16
	21.41	14.10	0.19
	24.47	16.90	0.20

Fig.6.Adsorption isotherms of TBO at various pHs at room temperature.

3.5.Surface study

One of the surface properties of metal oxides described was the apparant porosity which determined according to literature[28].The apparant porosity experiments showed that MnO_2/ZnO and MnO_2/TiO_2 possessed porosity (51.55%,37.14%) respectively as shown in table 5.

Table 5

Apparant porosity of adsorbents

Adsorbent	Apparant porosity (%)
MnO_2/ZnO	51.55
MnO_2/Al_2O_3	46.34
MnO_2/Cu_2O	40.43
MnO_2/TiO_2	37.14

3.6.Effect of the nature of adsorbent

The ability of adsorption of dye was greatly effected by the change in the kind of adsorbent, and this effect was studied using 0.6g from a group of adsorbents (MnO_2/Al_2O_3, MnO_2/Cu_2O, MnO_2/TiO_2 and MnO_2/ZnO) at pH=8 at room temperature with continuous stirring for 90min.

The results showed that the best adsorbent was MnO_2/ZnO at which the highest adsorption for dye happened due to the high quantity of adsorbed dye in comparison with other adsorbents where the value of Q_{eq} was $0.54mg.g^{-1}$ in MnO_2/ZnO while Q_{eq} was $0.12mg.g^{-1}$in MnO_2/TiO_2. This indicated that the nature and the kind of the adsorbent had a great effect on the adsorption process of the dye (table 6 and fig.7).The order of the adsorbents can be expressed according to thier porosities where MnO_2/ZnO had a high porosity while MnO_2/TiO_2 had a low porosity (table5), thefore the adsorbed quantity of the dye will be large by using MnO_2/ZnO as adsorbent in comparision with MnO_2/TiO_2.

Tabel 6
Values of initial conc.(C_o),free conc.(C_{eq})and adsorbed quantity(Q_{eq}) of TBO at various adsorbents at room temperature(pH=8).

Adsorbent	C_o(mg.L^{-1})	C_{eq}(mg.L^{-1})	Q_{eq}(mg.g^{-1})
MnO$_2$/ZnO	13.70	0.99	0.53
	18.04	4.84	0.55
	21.41	8.64	0.53
	24.47	11.60	0.54
MnO$_2$/Al$_2$O$_3$	13.70	10.60	0.24
	18.04	14.60	0.25
	21.41	18.20	0.26
	24.47	21.60	0.26
MnO$_2$/Cu$_2$O	13.70	9.58	0.17
	18.04	13.50	0.19
	21.41	17.00	0.18
	24.47	20.6	0.16
MnO$_2$/TiO$_2$	13.70	7.94	0.13
	18.04	12.00	0.14
	21.41	15.10	0.13
	24.47	18.30	0.12
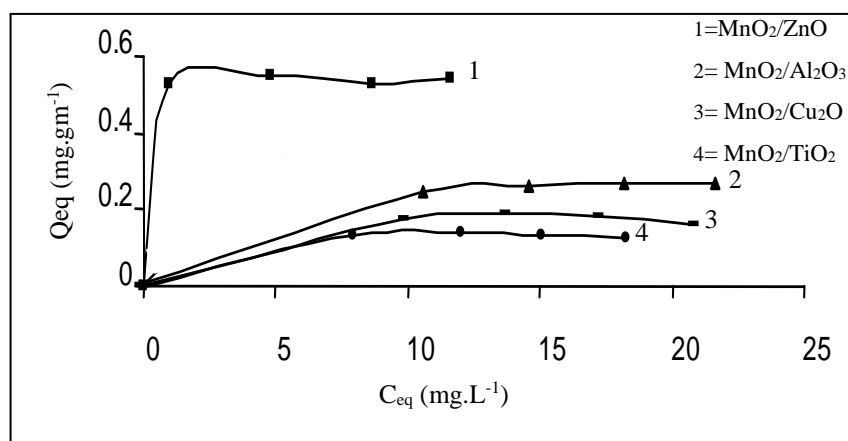
Fig.7.Adsorption isotherms of TBO using different adsorbents at pH=8 at room temperature.

3.7.Application of isotherm equations on the adsorption

Adsorption isotherms used to dascribe the relation between the adsorbate and the surface of the adsorbent. In this reseach two models of these isotherms: Freaundlich model and Langmuir model were used to describe the relation between the dye and the surface of adsorbent. These models can be represented by the following two equations:

Freundlich isotherm:

$$\text{Log } q_{eq} = \log k + 1/n \log C_{eq}$$

Langmuir isotherm:

$$C_{eq}/ q_{eq} = 1/b + C_{eq}/Q$$

Where (b) represents a Langmuir constant which has a relation with the energy of adsorption and (C_{eq}) is the concentration of the dye that dose not adsorbed- concentration of the dye in the equilibrium state (mg.L^{-1}). While (q_{eq}) represents the quantity of the adsorbed dy (mg.g^{-1}), Q represents the maximum capacity of adsorption (mg.g^{-1}) and (k) is Freundlich constant [26].

3.7.1.Adsorption states at various pH$_s$

1- The data showed linear relations in the application of Freundlich model (fig.8-11). These a good results which were affirmed by the values of the correlation factors (R^2).
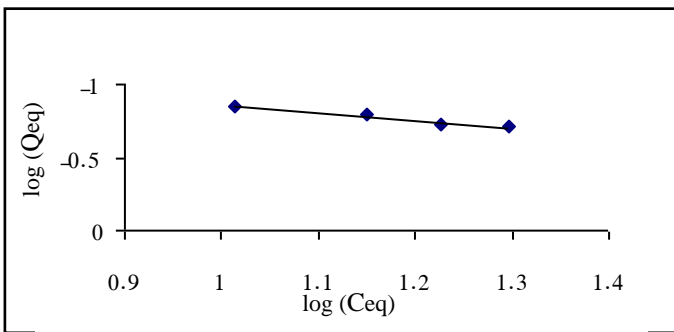
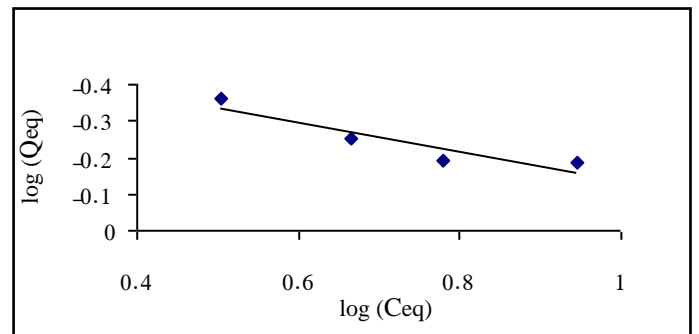**Fig.9. Freundlich isotherm of TBO at pH=6.**

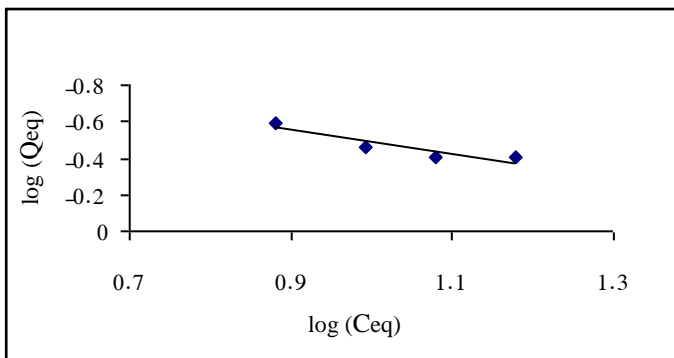**Fig.8. Freundlich isotherm of TBO at pH=8.**
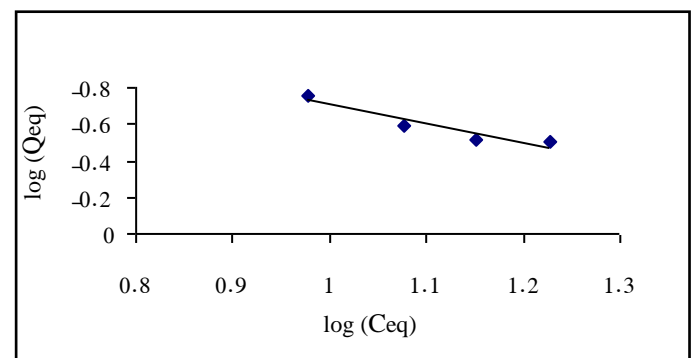

Fig.11. Freundlich isotherm of TBO at pH=10.

Fig.10. Freundlich isotherm of TBO at pH=12.

2- The values of Freundlich constants (n)-produced from the slope-and the values of (k)-produced from the intercept- were decreased (table 8) which are taken from the (table 7) in the high acid and basic media. The highest value of (n) and (k) was at pH= 8.

Tabel 7

Values of $Log(C_{eq})$ and $Log(Q_{eq})$ of TBO adsorbed onto MnO_2 surface at various pHs at room temperature.

pH	$Log(C_{eq})$	$Log(Q_{eq})$
8	0.51	-0.36
	0.66	-0.25
	0.78	-0.19
	0.95	-0.19
6	1.01	-0.85
	1.15	-0.79
	1.23	-0.72
	1.30	-0.71
10	0.88	-0.60
	0.99	-0.47
	1.08	-0.41
	1.18	-0.41
12	0.98	-0.76
	1.08	-0.60
	1.15	-0.52
	1.23	-0.50

Tabel 8

Values of Freundlich constants (n) and (k) and correlation factors (R^2) at various pHs at room temperature.

pH	R^2	k	n
8	0.8572	0.290	2.50
6	0.9663	0.040	1.88
10	0.8419	0.074	1.55
12	0.9079	0.017	0.95

3- The data showed a relatively good results due to somehow linear relations in the application of Langmuir model (fig.12-15) and these results were affirmed by the values of the correlation factors (R^2).
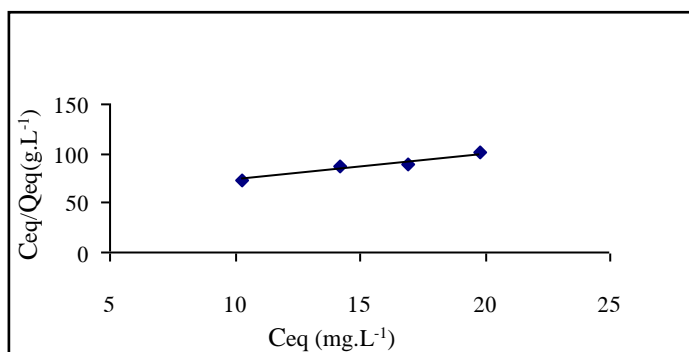

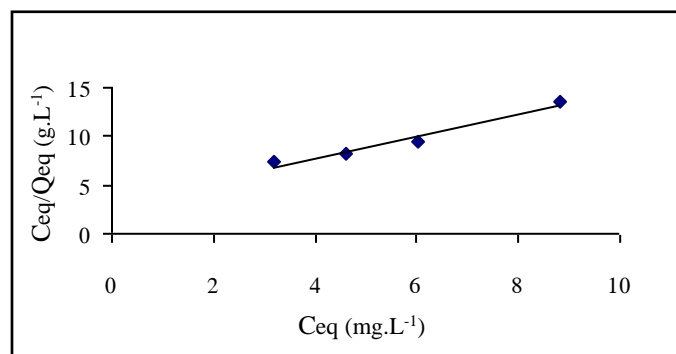**Fig.13. Langmuir isotherm of TBO at pH=6.**
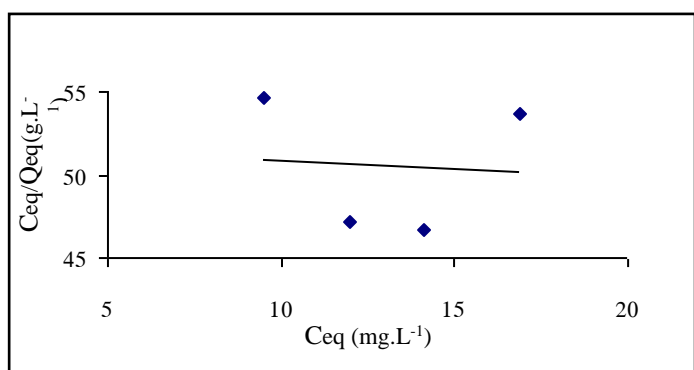

Fig.12. Langmuir isotherm of TBO at pH=8.

Fig.15. Langmuir isotherm of TBO at pH=12.

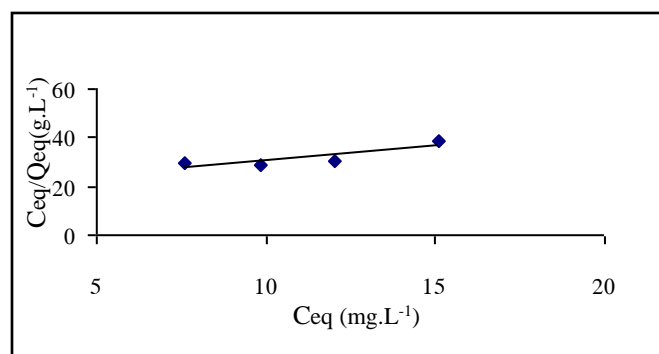

Fig.14. Langmuir isotherm of TBO at pH=10.

4- The values of Langmuir constant (b) and (Q) (table 10)were decreased in the high acidic and basic media and these data were obtained from the table 9. The values of (b) and (Q) were (0.340, 0.895mg.g^{-1}) respectively at pH= 8 wherase they were (0.059, 0.365mg.g^{-1}) respectively at pH= 6.

Tabel 9

Values of Log(C$_{eq}$) and Log(Q$_{eq}$) of TBO adsorbed onto MnO$_2$ surface at various pHs at room temperature.

pH	Log(C$_{eq}$)	Log(Q$_{eq}$)
8	7.32	3.20
	8.25	4.62
	9.37	6.01
	13.5	8.82
6	73.3	10.30
	87.4	14.20
	89.1	16.90
	101	19.80
10	30	7.61
	28.7	9.83
	30.7	12.00
	38.6	15.10
12	54.6	9.52
	47.2	12.00
	46.7	14.10
	53.7	16.90

Tabel 10

Values of Langmuir constants (b) and (Q) and correlation factors (R^2) at various pHs at room temperature.

pH	R^2	Q	b
8	0.9651	0.895	0.340
6	0.9542	0.365	0.059
10	0.7201	0.840	0.053
12	0.0047	10.940	0.002

3.7.2.Adsorption states at various adsorbents

1- In the application of Freundlich model,the results were passive according to non linear
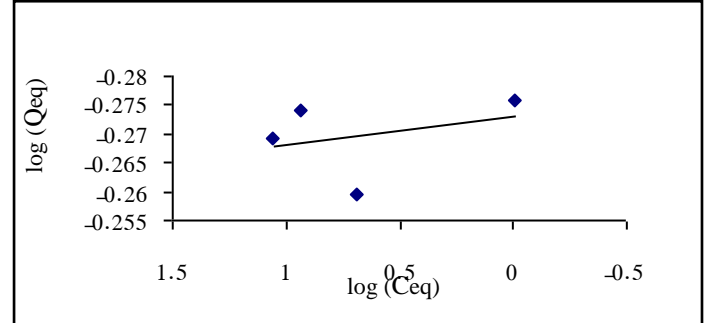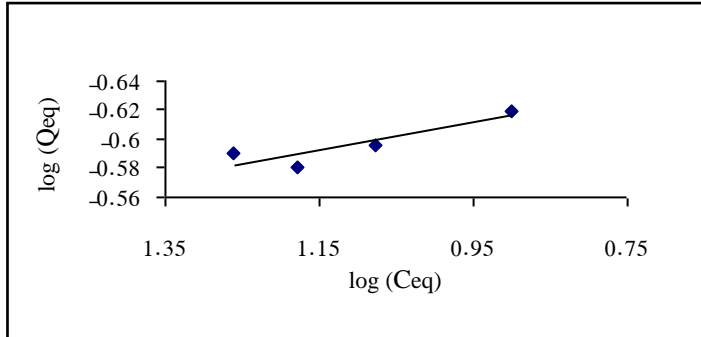   relations (fig.16-19) which were affirmed with correlation factors (R^2).

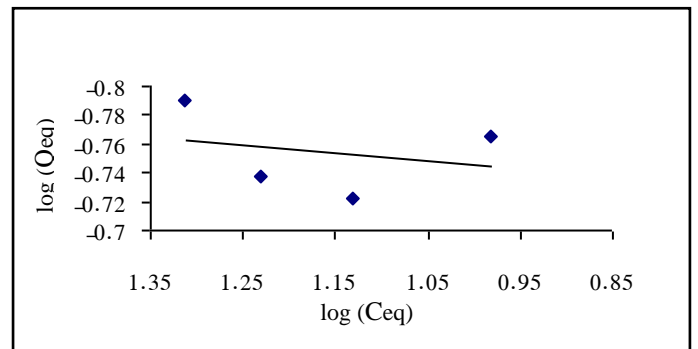**Fig.17. Freundlich isotherm of TBO with MnO_2/Al_2O_3.** **Fig.16. Freundlich isotherm of TBO with MnO_2/ZnO.**
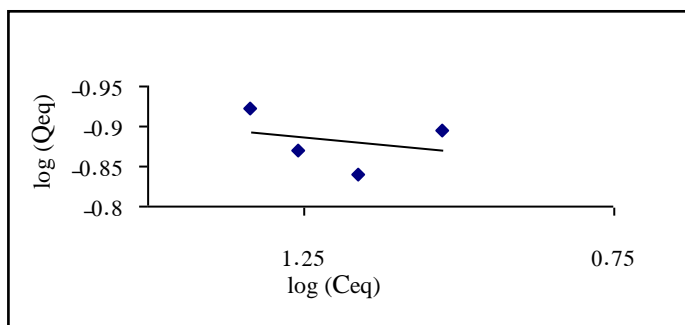

Fig.19. Freundlich isotherm of TBO with MnO_2/TiO_2. **Fig.18. Freundlich isotherm of TBO with MnO_2/Cu_2O.**

2- Generally there were decrease in Freundlich constants (k, n) (table 12) which were obtained
   from the table 11using the following adsorbents according to the order below:

MnO_2/ZnO, MnO_2/TiO_2, MnO_2/Cu_2O, MnO_2/Al_2O_3

$\longrightarrow$

generally decrease (k,n)

The highest value of (k,n) was obtained by the use of the MnO_2/ZnO as adsorbent which were
(0.53, 200) respectively.

Tabel 11

Values of Log(C$_{eq}$) and Log(Q$_{eq}$) of TBO adsorbed onto MnO$_2$ surface at various pHs at room temperature.

Adsorbent	Log(C$_{eq}$)	Log(Q$_{eq}$)
MnO$_2$/ZnO	-0.01	-0.28
	0.69	-0.26
	0.94	-0.27
	1.06	-0.27
MnO$_2$/TiO$_2$	1.03	-0.90
	1.16	-0.84
	1.26	-0.87
	1.33	-0.92
MnO$_2$/Cu$_2$O	0.98	-0.77
	1.13	-0.72
	1.23	-0.74
	1.31	-0.79
MnO$_2$/Al$_2$O$_3$	0.90	-0.62
	1.08	-0.60
	1.18	-0.58
	1.26	-0.59

Tabel 12

Values of Freundlich constants (n) and (k) and correlation factors (R^2) at various adsorbents at room temperature.

Adsorbent	R^2	k	n
MnO$_2$/ZnO	0.1061	0.530	200
MnO$_2$/TiO$_2$	0.0856	0.160	12.61
MnO$_2$/Cu$_2$O	0.0648	0.200	18.62
MnO$_2$/Al$_2$O$_3$	0.7830	0.198	10.56

3- very good linear relations were appeared in the application of Langmuir model (fig.20-23) were affirmed by the values of correlation factors (R^2).
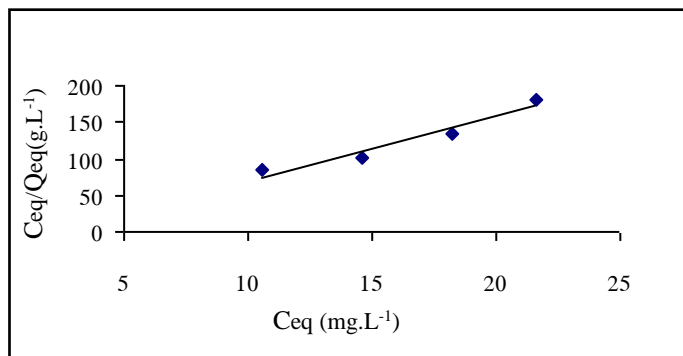

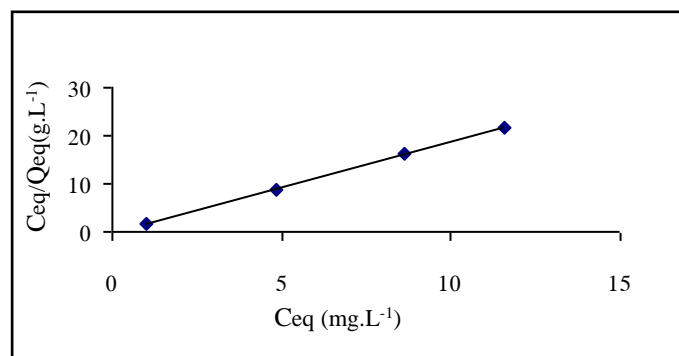**Fig.21. Langmuir isotherm of TBO with MnO₂/Al₂O₃.**

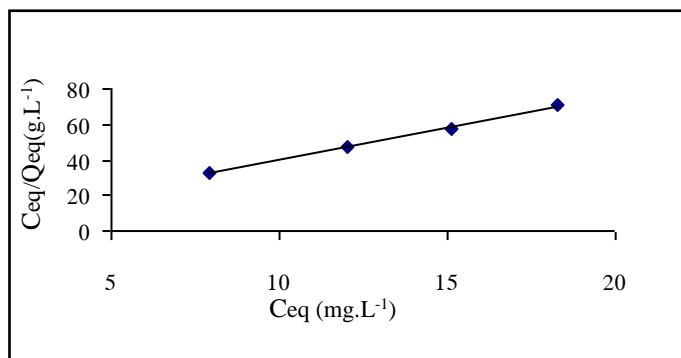**Fig.20. Langmuir isotherm of TBO with MnO₂/ZnO.**

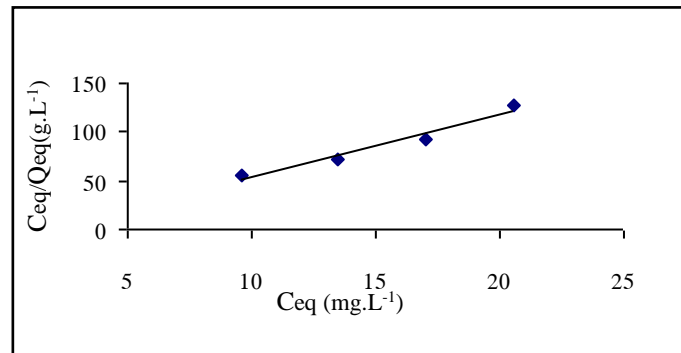**Fig.23. Langmuir isotherm of TBO with MnO₂/TiO₂.**

Fig.22. Langmuir isotherm of TBO with MnO₂/Cu₂O.

4- The values of (Q, b) (table14) were decreased which produced by the table13 . (Q) and (b) had alargest values (0.52, 48.99) respectively using MnO_2/ZnO as adsorbent while they became (0.11, 0.50) respectively using MnO_2/Al_2O_3 as adsorbent.

Tabel 13

Values of (Ceq) and (Ceq /Qeq) of TBO adsorbed at various adsorbents at room temperature (pH=8).

Adsorbent	Ceq/ Qeq $(g.L^{-1})$	Ceq $(mg.L^{-1})$
MnO_2/ZnO	1.86	0.99
	8.80	4.84
	16.20	8.64
	21.50	11.60
MnO_2/TiO_2	33.10	7.94
	47.20	12.00
	57.50	15.10
	71.20	18.30
MnO_2/Cu_2O	55.80	9.58
	71.30	13.50
	92.80	17.00
	127.00	20.6
MnO_2/Al_2O_3	83.70	10.60
	101.00	14.60
	135.00	18.20
	181.00	21.60

Tabel 14

Values of Langmuir constants (b) and (Q) and correlation factors (R^2) at various adsorbents at room temperature.

Adsorbent	R^2	Q	b
MnO_2/ZnO	0.9997	0.54	48.99
MnO_2/TiO_2	0.9969	0.27	0.99
MnO_2/Cu_2O	0.9621	0.16	0.60
MnO_2/Al_2O_3	0.9472	0.11	0.50

In generall, the adsorption of the dye was chemisorptions because the data obey Langmuir model which assumes that the molecules adsorb on fixed number of gaps on the adsorbent surface. These gaps are equivalent in energy and each gap carries one adsorbed molecule and there is no interaction among the molecules or with the molecules of the solution. Consequently, one molecular layer is formed on the adsorbent surface, while Freundlich model assumes that the surface of adsorbent is not homogenous generically [26].

Conclusion

From the experiments, it was found that the range of the dye concentration (0.31- 30.58 mg.L^{-1}) -which is used to determine the calibration curve of the dye- obeyed the Lambert- Beer law, while the high and low concentratios were excluded due to the deviations of the straight line. The best weight of the MnO_2 was (0.6g) at which the adsorbed quantity of the dye was large and reached the equilibrium state. Also, it was found that the equilibrium time of the dye was 90min. and the best pH for the adsorption process was at (pH =8) which was the natural medium of the dye, while the adsorbed quantity of the dye was decreased at the high acidic and basic media. The values of Langmuir and Freundilch constants and the adsorbed quantity, showed that the best adsorbent for the adsorption process of the dye was MnO_2/ZnO.

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