

# Chemical Treatment Of Jordanian Diatomaceous Clay And Its Use In Removal Of Some Pollutants From Aqueous Solutions

SALEM M. MUSLEH

(Acceptance Date 30th September, 2012)

## Abstract

Metal oxide of titanium was deposited on native Jordanian diatomaceous clay. The chemical and structural properties of the modified and the unmodified samples were characterized by XRF, XRD, SEM and FTIR techniques. The diatomaceous clay supported titanium oxide was used in preliminary experiments to study the interactions with aniline, N-methylaniline, and N,N dimethylaniline in aqueous solution. The results showed that titanium oxide interacted with diatomaceous clay and caused some structural changes. These were reflected in the surface area of the samples and their activity in the removal of aniline and its derivatives from aqueous solutions. The removal rate of aniline and its derivatives decrease with the increase of pH. Adsorption isotherms of modified diatomaceous clay indicates that aniline and its derivatives follow type 1, which is the Langmuir isotherms.

*Key words:* Diatomaceous clay, Titanium oxide, Aniline, Adsorption.

## 1. Introduction

Diatomite ( $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ) is a pale-colored and lightweight sedimentary rock composed principally of silica microfossils of aquatic unicellular algae. Diatomite consists of wide variety of shape and sized diatoms in a structure containing up to 80-90% void<sup>1</sup>. Diatomite's high porous structure, low density and high surface area results in a number of

industrial applications<sup>2-6</sup>. Diatomite exists in large deposits around the world, and it has wide future to apply diatomite in various industrial processes. Diatomaceous clay can be chemically heated with some functional groups to treat wastewater. Process of preparation for modified diatomite has been used as absorbent. On the process comprises immersing diatomite in intermediate base solution of magnesium ferric salt or manganese salts is represented as

precipitation agent. The process for modified diatomite composite absorbent is simple and low cost<sup>7,8</sup>.

Adsorption of arsenic on iron oxide coated diatomite was studied and its use in removal of some metals was studied<sup>9</sup>.

Characterization of diatomite with special attention was paid to the ability of its electro analytical performance at modified electrodes and to the potential application was studied<sup>10</sup>.

Diatomite components are used in the design of the thermal insulation for a high – temperature furnace; it is shown that the proposed concentration for the heat insulation has an advantage over existing ones<sup>11</sup>.

Natural and the surfactant modified diatomite have been tested for ability to remove uranium ions from aqueous solutions<sup>12</sup>.

Method for preparing modified diatomite for waste water treatment. Modified diatomite is prepared from diatomite, lime and aluminum sulfate (or aluminum chloride, ferric chloride, ferrous sulfate, etc...). The method can be used in treating city wastewater with high safety, high reliability and high efficiency<sup>13</sup>.

Removal of chromium and other metals from aqueous solutions by diatomite treated with micro emulsion was used.<sup>14-16</sup>

The feasibility of using raw and modified diatomite for advanced treatment of secondary sewage effluents (SSE) was investigated<sup>17-20</sup>.

The feasibility of using diatomite and Mn-diatomite for remediation of  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cd^{2+}$  shows that diatomite and manganese oxide- modified diatomite (Mn-diatomite) were tested as adsorbents for  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cd^{2+}$  removal from water<sup>21</sup>.

Application for modified diatomite concentrate in wastewater treatment was introduced based on practice. The modified diatomite concentrate was prepared from raw diatomite by wet ore beneficiation, and modifying with surface treating agent<sup>22</sup>.

This paper reports on the titanium dioxide treated Jordanian diatomaceous clays and their possible use in the removal of aniline and its derivatives from aqueous solutions.

## 2. Material and Methods

### 2.1 Preparation of Diatomaceous Earth Samples :

The samples of Diatomaceous earth were donated by natural resources authority from Al-Azraq region (Pore hole BT-34, at depth of 42-45 m) and samples were chosen to have average silica content, which were then homogenized and their chemical composition was ascertained by XRF analysis. These samples were labeled D.

Quantities of D were cleaned by successive washing with 1.8 liter of distilled water. The sample was further washed by a solution consisting of tetra sodium pyrophosphate (0.05M) and NaOH (0.05M) (1:1 v/v). This was followed by shaking with sodium hydroxide solution (0.05M), and finally by washing twice

with 1.8 L distilled water. The filtered sample was dried overnight at 105°C and was kept desiccated over anhydrous CaCl<sub>2</sub>. particles larger than 250 µm were removed by mechanical sieving . The sample prepared by this method was labeled Dw .

### 2.2 Preparation of Titanium dioxide :

Titanium dioxide was prepared by means of TiCl<sub>4</sub> hydrolysis at room temperature, 10 ml of it was gradually added to 400 mL of distilled water. The mixture was subsequently neutralized with 50 mL of 25% ammonia solution and stirred for 2 h, filtered, dried at 105°C and kept at 250°C in muffle furnace for 16 h and kept desiccated over anhydrous CaCl<sub>2</sub>.

### 2.3 Modification of diatomaceous earth with titanium dioxide :

The deposition of the titanium oxide on diatomaceous clay was affected in situ by the hydrolysis of titanium tetrachloride for rutile form . Thus 15 g portion of the prepared earth samples were stirred with distilled water (400 ml) for 10 min then, 15 ml of TiCl<sub>4</sub> (0.091 mol) was added gradually to the mixture at room temperature. The mixture was subsequently neutralized with 60 ml of 25% ammonia solution and stirred for 3 hours, filtered, dried at 105°C and kept at 250°C in muffle furnace for 12-15 hours, the above procedure gave the TiO<sub>2</sub> loaded sample Dt .

### 2.4 Characterization of the Diatomaceous earth samples:

All diatomaceous earth samples were characterized by ascertaining their chemical

composition, mineral constitution and chemical characterizations, as well as their surface morphology and adsorption capacity. The chemical composition was determined by XRF, at Natural Resources Authority(NRA), Amman, Jordan. The instruments used were Diano model 2023 model.

A 0.8g sample was mixed well with 7.2g of lithium tetra borate (Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) in platinum crucible. The crucible was then introduced into an automatic fluxer (LECO Corp. FX-200) where a temperature programming was affected starting from room dish and allowed to cool . the resulting glassy disc was subsequently used for XRF analysis, using united states geologically survey (USGS) standard for calibration.

The mineral constitution of the samples was determined at NRA by powder XRD technique, using X' pert instrument fitted with Philips X-ray tube giving CoK  $\alpha$  radiation at  $\lambda=1.77892 \text{ \AA}$ , at 40 Kv and 40 Ma. The chemical characterization of the samples was investigated by FTIR spectrometry using KBr matrix. The instrument used was aJasco FTIR -410 spectrophotometer, of scanning range 400-4000 cm<sup>-1</sup>. The surface morphology of the samples was studied using scanning electron microscope(SEM) type XL-30 W/TMP/200 at 20 kV. All samples are carbon plated.

### 2.5 Surface Area Estimation :

The surface area for samples were estimated using methylene blue (MB) method<sup>23</sup>. Methylene blue adsorption can be used for the measurement of surface areas of clay minerals. The method has advantage over BET gas adsorption measurements in being readily

applicable to a wide range of areas and especially to minerals under aqueous conditions. The method is simple, rapid and economical<sup>24</sup>. Weight samples of adsorbent in the range 15-105 mg were placed separately in 250 mL stoppered Erlenmeyer flasks and 100 mL of 50 ppm methylene blue solution was added to each. To achieve equilibrium for adsorption of dyes by clay minerals an incubation period of 12-24 days has been reported<sup>25</sup>. In the present study the mixtures, together with a control sample of MB, were left in subdued light at room temperature for a long period of six weeks to be sure that equilibrium is reached. Standard solutions of methylene-blue 1, 2, 4, 6, 8, 10, 12.5 and 15 ppm were prepared to construct a calibration curve using  $\lambda = 612$  nm.

Adsorption of organic pollutants such as aniline, N-methyle aniline and N-N dimethyle aniline reactions in the presence of modified and non-modified diatomite were carried out as follows:

The prepared organic pollutants in the range of 5-200 mg/L, were chosen to investigate their adsorption behavior on raw diatomite, washed and modified diatomite samples. The analysis of the adsorbate solutions were carried out using a calibrated Beer's Lambert law plot at  $\lambda_{max}$  254, 270 and 280 nm figures (1-3) respectively.

### 3. Results and Discussions

#### 3.1 Characterization of titanium dioxide sample:

XRD pattern of the prepared  $TiO_2$  sample is found to be identical with anatase in

the XRD card no 21 – 1272 joint committee of powder diffraction (JCPDS) as shown in the table (1):

The FTIR results showed in figure (4) a broad band one about  $466\text{ cm}^{-1}$  while the other weaker about  $690\text{ cm}^{-1}$  and a weak shoulder at  $787\text{ cm}^{-1}$ , these peaks agree with reported values of anatase  $TiO_2$  peaks, which are strong bands between  $525 - 460\text{ cm}^{-1}$ , broad band at  $700\text{ cm}^{-1}$  and shoulder at  $790\text{ cm}^{-1}$ .

#### 3.2 Chemical Composition of Diatomite Samples:

All diatomite samples were analyzed by XRF to determine their composition. The results are given in table (2), the difference from 100% is the loss on ignition (L.I.O). The chemical composition of the samples was discussed in terms of the change in relative presence of the main constituent to silica ( $SiO_2$ ).

The main effect of the raw material treated is the decrease in sodium content and increase in calcium content, this treatment seems to have also moved the  $MgO / CaO$  ratio close to that obtained in dolomite (i.e 0.72). The titanium sample shows clearly this effect in its preparation. The indicator ratio in table (3) shows that there is a drop down in  $Al_2O_3 / SiO_2$  for the modified sample from 0.22 to 0.03 due to the decrease in silica content. The  $Fe_2O_3 / SiO_2$  ratio remains nearly the same, while the  $TiO_2 / SiO_2$  increase remarkably from 0.03 to 0.91 due to the deposition of titanium oxide on the diatomite sample.

Table 1. Powder XRD peaks for TiO<sub>2</sub>

TiO <sub>2</sub> sample	JCPDS(card no 21 -1272)
2θ I/I□*	2θ I/I□*
29.45 100	29.44 100
44.31 39	44.20 20
56.37 31	56.43 35
63.87 24	63.49 20

\*Normalized values .

Table 2. Chemical composition of modified and unmodified samples is shown

Oxide %	D	DW	DT
Fe <sub>2</sub> O <sub>3</sub>	5.42	5.16	3.91
TiO <sub>2</sub>	1.46	1.38	37.86
CaO	0.52	0.31	1.72
K <sub>2</sub> O	1.65	1.42	0.75
SiO <sub>2</sub>	56.73	61.16	41.32
Al <sub>2</sub> O <sub>3</sub>	12.46	11.33	1.21
MgO	1.32	1.21	1.16
Na <sub>2</sub> O	5.81	2.01	1.71
L.O.I	14.63	15.97	10.36

Table 3. Indicator Ratios

	D	DW	DT
Al <sub>2</sub> O <sub>3</sub> / SiO <sub>2</sub>	0.22	0.19	0.03
Fe <sub>2</sub> O / SiO <sub>2</sub>	0.09	0.10	0.09
TiO <sub>2</sub> / SiO <sub>2</sub>	0.026	0.023	0.91

### 3.3 Mineral Constitution of Diatomite Samples :

The mineral constitution of the samples D,DW and DT are summarized in

table (3). From the results above as shown in figures (5-6) it is clear that the major crystalline mineral is Quartz as expected due to the important part of the amorphous silica of diatomite which under goes transformation to Quartz. Kaolinite become trace in the washed and the modified sample, Halite is trace in the raw sample while on washing as expected, it disappeared, the deposition of TiO<sub>2</sub> on the diatomite sample effects the relative presence of minerals, thus Anatase is the major mineral in the modified samples, while Muscovite has remained the same as before modification.

Table 4. The mineral constitution of the samples D, DW and DT

Mineral	D	DW	DT
Quartz	xxx	Xxx	xx
Kaolinite	xx	X	x
Muscovite	x	X	x
Halite	x	-	-
Anatase	-	-	xxx

Major = xxx

Minor = xx

Trace = x

### 3.4 Chemical Constitution of Diatomite Samples :

The FTIR spectra in figure (4) of raw diatomite, washed diatomite and TiO<sub>2</sub> modified diatomite are shown in table (4). The vibration of Si-OH bond results in the band  $\approx 3700 \text{ cm}^{-1}$ , together with doublet due to OH deformation at approximately  $800 \text{ cm}^{-1}$ , the main adsorption bands of diatomite occurs at 3690,1113,1047, 789 and  $714 \text{ cm}^{-1}$ .

Table 5. Infrared Absorption Bands ( $\text{cm}^{-1}$ ) of Diatomite Samples

Sample	*	Assignment
3694,3650, 362	ms	OH-stretching vibration of Si-OH of Kalonite and Diatomite
3430	m	OH- stretching of Si-OH, water vibration (crystalline water)*
1650	w	$\beta$ ( $\text{H}_2\text{O}$ ) of diatomite (1630)*
1107, 1035	m	Asymmetric stretching of Si-O-Si of diatomite* and Kaolinite**
800, 695	s	Asymmetric stretching of Si-O-Si of diatomite*
669, 536, 474	w	Bending of Si-O-Si of Quartz *, Muscovite* and diatomite*

\* Marel *et al.*, (1976)

\*\* Gadsden, (1975)

Table 6. Adsorption of MB on diatomite and modified diatomite

Sample	monolayer capacity ( $\text{Xm} \cdot 10^{-4}$ mole/g)	Surface area ( $\text{m}^2/\text{g}$ )
D	2.06	153
DW	2.09	176
DT	2.42	157

Diatomite modified  $\text{TiO}_2$  exhibit two clear peaks at 793 and 704  $\text{cm}^{-1}$  of OH vibration, similar effect was observed for main Si-OH vibration at  $\approx 3700 \text{ cm}^{-1}$ , This peak shifted to 3695 comparing the D and DT samples. Shows that for D and DW bands for  $\alpha$ - quartz at 695 and 669  $\text{cm}^{-1}$  have disappeared due to modification<sup>26,27</sup>.

Furthermore broadening in the peaks laying 550-450  $\text{cm}^{-1}$  has occurred.

The absorption peak at 474  $\text{cm}^{-1}$  which represents bending vibration of Si-O-Si in  $\alpha$ - Quartz, diatomite and muscovite have

Table 7. The Removal Percentage for Different Concentration

Adsorbent	Organic Pollutant	Removal %		
		100 ppm	50 ppm	25 ppm
Raw Diatomite	Aniline	76.0	64.1	40.3
	N-Methyele Aniline	71.2	57.6	31.0
	N-N Dimethyele Aniline	63.1	41.7	28.3
Washed Diatomite	Aniline	73.6	46.2	21.5
	N-Methyele Aniline	64.1	35.0	20.1
	N-N Dimethyele Aniline	65.3	50.0	33.6
Modified Diatomite	Aniline	90.7	87.4	65.8
	N-Methyele Aniline	82.1	67.1	41.6
	N-N Dimethyele Aniline	78.2	55.3	29.2

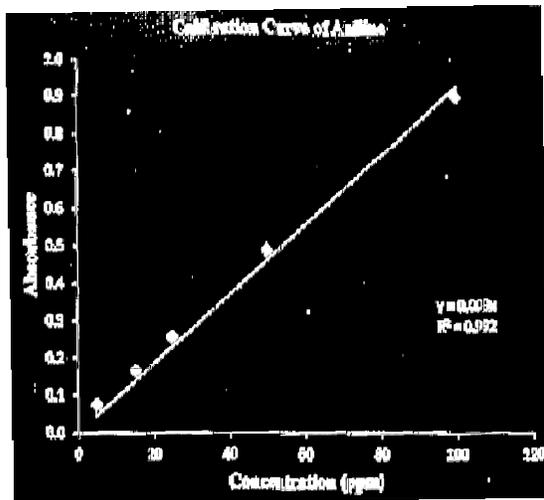


Figure 1. Calibration Curve of Standard Aniline Solution At 254nm.

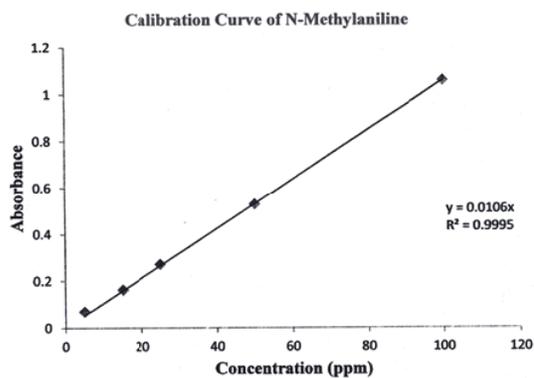


Figure 2. Calibration Curve of Standard N-Methylaniline Solution At 270nm.

remained strong, the broadening of the peak at  $700\text{ cm}^{-1}$  and the appearance of shoulder peak at  $793\text{ cm}^{-1}$  and the broadening in the region  $550\text{--}450\text{ cm}^{-1}$  indicates the presence of  $\text{TiO}_2$  in the modified sample.

### 3.5 Surface Morphology :

The scanning electron micrographs

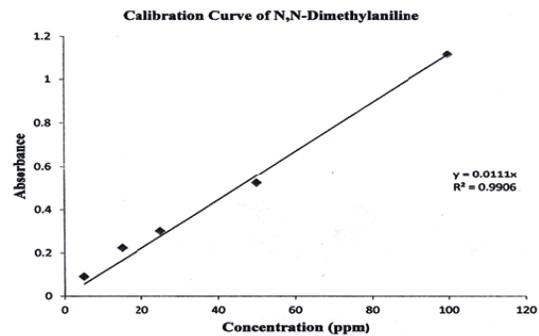


Figure 3. Calibration Curve of Standard N,N-Dimethylaniline Solution At 280 nm.

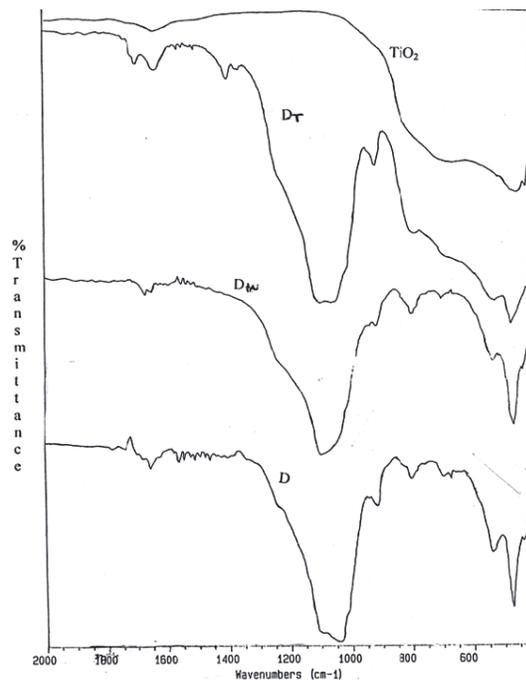


Figure 4. Infrared Spectra of D, DW, DT and  $\text{TiO}_2$  at ( $2000\text{--}400\text{ cm}^{-1}$ ) region.

gave good picture of the surface morphology. Figures (7) shows clearly the porous nature with sieve like structure of diatomite. The modified diatomite shows that Porous structure

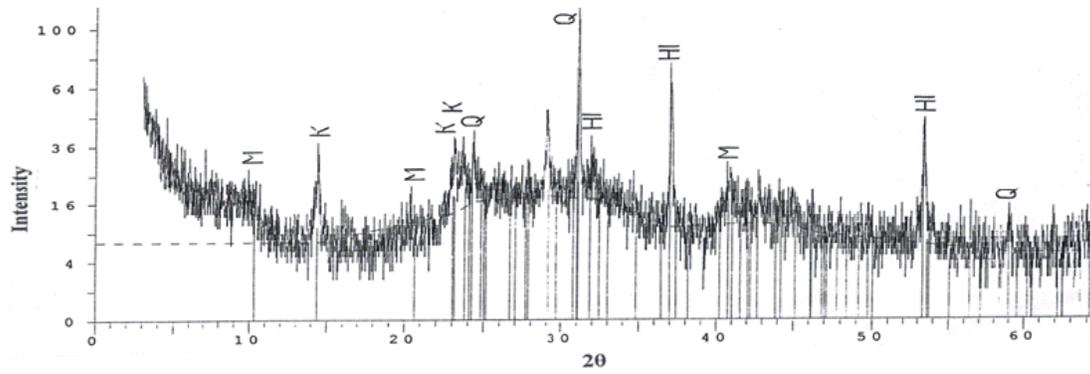


Figure 5. XRD of Sample D.

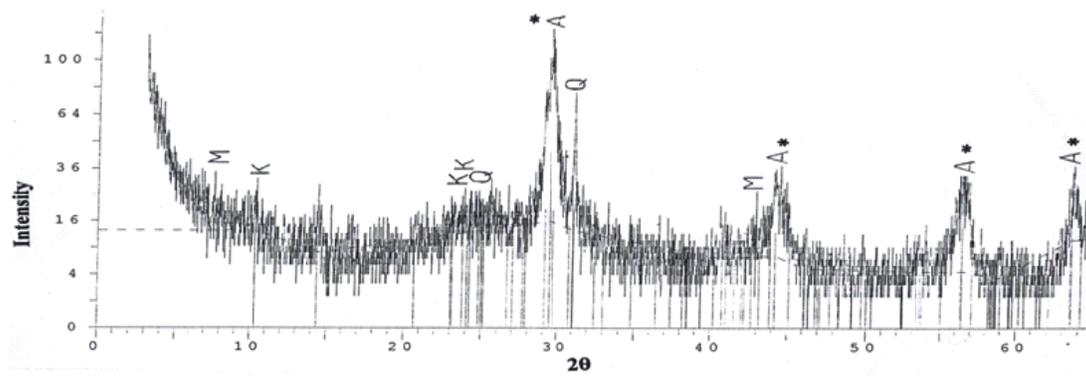


Figure 6. XRD of Sample Dt.

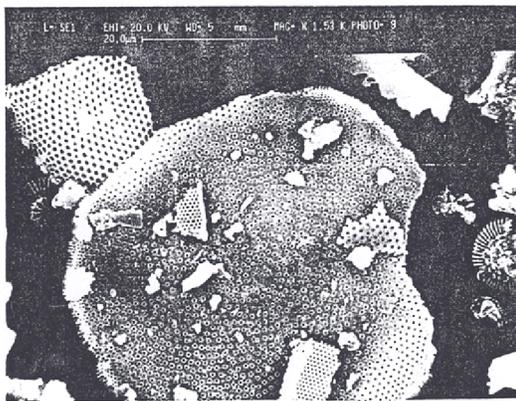


Figure 7. Scanning Electron Micrograph of D Sample.

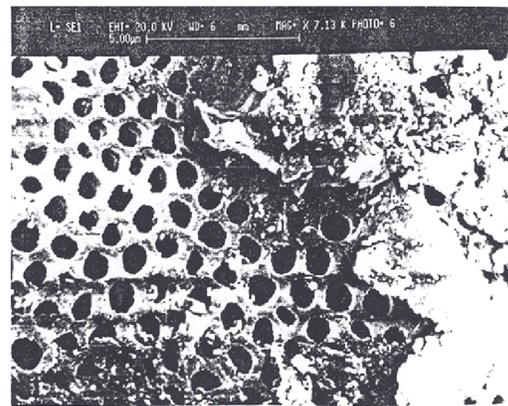


Figure 8. Scanning Electron Micrograph of Dt Sample.

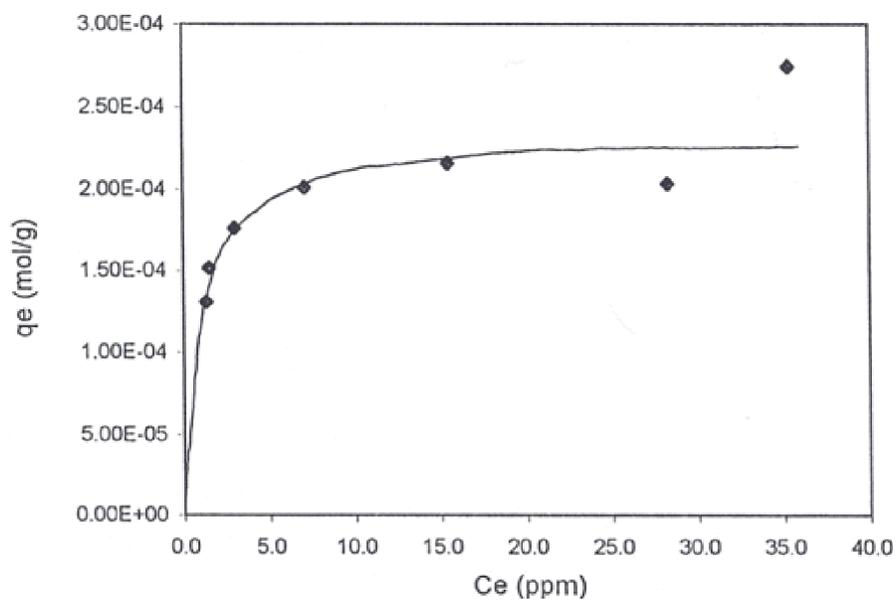


Figure 9. Adsorption of MB on D.

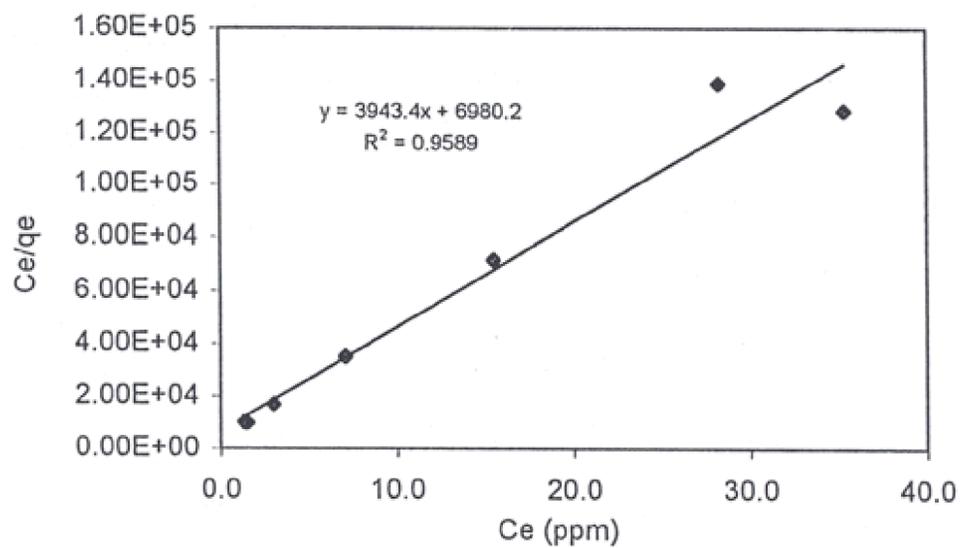


Figure 10. Adsorption Isotherm of MB on D.

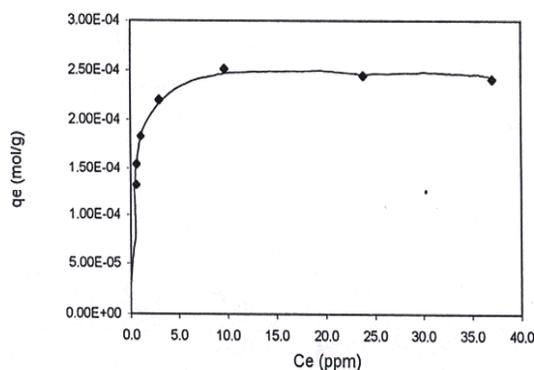


Figure 11. Adsorption of MB on Dt.

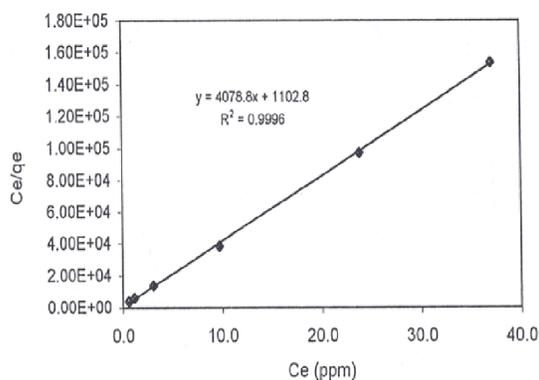


Figure 12. Adsorption Isotherm MB on Dt.

of diatomite was either destroyed or extensively covered by the deposited ( $\text{TiO}_2$ ) as shown in figure (8). This may be due to the use of NaOH in the sample preparation which may affect the diatomite surface.

### 3.6 Surface Area :

Methylene-Blue (MB) adsorption shown in figures (9-10) for D was used to obtain surface areas of the samples, from which relative values are obtained for comparison.

The surface area (A) decrease with the deposition of  $\text{TiO}_2$  as shown in figures (11-12), the monolayer capacity ( $X_m$ ) shows increase as given in the table (5). It is interesting to note that the washed diatomite sample has higher surface compared to the raw one. This reflects the effect of removal of clay and other contaminants by the washing procedure and the remarkable increase in silica content as revealed by XRF results.

### 3.7 Removal of Aniline and its Derivatives:

Preliminary work was carried out to instigate the possible effect of  $\text{TiO}_2$  supported on diatomite on the removal of aniline, N-methyle aniline and N-N- dimethyle aniline from aqueous solutions at different pH. The result show the optimum pH for the removal of aniline and its derivatives are almost acidic and as the pH increase, also it is found that the removal of the organic pollutants increase for diatomite modified of  $\text{TiO}_2$ . It is also noticed that increase of the surface area. The effect of initial aniline, N-methyle aniline and N-N- diamethyl aniline and the percentage of removal by diatomite and  $\text{TiO}_2$  modified diatomite are given in table (6).

It is noticed that the removal % of aniline and its derivatives are greater using the modified diatomite, while for the pollutants the removal of aniline is the most, this may attributed to the presence of  $\text{CH}_3$  group on the nitrogen atom which might be hindered on the surface of diatomite.

For the concentrations (100) ppm the removal percentage as shown in the table (6).

The experimental conditions where the same for all experiments, one gram of

diatomite was mixed with 10 ml of pollutant with different concentrations, the samples were shaken at 25°C and 150 rpm for 24 hours on a thermostatic shaker. The sample were filtered using syringe filter 0.45µm to yield a clear supernatant for analysis of equilibrium solute concentrations.

#### 4. Conclusion

The Jordanian diatomaceous clay earths contain mainly discus and pinnate diatomite forms, with quartz as major crystalline content, beside kaolinite and muscovite as minor. Modifying with TiO<sub>2</sub> effects the chemical and the mineral compositions Surface adsorptions indicate that depositions of the metal oxide will increase the adsorption of aniline and its derivatives from aqueous solutions.

#### 5. Acknowledgment

This work has been carried out during sabbatical leave granted to me from Al-Balqa Applied University(BAU)during the academic year 2011/2012. The author would like to thank university of Petra-Amman, for laboratory equipments, The Natural Resources Authority (NRA) for the donation of the diatomite samples and using their analytical facilities.

#### 6. References

1. Korunic Z. J. *Stored Prod. Res.* 34, 87, (1998).
2. Yuan P., D.Q. Wu, He H.P. and Lin Z. Y., *Appl. Surf. Sci.* 227, 30 (2004).
3. Lemonas J.F., *Carem Am. Soc. Bull.* 76 (6), 92 (1997).
4. Khraisheh M.A.M., Al-degs Y.S. and Mcminn W.A.M., *J. Chem. Eng.* 99, 177, (2004).
5. Huttenloch P., Roehl K. E. and Czurda K., *J. Environ. Sci. Technol.* 35, 4260 (2010).
6. Gu J., Liu Y. and Zhang Y., Chin., *J. Non Met. Mines* 26 (1), 46, (2003).
7. Weng H., Shen Z. and Zhang X., *J. Chin. Ceram. Soc.* 30(3), 366 (2002).
8. Pan Y.F., Chiou C.T., Lin T.F., *Environ. Sci. pollut. Res. Int.*, 17(8),1401-10 (2010).
9. Hajar H., Hamdi B., Ania C.O., *J. Hazard Mater., Vol.* 188(1-3), 304 (2011).
10. Caliskan N., Sogut E., Saka C., Yardim Y., Senturk Z., *Comb Chem High Througput Screen*, 13 (8), 703-11 (2010).
11. Kashcheev I.D., Popov A. G., Ivanov S.E., *J. Refractories and Industrial Ceramics*, 50, (2), (2009).
12. Sprynsky M., Kovalchuk I., Buszewski B., *J. Hazard Material*, Vol (181) (1-3) p 707-7. CAPLUS., (2010).
13. De Castro Dantas. T.N., Neto A. A. D., De A. Moura, M. C. P. *water Research*, 35(9), 2219-2224 (2001).
14. Wu, C.C., Wang, Y. C., Lin, T.F., Liang, S.Y. Proceedings of the International Symposium on East Asian Resources Recycling Technology, 8<sup>th</sup>, Beijing, China, Nov. 9-15,2005, 165-169 (2005).
15. Wu, Jinlu; Yang, Y. S., Lin, Jinhua. *Journal of Hazardous Materials*, 127 (1-3), 196-203 (2005).
16. Khraisheh, M. A. M., Al-Ghouti, M. A., Allen, S. J., Ahmad, M. N. M. *water Environment Research*, 76(6), 2655-2663 (2004).
17. Li, Menlou. *Peop. Rep. China.*, 19(3), 81-84 (2004).

18. Kaleta, Jadwiga, Puskarewicz, Alicja. *Archiwum Ochrony Srodowiska*, 31(1), 107-113 (2005).
19. Al-Degs, Yahya Salim, Tutunju, Maha Farooq; Shawabkeh, Reyad Awwad. *Separation Science and Technology*, 35 (14), 2299-2310, (2000).
20. Zheng, Shuilin, Wang, Qingzhong. *Peop. Rep. China*, 23(4), 36-37 (2000).
21. Hang, P.T. and Birindley, G.W., Methylene Blue Absorption by Clay Minerals. Determination of Surface Area And Cation Exchange Capacities, *Clay And Clay Minerals*, (18), 203-212 (1970).
22. Marel, H.W. and Beutelspacher, H., Atlas of Infrared Scientific publishing company (1976).
23. Gadsden, J.A., *Infrared Spectra of Minerals And Related Inorganic Compounds* (1975)
24. Pusit P., Pilaiporn T., Sukon P., *Journal of The Microscopy of Thailand*, 24(2), 99-102 (2010).
25. Pookmanee P., Thippraphan P., Jansanthea P., Phanichphant S., *Advanced Materials Research*, 506, 425 – 428 (2012).
26. Jian Z., Ping W., Xiaofu W., Mingjing L., *African Journal of Agriculture Research*, 7(24), 3614-3620 (2012).
27. Datsko ,Zelentsov V. I., Dvornika E. E., *Surface Engineering and Applied Electrochemistry*, 47(6), (2011).