Asian Journal of Chemistry; *Vol. 24, No. 1 (2012), 89-92*

ASIAN JOURNAL OF CHEMISTRY

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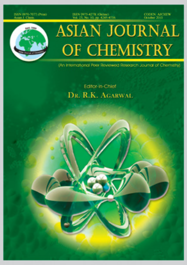

Adsorption of the 2,4-Dichlorophenoxyacetic Acid Dimethylamine by Raw and Modified Bentonite

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(*Received*: 8 November 2010; *Accepted*: 9 September 2011) AJC-10377

The adsorption of the 2,4-dichlorophenoxyacetic acid dimethyl amine on raw bentonite (Tokat, Turkey), modified bentonite with base and modified bentonite with acid has been studied using high pressure liquid chromatography (HPLC) and FT- infrared spectrophotometer. Sorption of 2,4-dichlorophenoxyacetic acid dimethyl amine on raw bentonite, modified bentonite with base and modified bentonite with acid was compared solving in different solutions such as aqueous and aqueous-ethanol solutions based on adsorption isotherms. The effect of temperature, time and pH were observed on adsorption of 2,4-dichlorophenoxyacetic acid dimethyl amine. Sorption mechanisms in soils, the effect of surface functional groups as well as parameters influencing adsorption were discussed. Then maximum adsorption of 2,4-dichlorophenoxyacetic acid dimethyl amine capacity was measured on modified bentonite with base in pH 5 at 40 ºC for 24 h. The modified bentonite with base used in experimental work played a major role than on the adsorption of 2,4-dichlorophenoxyacetic acid dimethyl amine so, the modified bentonite with base has better characteristics than raw bentonite and modified bentonite with acid adsorbents. The Freundlich isotherms of aqueous-ethanol solution was better than isotherms of aqueous solution for much better to adsorb of 2,4-dichlorophenoxyacetic acid dimethyl amine.

Key Words: Adsorption, Bentonite, Pesticides, 2,4-dichlorophenoxyacetic acid dimethyl amine.

INTRODUCTION

The environmental contamination associated with the presence and accumulation of poison and dangerous chemicals in soil as well as in surface and ground waters may be considered. Chemicals are highly soluble in water, minimally adsorbed by soil particles, not readily degradable, can move rapidly with the infiltrating water and hence, are likely to be found in ground water[1-3]. One of the contamination chemicals are herbicides. Many acidic herbicides used in agriculture such as dicamba, 2,4-dichlorophenoxyacetic acid dimethyl amine, clopyralid, bentazone and picloram have these characteristics and thus, if they accidentally reach high concentration in soil, they have to be immobilized as soon as possible to avoid further contamination in water. They cause some chronic diseases that are mortal for humans and animals. Among these herbicides, 2,4-dichlorophenoxyacetic acid is an anionic herbicide whereby the water solubility bases on the pH of solution. It is widely used on wheat, maize and rice to control broad-leaf weeds. As most anionic contaminants, 2,4-dichlorophenoxyacetic acid is also weakly adsorbed by soil particles and poses a threat of surface and ground water contamination[4]. This risk is concerned with both the 2,4-dichlorophenoxyacetic acid dimethyl amine and 2,4-dichlorophenoxyacetic acid esters used in commercial formulations. The available information regarding the acute toxicity of 2,4-dichlorophenoxyacetic acid covers various forms of 2,4-dichlorophenoxyacetic acid including the acid, *iso*-octyl, butyl and propyl esters and the sodium and 2,4-dichlorophenoxyacetic acid dimethyl amine. Hence it is important to consider the extent to which toxicity data on one form of 2,4-dichlorophenoxyacetic acid can be used to assess the consequences associated with exposure to other forms of 2,4-dichlorophenoxyacetic acid. There is at least some evidence for 2,4-dichlorophenoxyacetic acid that the presence of emulsifiers with 2,4-dichlorophenoxyacetic acid dimethyl amine will substantially enhance the toxicity of the 2,4-dichlorophenoxyacetic acid dimethyl amine to aquatic species[5]. In order to contribute to the understanding of the interaction phenomenon, we have undertaken a study of the retention of pesticides by simple and easily synthesized materials known the clays. These materials can be considered as the most suitable adsorbents for herbicides. Many investigations, performed during the last decade, have shown that these materials are promising for environmental remediation, in particular for the removal of organic and inorganic pollutants from water[6-11]. Clay minerals have high specific surface areas associated with their small particle size. After surface modification with inorganic or organic cations, they can be used as adsorbents for many hazardous herbicides to eliminate these pollutants from water[12-15].

The present study was performed to investigate the adsorption of 2,4-dichlorophenoxyacetic acid dimethyl amine in aqueous and aqueous-ethanol solution based on adsorption isotherms. The Freundlich isotherm was chosen the best adsorbing isotherm constants. Three different adsorbent raw bentonite, modified bentonite with base and modified bentonite with acid were studied on adsorption of 2,4-dichlorophenoxyacetic acid dimethyl amine. The effect of temperature, time and pH were measured for adsorption of 2,4-dichlorophenoxyacetic acid dimethyl amine in aqueous solution.

EXPERIMENTAL

2,4-Dichlorophenoxyacetic acid dimethyl amine (molecular mass 266.1) were supplied from Koruma Agriculture Medicines Industry (Izmit, Turkey) (Fig. 1). These pesticides are widely used in agriculture and are potential contaminants of ground waters. Bentonite was obtained from The Department of Mine Technology (Tokat, Turkey). Per cent of oxide present in raw bentonite was shown in Table-1. The other chemicals used in this work HCl, Na_2CO_3, HNO_3, NaOH, Acetonitrile were purchased from Merck (Darmstadt, Germany).

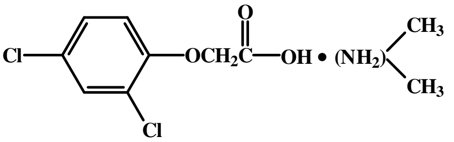

Fig. 1. Structure of 2,4 dichlorophenoxy acetic acid dimethylamine

TABLE-1
PER CENT OXIDES OF RAW BENTONITE (TUBITAK)

	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	CaO	MgO
Raw bentonite	60/62	16/17.5	3/3.5	2.2/2.7	0.9/0.95	2.5/3.5	1.5/2

Preparation of raw bentonite, modified bentonite with base and modified bentonite with acid: 200 g of raw bentonite was eliminated by 200-400 mesh sieves and stored at 100 ºC for 48 h. The procedure for the production of modified bentonite with base was that 0.8 g Na_2CO_3 was solved in water and 40 g raw bentonite were added to solution of base solution. It was centrifugated at 450 rpm for 1 h. The samples were taken into the oven at 800 ºC for 2 h. The calcined bentonite was washed with 3 % HCl and dried at room temperature and then stored in the desiccators for further uses. 0.75 M HNO_3 was added to 25 g of raw bentonite for the production of modified bentonite with acid. The colloidal complex was boiled for 1 h with back colding and they were taken into the oven 300 ºC for 1.5 h.

Capacity of cation enhance (CCE) of raw bentonite, modified bentonite with base, modified bentonite with acid: This method was based on adsorption of methylene blue on some particular adsorbents. The suspension of 1 g clays and 150 mL distilled water were prepared in the laboratory. The pH of suspension was adjusted to 3.8 with H_2SO_4. The methylene blue was added to the suspension with 3 or 5 mL to shaker for 3 min. This process was ended, when a clear blue was observed. The CCE enhance of raw bentonite, modified bentonite with base and modified bentonite with acid were calculated the same as this method shown in eqn. 1. We used raw bentonite, modified bentonite with base and modified bentonite with acid bentonite from Tokat, Turkey. The bentonite was modified by Na_2CO_3 had a cation exchange capacity, CEC, of 0.86 meq/g. The cation exchange of modified bentonite with acid was 0.68 meq/g. The CEC of the montmorillonite fraction was 0.85 meq/g[16]. Thus, the bentonite contained about 85 % montmorillonite. The CCE of the raw bentonite was calculated 1.13 meq/g. The CCE of bentonite was found 0.72 meq/g to modify it[17].

$$CCE = E.\ V / W \tag{1}$$

Adsorption experiments: The change of adsorption on clays was performed in three ways; time, pH and concentration dependent on adsorption. The suspensions were prepared with 1 g clays as a sorbent and 2, 4, 6, 8, 12, 14, 16, 18, 20 µL 2,4-dichlorophenoxyacetic acid dimethyl amine solutions in aqueous solution and aqueous-ethanol solution separately. They were shaken at 20, 25, 30, 35 and 40 ºC temperatures. pH were chosen 3, 4, 5, 7, 8 and 9 with 0.05 M HCl or NaOH to adjust pH. These suspensions were shaken for 24 h and centrifuged under the same conditions as the adsorption isotherm experiments. The equilibrium pH and 2,4-dichlorophenoxyacetic acid dimethyl amine concentrations were calculated for the supernatants in different times and temperature[18]. A method used by Battal *et al.*[19], was modified to determine the amount of adsorbed herbicide on bentonite. The column for herbicides during certain periods is expressed as transition periods. We have performed this study as taken a reference on this work. After equilibrium, the dispersions were centrifuged and the supernatant was filtered. The amount adsorbed (Q_e) was calculated from the difference in concentration between the initial (C_o) and the equilibrium (C_e) solutions. Blanks without herbicide and triplicates of each adsorption point were used in each series of experiments. The supernatants were filtered to determine the contaminant concentration using a Shimadzu HPLC (Kyoto, Japan) system with an µ bondapak C_{18} column, 18 % acetonitrile water at 1.5 mL/min was used as an eluent, detection was made by UV and column temperature was fixed as 55 ºC. Infrared spectra were recorded on a FT-IR spectrometer (Bio Rad, England, London) purged with dried air. Solids were examined in the form of KBr discs.

RESULTS AND DISCUSSION

Infrared spectra of raw bentonite show that the stretching absorption band of OH^- within the crystal texture is constituted at 3643 cm^{-1}, while the stretching absorption band of hydroxy bound and zeolitic shapes of water are formed at 3464 cm^{-1} The adsorption bands at 3643 and 3464 cm^{-1} decreased when the surface of bentonite was exchange by nitric acid (modified bentonite with acid). These bands are intended to detect water usually bonded as water of crystallization in salts and metal oxides. Then hydrated silicates and phosphates cause significant interference with this band. The other absorption band at 1394 cm^{-1} belonging to the NO_2^- group of nitric acid was also observed at 1394 cm^{-1}. This can be interpreted as meaning that the groups of crystal texture of bentonite and -OH groups belonging to the bound and zeolitic waters have formed with nitric acid. The absorption band at 1490 cm^{-1} belonging to the raw bentonite and modified bentonite with acid disappeared on the modified bentonite with base. It is indicated that C=C bond disappeared on modified bentonite with base. However the surface of bentonite is exchanged by Na_2CO_3 on modified bentonite with base. The absorption band at 1083 cm^{-1} covers many phosphates that are moderately hydrated or are anhydrous. Heavily hydrated salts such as dodecahydrates are possibly not consist of here. The texture of OH^- bond on raw bentonite and modified bentonite with acid are similar and more different than modified bentonite with base. Then, the adsorption capacity of modified bentonite with base is bigger than raw bentonite and modified bentonite with acid.

Adsorption isotherms of 2,4-dichlorophenoxyacetic acid dimethyl Amine on raw bentonite, modified bentonite with base and modified bentonite with acid: The data at the equilibrium point is known as adsorption isotherms. It has been explained due to the shapes isotherms as positive, smooth and concave. The amount of adsorbed herbicide increases with the equilibrium concentrations of herbicides. Fig. 2, represents Freundlich adsorption isotherms of 2,4-dichlorophenoxyacetic acid dimethyl amine on raw bentonite, modified bentonite with base and modified bentonite with acid in aqueous solution. It has been observed that the capacity of adsorption on modified bentonite with base was better than the capacity of adsorption on raw bentonite and modified bentonite with acid. In Fig. 2, the maximum Q_e was measured 7.56 mmol/g on modified bentonite with base respectively. Then Q_e reaches a plateau. When C_e value increased, Q_e increased more rapidly than at low C_e value. This can be explained that the adsorption continues in two steps, saturation of the external sites is followed by an interlayer process performs at high C_e values[20]. Some models were matured to describe adsorption condition. Owing to the shape of the isotherms, the sorption data were analyzed according to Freundlich equation as given in below (2).

$$q_e = K_f C_e^{1/n} \quad (2)$$

where K is the amount of pesticide per unit weight of the clay, C_e the equilibrium concentration of the adsorbate, while K and n are constants that give estimates of the adsorption capacity and intensity, respectively[20]. The linear equation of isotherm is given below (3).

$$\log q_e = \log K_f C_e^{1/n} \quad (3)$$

Constants of isotherm using the linear equation are shown in Table-2. Fig. 3 shows the Freundlich adsorption isotherms of 2,4-dichlorophenoxyacetic acid dimethyl amine on raw bentonite, modified bentonite with base and modified bentonite with acid in aqueous-ethanol solution. The maximum adsorbing of 2,4-dichlorophenoxyacetic acid dimethyl amine was achieved 14.4 mmol/g by modified bentonite with base approximately. The adsorbing capacity of modified bentonite with base was better than raw bentonite and modified bentonite with acid in aqueous-ethanol solution. The higher content of 2,4-dichlorophenoxyacetic acid dimethyl amine in aqueous-ethanol compared to the aqueous is beneficial for adsorption of 2,4-dichlorophenoxyacetic acid dimethyl amine in Figs. 2 and 3.

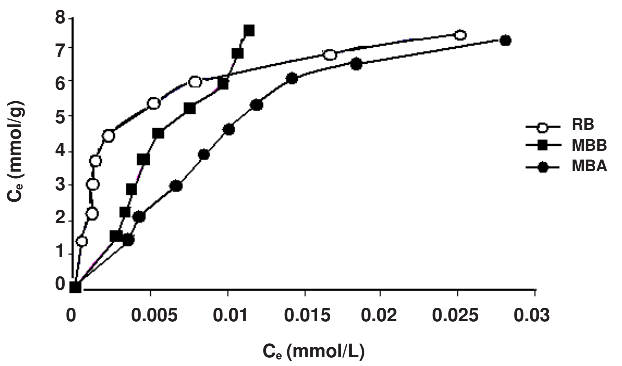

Fig. 2. Adsorption isotherms of 2,4-dichlorophenoxyacetic acid dimethyl amine on raw bentonite, modified bentonite with base and modified bentonite with acid in aqueous

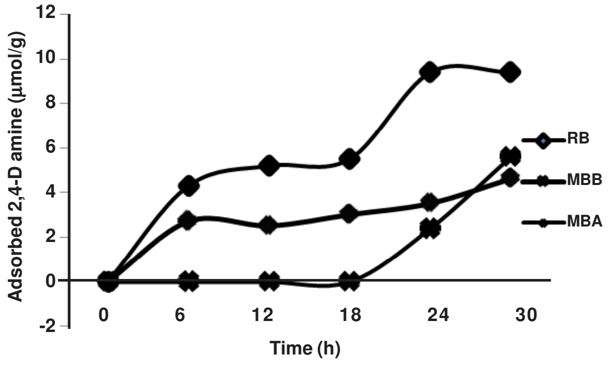

Fig. 3. Adsorption isotherms of 2,4-dichlorophenoxyacetic acid dimethyl amine on raw bentonite, modified bentonite with base and modified bentonite with acid in aqueous-ethanol solutions

TABLE-2
FREUNDLICH PARAMETERS FOR HERBICIDE ADSORPTION ON RB, MBB AND MBA IN AQUEOUS AND AQUEOUS-ETHANOL SOLUTIONS.

Adsorbent	Aqueous solution			Aqueous-ethanol solution		
	K_f (mmol/g)	n	R^2	K_f (mmol/g)	n	R^2
RB	18. 15	4.21	0.978	46.48	0.811	0.9951
MBB	165. 18	1.42	0.971	318.09	0.595	0.9717
MBA	101.19	1.47	0.994	823.71	0.699	0.9128

Kinetic study: The maximum capacity of adsorption of 2,4-dichlorophenoxyacetic acid dimethyl amine was studied at 40 ºC on raw bentonite, modified bentonite with acid and modified bentonite with base (Fig. 4). When the temperature was increased, the capacity of adsorption was increased too. The increasing of equilibrium adsorption with temperature showed that the process of adsorption was endothermic. The increasing and decreasing of adsorption at some temperature provided that not only physically adsorption exists but also chemical adsorption[21].

The interaction of herbicide with clays at the different concentrations was investigated as a contact period's function. The adsorbed herbicide for each clay and their times are given in Fig. 5. It represented that maximum adsorption of herbicide reached on 30 h.

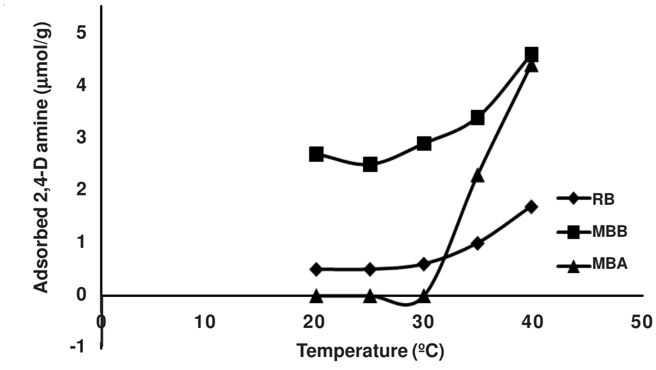

Fig. 4. Effect of temperature on adsorption of 2,4-dichlorophenoxyacetic acid dimethyl Amine by raw bentonite, modified bentonite with acid and modified bentonite with base

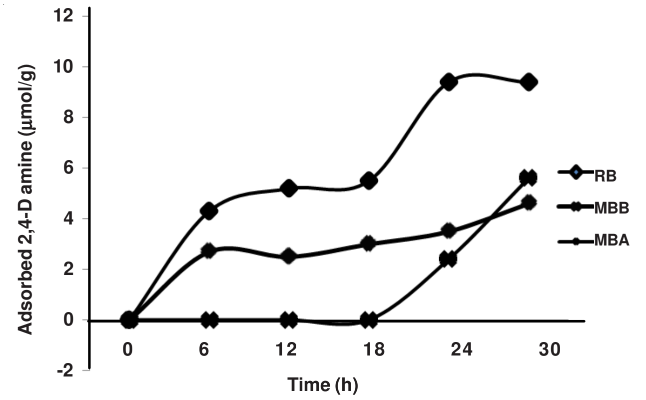

Fig. 5. Effect of time on adsorption of 2,4-dichlorophenoxyacetic acid dimethyl Amine by raw bentonite, modified bentonite with acid and modified bentonite with base

The adsorption of 2,4-dichlorophenoxyacetic acid dimethyl amine at distinct pH are given in Table-3. The maximum adsorption of herbicide was observed at pH 8 on raw bentonite. pH 9 was best pH to adsorb 2,4-dichlorophenoxyacetic acid dimethyl amine by modified bentonite with acid. The maximum adsorption capacity of the modified bentonite with base was occurred[20] at pH 5.

TABLE-3
EFFECT OF pH ON ADSORPTION OF 2,4–D AMINE BY RB, MBA AND MBB.

pH	RB (µmol/g)	MBA (µmol/g)	MBB (µmol/g)
3	5,45	5,72	7,01
4	5,93	5,98	5,93
5	6,83	7,38	7,80
7	7,01	5,76	6,57
8	7,58	6,69	7,10
9	6,07	7,45	6,81

Conclusion

The modified bentonite with base ensures a simple probability to alter the adsorption characteristic of this clay mineral. The increment of the mesopore surface area with the calcinations temperature derives the sites for an enhanced 2,4-dichlorophenoxyacetic acid dimethyl amine adsorption. The adsorption of this herbicide on modified bentonite with base shows higher adsorption than on raw bentonite and modified bentonite with acid. The combination of the results from aqueous-ethanol solutions employed to study the adsorption of 2,4-dichlorophenoxyacetic acid dimethyl amine on raw bentonite, modified bentonite with acid and modified bentonite with base samples leads to the following conclusions. The use of ethanol in place of water is better than using water. So, we used little ethanol with water while 2,4-dichlorophenoxyacetic acid dimethyl amine is used on agriculture areas. Thus, the controls of removing hazardous pollutants were provided by modified bentonite with base used in this study with aqueous-ethanol solutions. The results illustrated that modified bentonite with base is quite good adsorbent for 2,4-dichlorophenoxyacetic acid dimethyl amine from aqueous solution. Research is needed to optimize the application of this compound as adsorbent of these herbicides from contaminated waters.

ACKNOWLEDGEMENTS

The authors thank Yüzüncü Yil University for providing the laboratory facilities and funding for this study.

REFERENCES

1. J.A. Goodrich, B.W. Lynkis Jr. and R.M. Clark, *J. Environ. Qual.*, **20**, 707 (1991).
2. D.W. Kolpin, J.E. Barbash and R.J. Gillion, *Environ. Sci. Technol.*, **32**, 558 (1998).
3. S.J. Kalkhoff, D.W. Kolpin, E.M. Thurman, I. Ferrer and D. Barcelo, *Environ. Sci. Technol.*, **32**, 1738 (1998).
4. R.A. Rebich, R.H. Coupe and E.M. Thurman, *Sci. Total Environ.*, **321**, 189 (2004).
5. 2,4-dichlorophenoxyacetic acid dimethylichlorophenoxyacetic acid Formulations Human Health and Ecological Risk Assessment. L.R. Cotr., (1998). Syracuse Environmental Research Associates, Inc. 5100 Highbridge St., 42C, Sera TR 95-21-09-01d.
6. C. Barriga, M. Gaitan, I. Pavlovic, M.A. Ulibarri, M.C. Hermosin and J. Cornejo, *J. Mater. Chem.*, **12**, 1027 (2002).
7. M.A. Ulibarri, I. Pavlovic, C. Barriga, M.C. Hermosin and J. Cornejo, *Appl. Clay Sci.*, **18**, 17 (2001).
8. B. Houri, A. Legrouri, A. Barroug, C. Forano and J.P. Besse, *J. Chim. Phys.*, **96**, 455 (1999).
9. F. Kovanda, E. Kovacsova and D. Kolousek, *Coll. Czech. Chem. Commun.*, **64**, 1517 (1999).
10. Y. Seida and Y. Nakano, *Water Res.*, **36**, 1306 (2002).
11. R. Nomura, T. Mori, E. Kanezaki and T. Yaburani, *Int. J. Mod. Phys.*, *B*, **17**, 1458 (2002).
12. M.C. Hermosin and J. Cornejo, *Chemosphere*, **24**, 1493 (1992).
13. O.R. Pal and A.K. Vanjara, *Sep. Purif. Technol.*, **24**, 167 (2001).
14. D. Yaron-Marcovich, S. Nir and Y. Chen, *Appl. Clay Sci.*, **24**, 167 (2004).
15. S.L. Neitsch, K.J. McInnes, S.A. Senseman, G.N. White and E.E. Simanek, *Chemosphere*, **64**, 704 (2006).
16. H. Tributh and G. Lagaly, *GIT Fachzeitschrift Fuer Das Laboratorium* **30**, 524; 771 (1986).
17. E. Bojemueller, A. Nennemann and G. Lagaly, *Appl. Clay Sci*. **18**, 277 (2001).
18. Y.H. Hsu, M.K. Wang, C.W. Pai and Y.S. Wang, *Appl. Clay Sci.*, **16**, 147 (2000).
19. H. Ceylan, P. Battal, S. Kubilay and T. Sahan, III. Ulusal Kromatografi Kongresi, Isparta (2002).
20. C.J. Inacio, C. Taviot, C. Forano and J.P. Besse, *Appl. Clay Sci.*, **18**, 255 (2001).
21. H. Arnolds, *J. Phys. Chem., B*, **108**, 14311 (2004).