

ADSORPTION STUDY OF RHODAMIN B DYE ON IRAQI BENTONITE AND MODIFIED BENTONITE BY NANOCOMPOUNDS TiO_2 , ZnO , Al_2O_3 AND SODIUM DODECYL SULFATE

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ABSTRACT

The adsorption of Rhodamin B on Iraqi bentonite at the concentration range from 50 to 250 $\mu\text{g mL}^{-1}$ was studied, Nano compounds; ZnO , TiO_2 , Al_2O_3 and SDS in different amounts 0.01-0.1 g 10^{-1} g of Bentonite were used to modified the adsorption capacity of bentonite to remove the Rhodamin B from aqueous solutions. The study indicated that using 0.05 g and 0.1 of Sodium Dodecyl Sulfate (SDS) lead to increase the percentage removal (%R) from 79.3% for pure bentonite to 99.3%. While using 0.05 g TiO_2 lead to increase the %R to 98.9%, 0.05 of ZnO to 98.6%. The other amount additives and Al_2O_3 using was not success to increase the %R for the Rhodamin B on bentonite surface. SEM measurement was achieved to discover the Nanoparticl exists in the bentonite surfaces.

Keywords: Adsorption, Rhodamine B, Dye, Bentonite, Modified Bentonite

1. INTRODUCTION

Textile industry wastewaters cause considerable environmental problem in all world. Particularly, wastewaters containing soluble dyes must be cleaned before they discharge to nature (Gulgonul, 2012; Kareem and Abd-Al-Hussin, 2012; Wang and Zhu, 2007; Errais *et al.*, 2011).

Therefore, textile dyeing processes as well as the chemical content of dyeing components are very important. The dyed wastewaters consist of generally acids, bases, dissolved solid toxic compounds and considerable colore pollutants (Armagan *et al.*, 2004) moreover many dyes are toxic and obstruct catalytic effects and also cause severe damages to the human bodies (Baskaralingam *et al.*, 2006; Ozcan *et al.*, 2007), the discharge of colored wastewater even at very low concentrations from the problems such as increasing toxicity and chemical oxygen demand of the effluent and also reducing light penetration, which has a derogatory

effect on photo synthetic phenomena (Karaoglu *et al.*, 2010; Hameed and Ahmad, 2004).

Rhodamine B has moderate wash and light fastness properties on wool. It's also a useful analytical reagent for the detection and determination of metals. However, the use of rhodamin B as a food color has been discontinued for a number of years on account of its suspected carcinogenic nature (Gupta *et al.*, 2004; Venkataraman, 1971; Sharma *et al.*, 2011; Attia *et al.*, 2008). There are various conventional methods of removing dyes including coagulation and flocculation, oxidation or zonation and membrane separation. However, these methods are not widely due to their high cost and economic disadvantage chemical and electrochemical oxidation coagulation are generally not feasible on large scale industries (Arivoli *et al.*, 2009; Turabik, 2008).

Adsorption is an important method commonly used for cleaning of wastewater for treatment and separation of colorant in industrial processes. Bentonite (Espantaleon *et al.*, 2003; Özcan *et al.*, 2004; Eren and

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Afsin, 2008; Atia *et al.*, 2006; Volzone and Garrido, 2002; Karahan *et al.*, 2006) has been used directly or after modified for remove textile industry dyes from wastewater. Bentonite may be attributed to its high surface area, high chemical and mechanical stability and to a variety of surface and structural ability (Mockovciakova and Orolinova, 2009; Zhao *et al.*, 1998) by surfactants to be efficient in the treatment of various pollutants (Ma *et al.*, 2011).

The aim of this Study is to examine the adsorption mechanism of Rhodamine B dye by using natural and modified bentonite by Sodium Dodecyl Sulfate (SDS), Nano; TiO₂, ZnO and Al₂O₃.

The surfactant, sodium dodecyl sulfate and bentonite was prepared by insertion of SDS between the layers of the bentonite by a simple anionic exchange. Another modification was used in this study involved adding three Nano composite; ZnO, Al₂O₃ and TiO₂ to increase the adsorption bentonite surface area and modified adsorption surface ability and to find out the applicability to textile wastewaters.

The effects of parameters such as solid: dye ratio, contact time, removal percentage %R by bentonite and modified bentonite were investigated.

2. MATERIALS AND METHODS

2.1. Adsorbent

2.1.1. Natural Bentonite

The bentonite clay was supplied from the state company for geological survey and mining-Iraq. The bentonite had the following composition with particle size less than 75 µm:

Constituent	SiO ₂	Al ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	Fe ₂ O ₃	L.O.I
%Wt	56.77	15.67	4.48	3.42	0.60	1.11	5.02	12.49

The molecular formula of bentonite could be written as:



2.1.2. Preparation of the Modified Bentonite

Preparation of modified benonite involves mixing different weight 0.01, 0.05 and 0.1 g of modifier SDS, Nano TiO₂, ZnO and Al₂O₃ with 10 g of natural

bentonite and 100 mL of deionized water. This content was shake about 3 h and then separated and dried.

2.2. Adsorbate

The dye used in this work was Rhodamine B, it was choice in this study because it has a strong adsorption onto solids and also for its high solubility in water. The characteristics and chemical structure of this dye are listed in **Table 1**.

A stock solution of Rhodamin B was prepared by dissolving its 1.0 g in 100 mL distilled water. The stock solution was diluted accordingly to obtain fresh solutions of desired concentrations.

2.3. Batch Kinetics Experiments

Adsorption experiments were carried out batch wise. A specific amount of benotine and modified benotine was added in 250 mL round bottom flasks containing 50 mL of Rhodamine B aqueous solution of desired concentrations 50-250 mg L⁻¹. The bottles were subsequently capped and placed on a mechanical shaker at a speed of 500 rpm at 25°C for intervals time. The resultant solutions were filtered using Millipore membrane filter of 0.2 µm before analyses.

The residual dye concentrations of each solution were determined by measuring their characteristic absorbance using a double beam UV-Vis Spectrophotometer (Shimadzu, UV-160A) at a wavelength 554 nm. The calibration curve at this wavelength was established as a function of Rhodamine B dye concentrations is shown in **Fig. 1**.

The amount of adsorbed Rhodamine B at any time Q_e (mg/g) was calculated using Equation 1:

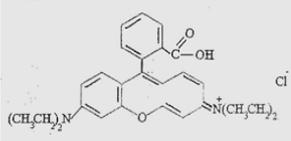
$$q_e = \frac{(C_o - C_t)}{m} \cdot V \quad (1)$$

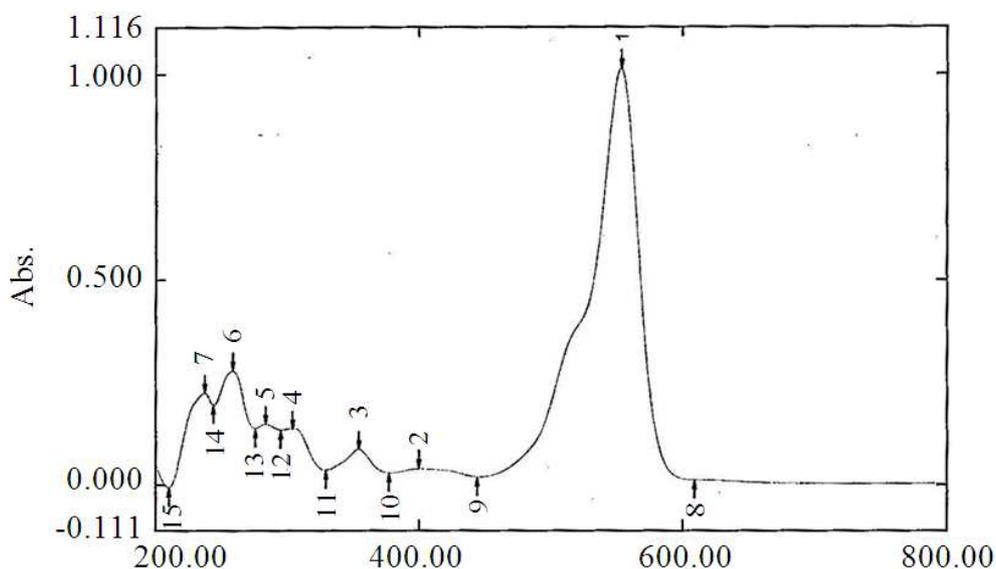
where, C_o and C_t are the initial and liquid-phase concentrations at any time t of dye solution (mg/l), respectively, V is the volume of dye solution (L) and m is the mass (g) of the benotine used.

The removal efficiency, $R(\%)$ of the system, was expressed as Equation 2:

$$\% R_e = \frac{(C_o - C_t)}{C_o} \times 100 \quad (2)$$

Table 1. Physical properties and molecular structure of Rhodamine B (Ding *et al.*, 1999)

Dye name	Rhodamine B
Colorindex number	45170
Chemical formula	C ₂₈ H ₃₁ ClN ₂ O ₃
IUPAC name	[9-(2-carboxy phenyl)-6-diethylamino-3-Xanthenylidene]-diethylammonium Chloride
Molecular weight (g/mol)	479.02
Max wavelength	554 nm
Solubility in water	50 g/L
Molecular structure	

**Fig. 1.** UV-Visible absorption spectrum for Rhodamine B dye with concentration

3. RESULTS AND DISCUSSION

3.1. Effect of Contact Time

Rhodamine B at a wavelength 554 nm attained versus contact time was attained equilibrium at 30 min for natural and modified bentonite at the same conditions. The results also indicated that the amount of retained dye increased with the increase of initial dye concentration. Although the rate behavior of both bentonite and modified bentonite was the same, but has been found that under identical conditions the modified bentonite presented higher adsorption capacity. The rate of adsorbed Rhodamine B onto natural and modified bentonite was initially rapid and then it slowed down

gradually until equilibrium was attained. It would be for that a large number of vacant surface sites were available for adsorption during the initial stage of the treatment time and after elapse of time, less remaining vacant were available (Dhahir, 2007). Increase in the adsorption capacity of modified bentonite may be attributed to many factors; SDS modified, converted the surface of bentonite from hydrophilic to hydrophobic (Al-Khatib *et al.*, 2012) and the Nano, TiO₂ and ZnO of a few nanometers in size are dispersed among the silicate platelets on bentonite clay so that high surface area of TiO₂ and ZnO is available for the adsorption capacity and removal percentage (Jie and Jiafen, 2010; Lien and Zhang, 2002), as illustrate by SEM images in **Fig. 2**.

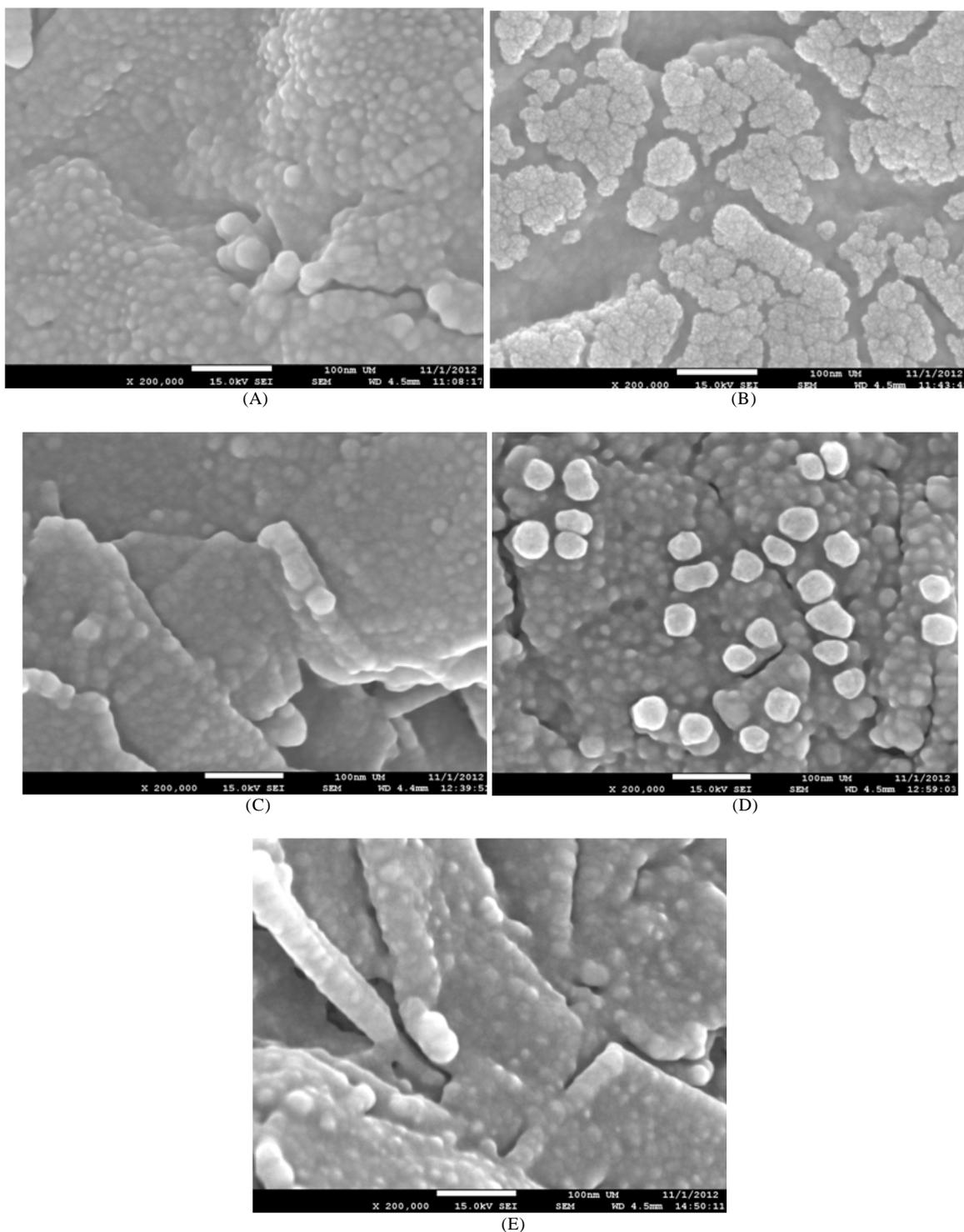
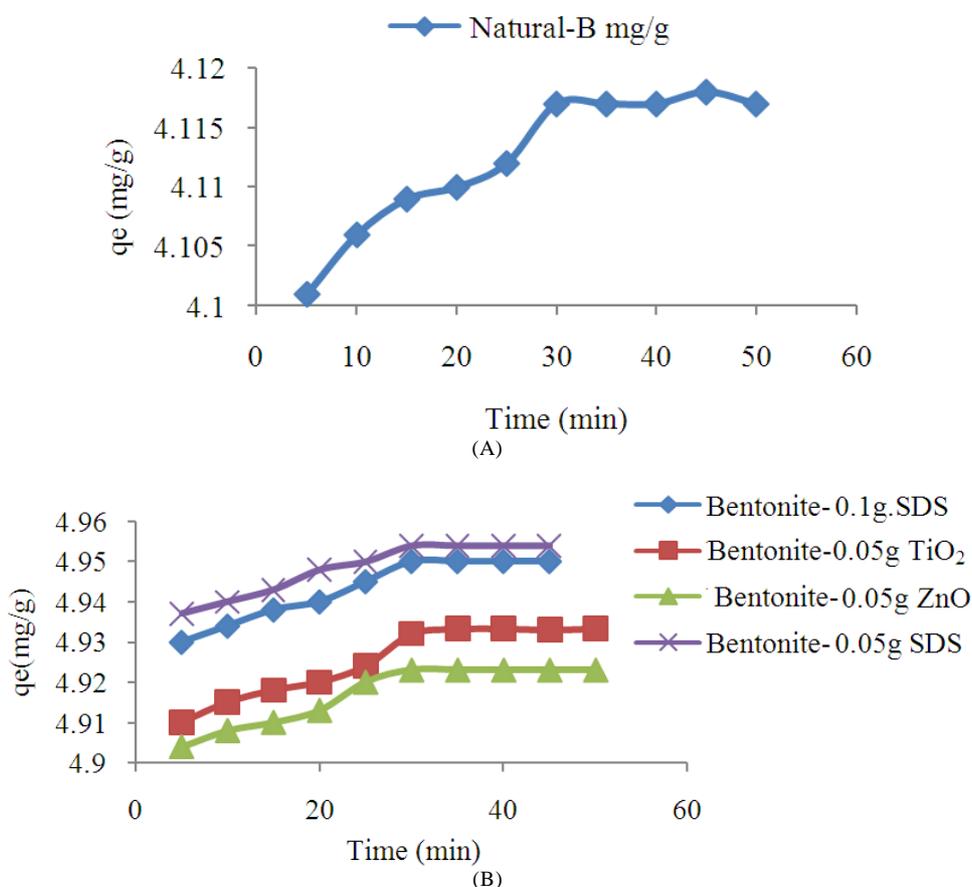


Fig. 2. SEM surface morphology of (A) natural bentonite (B) bentonite-0.05g TiO₂ (C) bentonite-0.05g ZnO (D) bentonite-0.05g SDS (E) bentonite-0.01g SDS

Table 2. Effect of the adsorbent mass on the adsorption of rhodamine B

Dose of adsorbent (g)	Removalpercentage (%R)				
	Natrnal bentonite	B-0.05g TiO ₂	B-0.05g ZnO	B-0.05g SDS	B-0.1g SDS
0	0.0	0.00	0.0	0.0	0.0
0.1	20.7	25.30	25.3	30.7	23.8
0.2	45.5	52.30	50.5	48.2	52.3
0.3	69.3	75.20	75.0	80.1	82.4
0.4	80.1	95.21	94.6	92.3	90.7
0.5	82.3	98.60	98.4	99.0	99.0
1	82.3	98.60	98.6	98.6	99.0

**Fig. 3.** Effect of contact time on Rhodamine B adsorption on, (A) natural bentonite (B) Modified bentonite

3.2. Effect of Adsorbent Dose

The effect of adsorbent dose on the amount of dye adsorbed at initial 50 mL of 50 mg L⁻¹ of adsorbate is shown in **Table 2**. The percentage removal of Rhodamine B increased with the increasing the dose of adsorbent. This may be due to the increase in availability of surface active sites resulting from the increased dose

and conglomeration of the adsorbent. The increase in the extent of removal percentage %R of Rhodamine is found to be insignificant after 0.4 g for natural bentonite and modified bentonite. We obtained maximum removal (82.3%) of rhedamin B on naturalbentenite, while the maximum removal on bentonite with 0.05g TiO₂ (98.6%), on bentonite with 0.05g ZnO(98.4%) and on bentonite with (0.05,0.1)g SDS(99.0%).

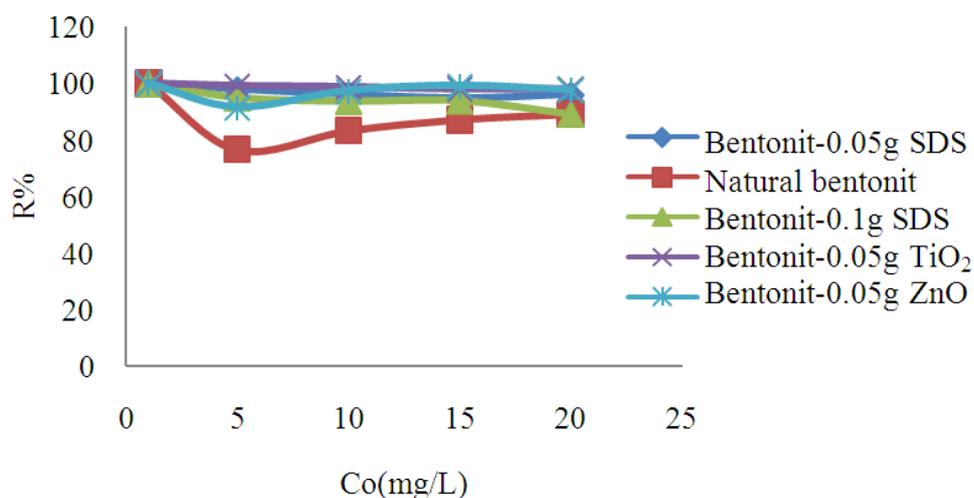


Fig. 4. Effect of adding different amount of modifier to bentonite on Removal percentage of Rhodamine B

3.3. Effect of Adding Different Amount of SDS and Nano TiO₂, ZnO and Al₂O₃ on the Removal Percentage

The adsorption of Rhodamine B on bentonite at the concentration rang 1-20 mg L⁻¹ when adding different amounts of SDS ranged from 0.01 to 0.1 g and NanoTiO₂, ZnO and Al₂O₃ to 10g of bentonite as shown in Fig. 3. The results indicated that the removal percentage (%R) of Rhodamine B dye increase from 89% to 98% for 20 mg L⁻¹ dye concentration when adding 0.05, 0.1 g of SDS to 10g of natural bentonite, while the removal percentage increased to 97.6% and 96.0% when 0.05 g of TiO₂, ZnO. There is no increase of %R of Rhodamine B on Bentonite surface when adding Al₂O₃. As a conclusion, the best amount of modifier SDS, ZnO, Al₂O₃ was 0.1, 0.05g of SDS and 0.05g of TiO₂, ZnO.

3.4. Effect of Bentonite Modification on Removal Percentage of Rhodamine B at the Best Amount of Modifier

Adding 0.05 and 0.1g of SDS to 10g of bentonite lead to increase the percentage removal from 79.3% to 99.3% for Rhodamine B concentrations 50-250 mg L⁻¹, while adding 0.05g of TiO₂ and ZnO to 10g of bentonite lead to increase %R to 98.9, 98.6% respectively, for 250 mg L⁻¹ dye concentration. This increase in the adsorption capacity of modifier bentonite may be attributed to many factors, like modifier converted the surface of bentonite from hydrophilic nanometers in size are dispersed among

the silicate platelets on natural bentonite resulted high surface area of TiO₂, ZnO (Chen *et al.*, 2008; Langmuir, 1918). This result as shown in Fig. 4 and illustrate by SEM images Fig. 2.

3.5. Adsorption Isotherms

3.5.1. Adsorption Isotherm

Adsorption isotherm model are very useful for predicting adsorption capacities and also for incorporating into mass relationships in the design of contacting equipment so, in order to optimize the design of an adsorption system to remove Rhodamine B dye from effluents, is to establish the most appropriate correlation for the equilibrium curves. In this respect, the equilibrium experimental data for adsorbed Rhodamine B onto natural and modified bentonite were compared using two isotherm models, Langmuir and Freundlich isotherms.

3.6. Langmuir Isotherm Model

The Langmuir adsorption model depends on the assumption that the intermolecular forces decrease rapidly with distance and consequently predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent. In addition, the isotherm model assume that adsorption occurs at specific homogeneous sites within the adsorbent (Frundlich, 1906). The Langmuir equation used based on the assumption of a structurally homogeneous adsorbent, where all sorption sites are identical and energetically equivalent.

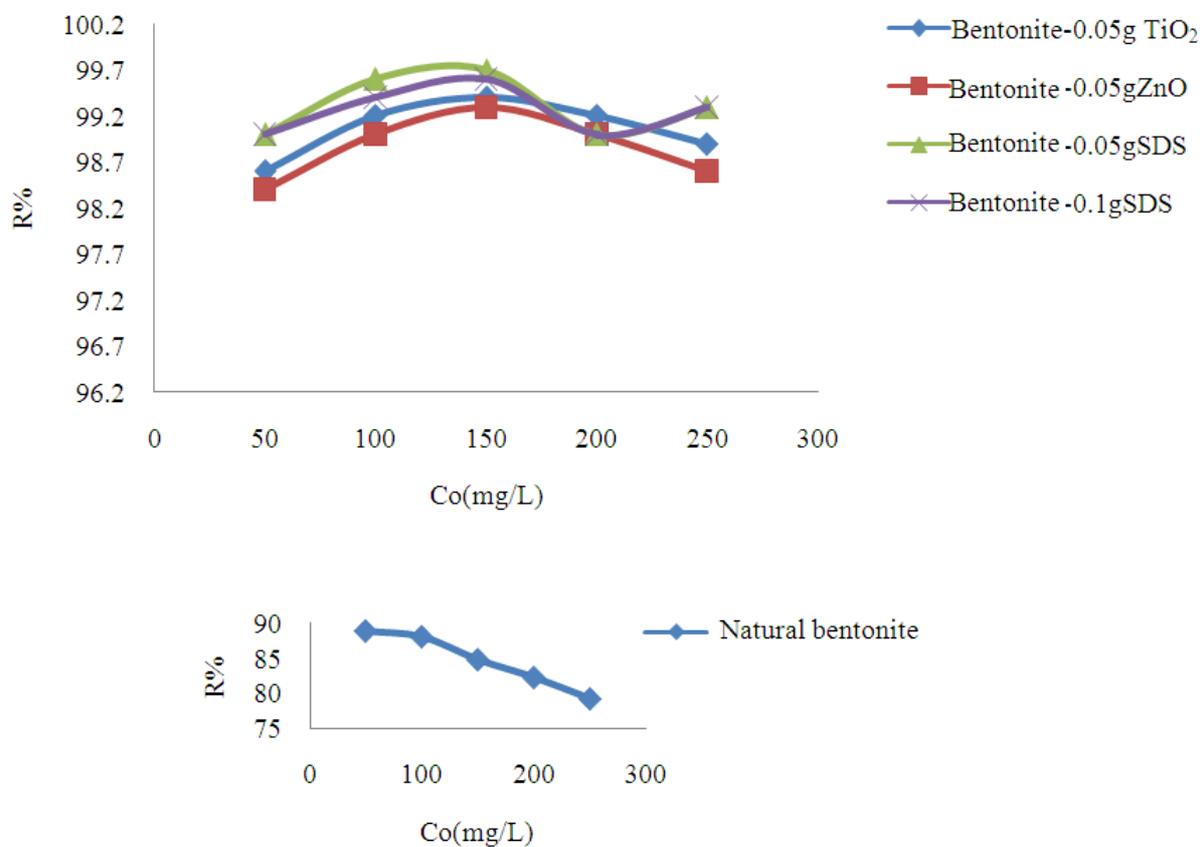
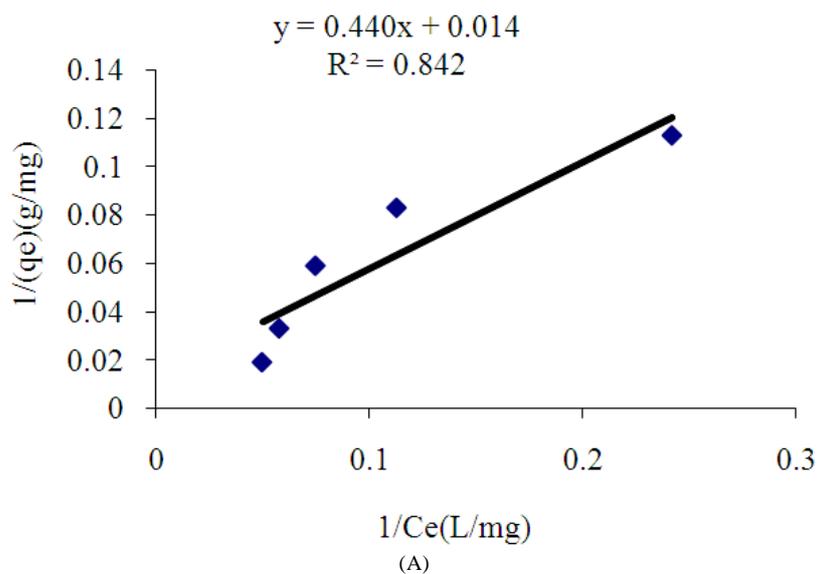
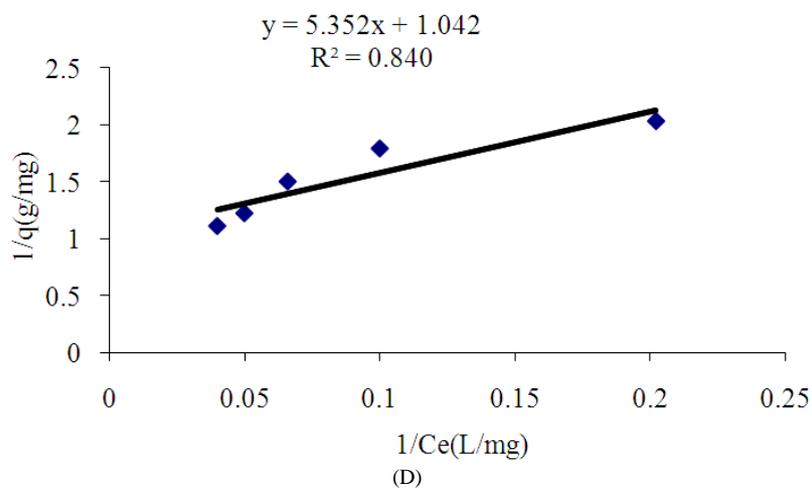
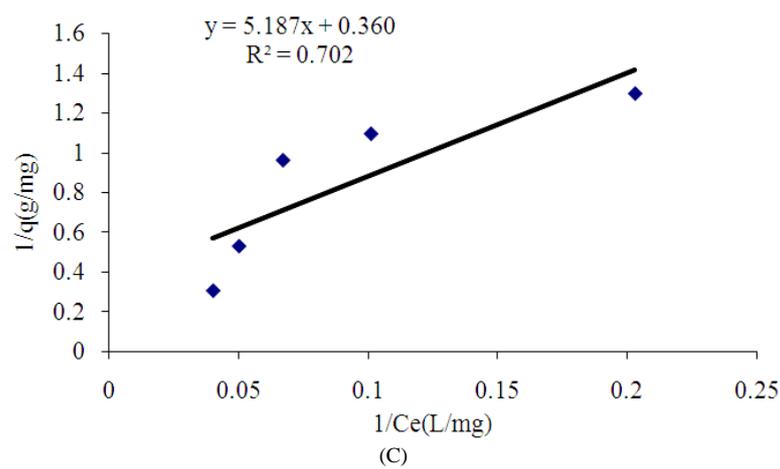
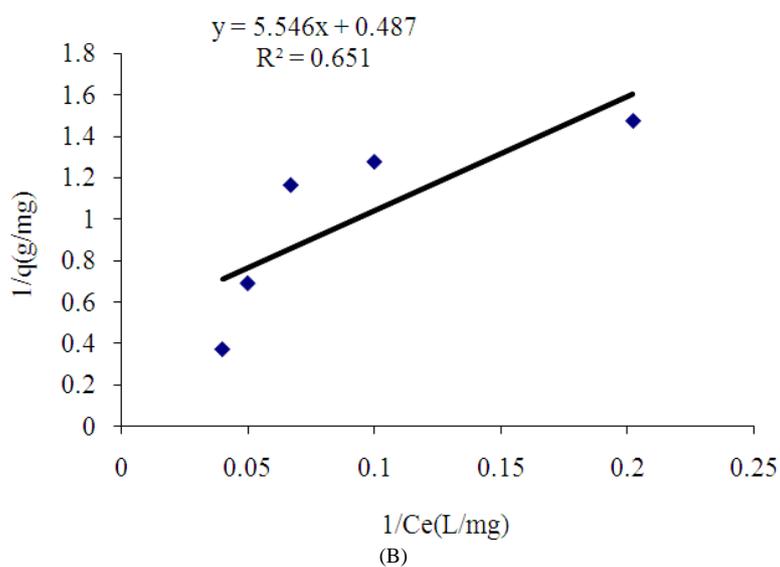


Fig. 5. Variation of removal percentage against Rhodamine B concentration on natural bentonite, bentonite-0.05g TiO₂, bentonite-0.05g ZnO, bentonite-0.05g SDS, bentonite-0.01g SDS





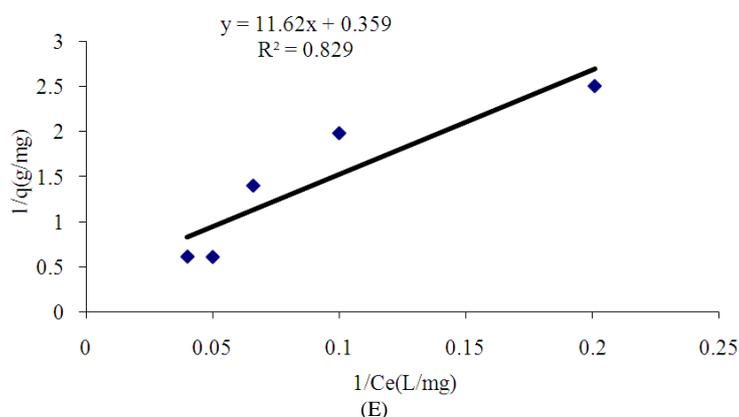


Fig. 6. Langmuir adsorption isotherms for Rhodamine B on (A) natural bentonite, (B) bentonite-0.05g TiO₂ (C) bentonite-0.05g ZnO (D) bentonite-0.05g SDS, (E) bentonite 01g SDS

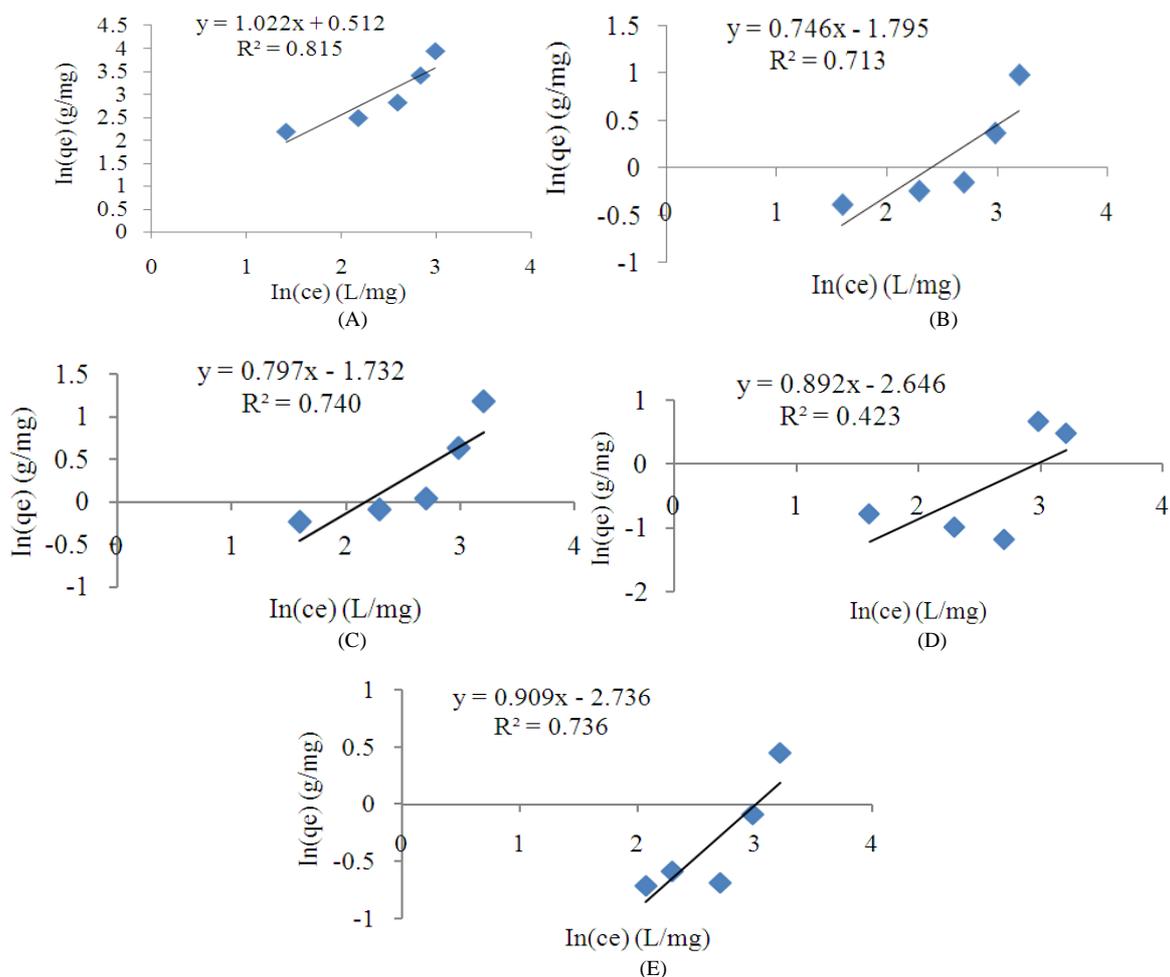


Fig. 7. Freundlich adsorption isotherms for Rhodamine B on (A) natural bentonite, (B) bentonite-0.05g TiO₂ (C) bentonite-0.05g ZnO (D) bentonite-0.05g SDS (E) bentonite-0.01g SDS

Theoretically, the sorbent has a finite capacity for the sorbet. Therefore, a saturation value is reached beyond which no further sorption can occur. The saturated or mono layer capacity can be represented as the known Langmuir Equation 3:

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \left(\frac{1}{q_{\max} K_L} \right) \frac{1}{C_e} \quad (3)$$

where, --- (mg/g) (L/mg) are the Langmuir constants and (mg/L) is the equilibrium dye concentration in the solution.

The Langmuir adsorption equilibrium isotherm of Rhodamin B dye onto bentonite and modified bentonite is presented in **Fig. 5**.

Regression analysis reveals that the Langmuir model fits the experimental data well with correlation factors higher than (0.6512) for natural and modified bentonite.

3.7. Freundlich Isotherm Model

This model describes heterogeneous adsorption system. The model is given in its linear using Equation 4:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

where, K_F is the Freundlich constant related to overall adsorption capacity mg/g and $1/n$ is a dimensionless constant related to the intensity of adsorption, or the heterogeneity factors describes reversible adsorption and is not restricted to the formation of the monolayer.

Figure 6 shows plots of $\ln q_e$ versus $\ln C_e$ for the adsorption of Rhodamin B dye on natural and modified bentonite. The values of K_F and n are obtained from intercept and slope, respectively. These are (1.66) and (0.97) for natural bentonite and (6.02), (1.33), (5.65), (1.52), (14.10) and (1.12) for modified bentonite. This indicates (**Fig. 7**) that both systems were favorable and the modified bentonite had a higher adsorption capacity.

4. REFERENCES

- Al-Khatib, L., F. Fraige, M. Al-Hwaiti and O. Al-Khashman, 2012. Adsorption from aqueous solution onto natural and acid activated bentonite. *Am. J. Environ. Sci.*, 8: 510-522. DOI: 10.3844/ajessp.2012.510.522
- Arivoli, S., M. Hema and P.M.D. Prasath, 2009. Adsorption of Malachite green onto carbon prepared from borassus bark. *Arabian J. Sci. Eng.*, 34: 120-129.
- Armagan, B., M. Turan and M.S. Elik, 2004. Equilibrium studies on the adsorption of reactive azo dyes into Zeolite. *Desalination*, 170: 33-39. DOI: 10.1016/j.desal.2004.02.091
- Atia, A.A., F.M. Farag and A.E.F.M. Youssef, 2006. Studies on the adsorption of dodecylbenzenesulfonate and cetylpyridinium bromide at liquid/air and bentonite/liquid interfaces. *Colloids Surfaces A: Physicochem. Eng. Aspects*, 278: 74-80. DOI: 10.1016/j.colsurfa.2005.11.091
- Attia, A.A., B.S. Girgis and N.A. Fathy, 2008. Removal of methylene blue by carbons derived from peach stones by H_3PO_4 activation: Batch and column studies. *Dyes Pigments*, 76: 282-289. DOI: 10.1016/j.dyepig.2006.08.039
- Baskaralingam, P., M. Pulikesi, D. Elango, V. Ramamurthi and S. Sivanesa, 2006. Adsorption of acid dye onto organobentonite. *J. Hazard. Mater.*, 128: 133-144. DOI: 10.1016/j.jhazmat.2005.07.049
- Chen, L.H., C.C. Huang and H.L. Lien, 2008. Bimetallic iron-aluminum particles for dechlorination of carbon tetrachloride. *Chemosphere*, 73: 692-697. DOI: 10.1016/j.chemosphere.2008.07.005
- Dhahir, S.A., 2007. Experimental and theoretical study of environmental path way Degradation for pesticides pollutant propanil and Dazomet. PhD Thesis, College of Science For Women, University of Baghdad.
- Ding, Z., H.Y. Zhu, G.Q. Lu and P.F. Greenfield, 1999. Photocatalytic properties of titania pillared clays by different drying methods. *J. Colloid Interface Sci.*, 209: 193-199. DOI: 10.1006/jcis.1998.5857
- Eren, E. and B. Afsin, 2008. Investigation of a basic dye adsorption from aqueous solution onto raw and pre-treated bentonite surfaces. *Dyes Pigments*, 76: 220-225. DOI: 10.1016/j.dyepig.2006.08.019
- Errais, E., J. Duplay, F. Darragi, I.M. Rabet and A. Aubert *et al.*, 2011. Efficient anionic dye adsorption on natural untreated clay: Kinetic study and thermodynamic parameters. *Desalination*, 275: 74-81. DOI: 10.1016/j.desal.2011.02.031
- Espantaleon, A.G., J.A. Nieto, M. Fernandez and A. Marsal, 2003. Use of activated clays in the removal of dyes and surfactants from tannery waste waters. *Applied Clay Sci.*, 24: 105-110. DOI: 10.1016/S0169-1317(03)00153-4
- Frundlich, H., 1906. Adsorption solution. *Z. Phys. Chem.*, 57: 384-470.

- Gulgonul, I., 2012. Evaluation of Turkish Bentonite for removal of dyes from textile wastewaters. *Physicochem. Probl. Miner. Process.*, 48: 369-380.
- Gupta, V.K., I. Ali and V.K. Saini, 2004. Removal of Rhodamine B, fast green and methylene blue from wastewater using red mud, an aluminum industry waste. *Ind. Eng. Chem. Res.*, 43: 1740-1747. DOI: 10.1021/ie034218g
- Hameed, B.H. and A.A. Ahmad, 2004. Batch adsorption of methylene blue from aqueous solution by garlic peel, an agricultural waste biomass. *J. Hazard. Mater.*, 164: 870-875. DOI: 10.1016/j.jhazmat.2008.08.084
- Jie, L. and P. Jiafen, 2010. Removal of carbon tetrachloride from contaminated groundwater environment by adsorption method. *Proceedings of the 4th International Conference on Bioinformatics and Biomedical Engineering (iCBBE)*, Jun. 18-20, IEEE Xplore Press, Chengdu, pp: 1-4. DOI: 10.1109/ICBBE.2010.5517280
- Karahan, S., M. Yurdakos, Y. Seki and K. Yurdakoc, 2006. Removal of boron from aqueous solution by clays and modified clays. *J. Colloid Interface Sci.*, 293: 36-42. DOI: 10.1016/j.jcis.2005.06.048
- Karaoglu, M.H., M. Dogan and M. Alkan, 2010. Kinetic analysis of reactive blue 221 adsorption on kaolinite. *Desalination*, 256: 154-165. DOI: 10.1016/j.desal.2010.01.021
- Kareem, S.H. and E. Abd-Al-Hussin, 2012. Adsorption of congo, red Rhodamine B and disperse blue dyes from aqueous solution onto raw flint clay. *J. Baghdad Sci.*, 9: 680-688.
- Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.*, 40: 1361-1403. DOI: 10.1021/ja02242a004
- Lien, H.L. and W. Zhang, 2002. Enhanced dehalogenation of halogenated methanes by bimetallic Cu/Al. *Chemosphere*, 49: 371-378. DOI: 10.1016/S0045-6535(02)00248-5
- Ma, J., B. Cui, J. Dai and D. Li, 2011. Mechanism of adsorption of anionic dye from aqueous solutions onto organobentonite. *J. Hazard. Mater.*, 186: 1758-1765. DOI: 10.1016/j.jhazmat.2010.12.073
- Mockovciakova, A. and Z. Orolinova, 2009. Adsorption properties of modified bentonite clay. *Chem. Technol.*, 50: 47-50.
- Ozcan, A., C. Omeroglu, Y. Erdogan and A.S. Ozcan, 2007. Modification of bentonite with a cationic surfactant: An adsorption study of textile dye Reactive Blue 19. *J. Hazard. Mater.*, 140: 173-179. DOI: 10.1016/j.jhazmat.2006.06.138
- Özcan, A.S., B. Erdem and A. Ozcan, 2004. Adsorption of Acid Blue 193 from aqueous solutions onto Na-bentonite and DTMA-bentonite. *J. Colloid Interface Sci.*, 280: 44-54. DOI: 10.1016/j.jcis.2004.07.035
- Sharma, P., H. Kour and M. Sharma, 2011. A review on applicability of naturally available adsorbents for the removal of hazardous dyes from aqueous waste. *Environ. Monit. Assess.*, 183: 151-195. DOI: 10.1007/s10661-011-1914-0
- Turabik, M., 2008. Adsorption of basic dyes from single and binary component systems onto bentonite: Simultaneous analysis of Basic Red 46 and Basic Yellow 28 by first order derivative spectrophotometric analysis method. *J. Hazard. Mater.*, 158: 52-64. DOI: 10.1016/j.jhazmat.2008.01.033
- Venkataraman, K., 1971. *The Chemistry of Synthetic Dyes*. 1st Edn., Elsevier, New York, ISBN-10: 0323142958, pp: 726.
- Volzone, C. and L.B. Garrido, 2002. Retention of chromium by modified Al-Bentonite. *Ceramica*, 48: 153-156. DOI: 10.1590/S0366-69132002000300008
- Wang, S. and Z.H. Zhu, 2007. Effects of acidic treatment of activated carbons on dye adsorption. *Dyes Pigments*, 75: 306-314. DOI: 10.1016/j.dyepig.2006.06.005
- Zhao, J., T. Wu, K. Wu, K. Oikawa and H. Hidaka *et al.*, 1998. Photoassisted degradation of dye pollutants. 3. Degradation of the cationic dye Rhodamine B in aqueous anionic surfactant/TiO₂ dispersions under visible light irradiation: Evidence for the need of substrate adsorption on TiO₂ particles. *Environ. Sci. Technol.*, 32: 2394-2400. DOI: 10.1021/es9707926