Asian Journal of Chemistry; Vol. 25, No. 2 (2013), 947-950

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.13201

Adsorption of the 2,2-Dichlorovinylphosphate on Raw and Modified Bentonites

VAHAP YÖNTEN[1,*] and SENOL KUBILAY[2]

[1]The Technology of Chemistry, Vocational School, Tunceli University, 62000 Tunceli, Turkey
[2]Department of Chemistry, Faculty of Art and Science, Yuzuncu Yil University, 65080 Van, Turkey

*Corresponding author: Tel/Fax: +90 428 2131757; +90 428 2131566; E-mail: vyonten@hotmail.com

(*Received*: 8 December 2011; *Accepted*: 27 August 2012) AJC-12017

This study aims to investigate the adsorption of the 2,2-dichlorovinylphosphate (DDVP) on raw and modified bentonite *via* high pressure liquid chromatography and infrared spectroscopy. The modified bentonites were prepared by adding HNO_3 and Na_2CO_3. The Freundlich adsorption isotherm defines 2,2-dichlorovinylphosphate adsorption in aqueous and aqueous ethanol solutions through raw and modified bentonite. Variables such as temperature, time and pH were observed on 2,2-dichlorovinylphosphate adsorption. Then the capacity for maximum 2,2-dichlorovinylphosphate adsorption was measured on modified bentonite with HNO_3 under the conditions of pH 3 and 40 ºC. The modified bentonite with Na_2CO_3 clay used in experimental work played a major role on the adsorption of 2,2-dichlorovinylphosphate; thus modified bentonite with Na_2CO_3 is considered to possess better characteristics than modified bentonite with HNO_3 and raw bentonite. The Freundlich isotherms of modified bentonite with Na_2CO_3 in aqueous-ethanol solution were found to be better than isotherms of aqueous solution for a much better 2,2-dichlorovinylphosphate adsorption.

Key Words: Adsorption, Bentonite, Insecticides, 2,2-Dichlorovinylphosphate.

INTRODUCTION

The environmental contamination associated with the presence and accumulation of toxic and dangerous chemicals in soil as well as at surface and within ground waters may be pondered. Chemicals that are highly soluble in water, minimally adsorbed by soil particles, not readily degradable, can move rapidly through the infiltrating water and hence, are likely to be found within ground waters[1-3]. Past few decades have witnessed to an increasing utilization of a wide range of pesticides in agriculture that have finally found their way directly or indirectly into soil. The risk for these compounds to contaminate human nutrition and drinking water necessitated a comprehensive research into the fate and behaviour of pesticides as well as other organic molecules. Organic molecules are not as dangerous as pesticides; nevertheless, they are encountered as degradation products of pesticides and are also able to behave as model compounds in soil. The fate and behaviour of pesticides in soil environments are governed by various retention, transportation and transformation processes. These processes determine both the efficacy of pesticides in controlling target organisms and their potential for environmental hazards. Transportation and transformation processes of pesticides in soil to a great extent depend on their retention by the solid organo-mineral phase. Despite retention includes all processes that prevent or delay the movement of pesticides in soil, the primary means of retention is the adsorption of pesticides on soil constituents. The most important soil constituents for adsorption are clay minerals and organic matter[1,2].

Many investigations have indicated that clay minerals are promising for environmental remediation, in particular for the removal of organic and inorganic pollutants from water[4-9]. Clay minerals have 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 in order to eliminate these pollutants from water[10-13].

This study was conducted in order to investigate the adsorption of 2,2-dichlorovinylphosphate pesticide from aqueous solutions based on adsorption isotherms. Three different clay types, raw bentonite, modified bentonite with HNO_3 and modified bentonite with Na_2CO_3 were studied concerning 2,2-dichlorovinylphosphate adsorption. Variables such as temperature and pH were measured.

EXPERIMENTAL

2,2-Dichlorovinylphosphate were delivered from Hektas (Kocaeli,Turkey). These insecticides are widely used in agriculture and in settlement areas. Bentonite was obtained from The Department of Mine Technology (Tokat, Turkey). Percentage of oxide over bentonite is indicated in Table-1. Other chemicals (HCl, Na_2CO_3, HNO_3, NaOH, Aceto nitrile *etc.*) used in this work were purchased from Merck (Darmstadt, Germany).

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 Na_2CO_3 and modified bentonite with HNO_3: 200 g of original bentonite was eliminated by 200-400 mesh sieves and stored at 100 ºC for a period of 48 h. The procedure for the production of calcined bentonite was stopped to be stored in a desiccator primarily for further uses. 0.8 g Na_2CO_3 was dissolved in water for modified bentonite with Na_2CO_3. After the solution of 40 g clay was added to solution, it was centrifugated at 450 rpm for 1 h. The samples were taken into oven at 800 ºC for 2 h. The calcined bentonite was washed with 3 % HCl, dried at room temperature and then stored for further use in desiccators. For the preparation of modified bentonite with HNO_3, 0.75 molar HNO_3 and 25 g clay were mixed and boiled for one hour with back fridge, centrifugated and heated for 1.5 h, and then stored to use in desiccators for such other clays.

Cation enhancing capacity of raw bentonite, modified bentonite with Na_2CO_3 and modified bentonite with HNO_3: This method is based on adsorption of blue methylene over some particles. A suspension of 1 g clay and 150 mL distilled water was prepared in the laboratory. The pH value of suspension was calibrated to 3.8 with H_2SO_4. Blue methylene was added to the suspension with 3 or 5 mL into the shaker for 3 min. This process was stopped, when a clear blue colour was observed. The cation enhancing capacity of raw bentonite, modified bentonite with Na_2CO_3 and modified bentonite with HNO_3 were calculated (Table-2) in the same manner with the method displayed in eqn. 1:

$$\text{Capacity of cation enhance (CCE)} = \frac{E \times V}{W} \qquad (1)$$

TABLE-2
CAPACITY OF CATION ENHANCE OF RAW AND MODIFIED BENTONITE

	E	v	w	CCE (meg/100 g clays)
RB	0.01	113	1.0	1.13
MBB	0.01	86	1.0	0.86
MBA	0.01	68	1.0	0.68

RB = Raw bentonite, MBB = Modified bentonite with Na_2CO_3 and MBA = Modified bentonite with HNO_3, CCE = Capacity of cation enhance.

Adsorption experiments: The change of adsorption on clays was performed in three ways *i.e.*, time, pH and temperature concentration based on adsorption. The suspensions were prepared with 1 g clays as a sorbent and 2, 4, 6, 8, 12, 14, 16, 18, 20 μL pesticide solutions in aqueous solution. They were shaken at 20, 25, 30, 35 and 40 ºC temperatures in pH 3, 4, 5, 7, 8 and 9 with 0.05 M HCl or NaOH. These suspensions were shaken for 24 h and centrifuged under the same conditions with the adsorption isotherm experiments. The equilibrium pH and 2,2-dichlorovinylphosphate concentrations were calculated for the supernatants at different times and temperatures[14]. A method used by Battal *et al.*,[15] was modified in order to determine the amount of adsorbed pesticide on bentonite. Specific insecticide was prepared in concentrations, the device could read the values in reference to the clay and the resulting supernatants were treated with HPLC. The chromatograms of these standards are presented in Fig. 1. The column for insecticide during certain periods refers to transition periods. We have carried out this study in the manner indicated on this graph. After equilibration, the dispersions were centrifuged and the supernatant was filtered. The adsorbed amount (Q_e) was calculated from the difference in concentration between the initial (C_o) and the equilibrium (C_e) solutions. Blanks without insecticide and triplicates of each adsorption point were used in each series of experiments. The supernatants were filtered so as to determine the contaminant concentration using a Shimadzu HPLC (Japon, Kyoto) system with an μBondapak C_{18} column, 18 % acetonitrile water at 1.5 mL/min was used as an eluent, detection was made *via* UV and column temperature was fixed to 55 ºC. Infrared spectra were recorded on a FT-IR spectrometer (Bio Rad, England, London) purged with dried air.

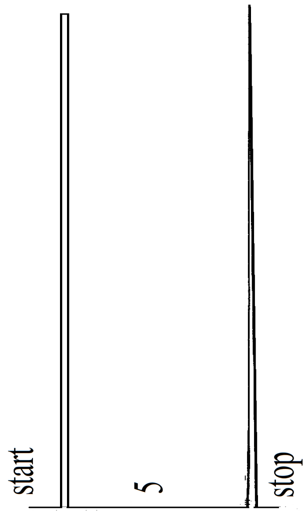

Fig. 1. Chromatogram of 2,2 Dichlorovinylphosphate on HPLC, UV detector

RESULTS AND DISCUSSION

Infrared spectra of raw bentonite lattice absorption in the OH-stretching band in 3643 cm^{-1} is indicated in Fig. 2. 3464 cm^{-1} was also bound and zeolitic water OH-stretching absorption bands were seen in Fig. 2. 2346 cm^{-1} was the next spectrum of the raw bentonite and pruning was the property of Si-H bond. 1667 cm^{-1} in the raw bentonite OH deformation of water occurs in Fig. 2 when the spectrum at 1625 cm^{-1} was treated with modified bentonite with Na_2CO_3, C=O bond was observed. Bentonite 476 cm^{-1} and the other two Si-O bonds as the deformation has occurred in Fig. 2.

Kinetic study: The interaction of insecticide with clays at different concentrations was examined as a function of the contact period. The adsorbed insecticide for each clay and their times are displayed in Fig. 3. It represented that maximum adsorption of 2,2-dichlorovinylphosphate was reached at 30th hours. The adsorption of 2,2-dichlorovinylphosphate at distinct

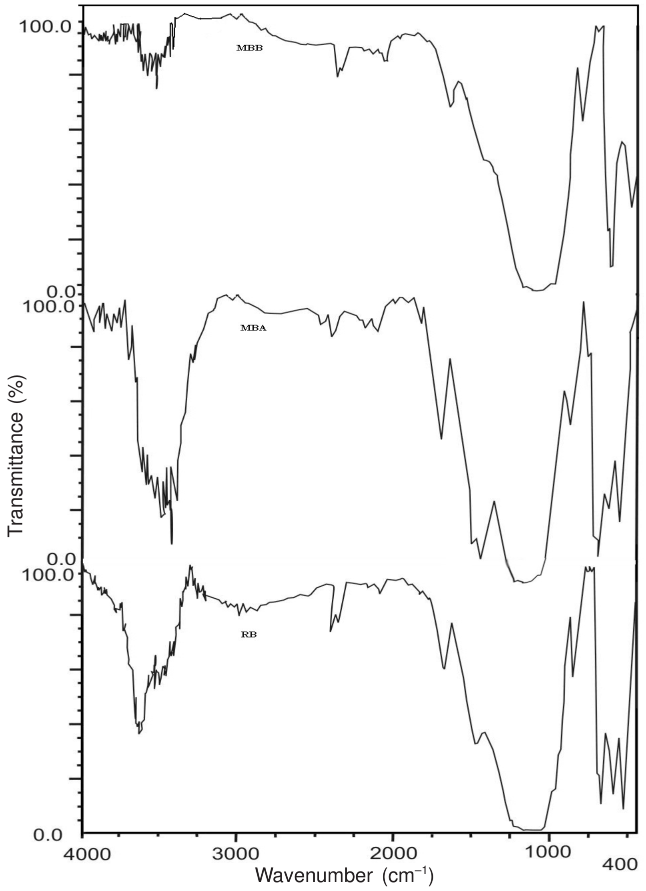

Fig. 2. FT-IR graphic of raw bentonite, modified bentonite with Na_2CO_3 and modified bentonite with HNO_3

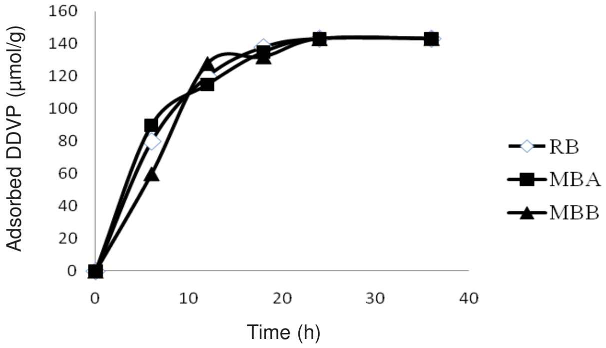

Fig. 3. Effect of time on adsorption of 2,2-dichlorovinylphosphate

pH values is given in Table-3. The maximum adsorption of insecticide was observed at pH 3.0 by modified bentonite with HNO_3. Adsorption of modified bentonite with HNO_3 on clays at pH 5 was observed at maximum levels[16].

TABLE-3
EFFECT OF pH ON ADSORPTION OF 2,2-DICHLOROVINYLPHOSPHATE BY RAW BENTONITE, MODIFIED BENTONITE WITH HNO_3 MODIFIED BENTONITE WITH Na_2CO_3

pH	Raw bentonite (µmol/g)	Modified bentonite with HNO_3 (µmol/g)	Modified bentonite with Na_2CO_3 (µmol/g)
3	118.5	143.8	138.5
5	119.4	140.0	140.8
7	130.0	120.7	115.5
9	125.6	123.4	112.6

The maximum 2,2-dichlorovinylphosphate adsorption capacity was examined at 40 ºC on raw and modified bentonite as indicated in Fig. 4. When the temperature increased, the capacity of adsorption increased as well. The increasing of equilibrium adsorption proportionally with the temperature showed that the process of adsorption was endothermic. The increasing and decreasing of adsorption at some temperature provided that not only physically adsorption but also chemical adsorption exists[17]. This figure indicated that maximum adsorption was reached at 40 ºC by modified bentonite with Na_2CO_3. At this temperature, the maximum adsorption capacity of modified bentonite with Na_2CO_3 was better than the maximum adsorption capacity of raw bentonite and modified bentonite with HNO_3.

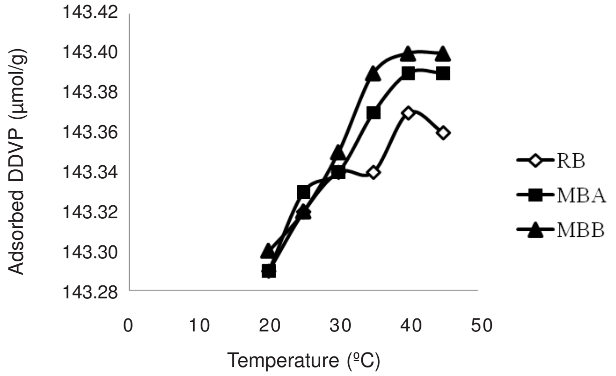

Fig. 4. Effect of temperature on adsorption of 2,2-dichlorovinylphosphate

Adsorption isotherms of 2,2-dichlorovinylphosphate on raw bentonite, modified bentonite with Na_2CO_3 and modified bentonite with HNO_3: The data at the equilibrium point is known as adsorption isotherms. Adsorption systems were set for main equipment. It has been explained to be due to different isotherm shapes as positive, smooth and concave. The amount of adsorbed 2,2-dichlorovinylphosphate increases with the equilibrium concentrations of 2,2-dichlorovinylphosphate.

Fig. 5 represented adsorption isotherms of pesticide on raw and modified bentonite. It has been observed that the capacity of adsorption on modified bentonite with Na_2CO_3 was better than the capacity of adsorption on raw bentonite and modified bentonite with HNO_3. In Fig. 5 the maximum mass of adsorption of pesticide on equilibrium (Q_e) was measured as 5.9 mmol/g, 5.4 mmol/g and 5.0 mmol/g on modified bentonite with Na_2CO_3, modified bentonite with HNO_3 and raw bentonite respectively. Then Q_e reaches a plateau. When concentration of pesticide on equilibrium (C_e) value increased, Q_e increased more rapidly than it does at a low C_e value. This can be explained as that the adsorption continues through two steps, saturation of the external sites is followed by an interlayer process that operates at high C_e values[16]. Some models were developed to describe adsorption condition. Due to the shape of the isotherms, the sorption data were analyzed according to Freundlich equation as given below (2).

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

where, K is the amount of pesticide per unit weight of the clay, C_e the equilibrium concentration of the adsorbate, while

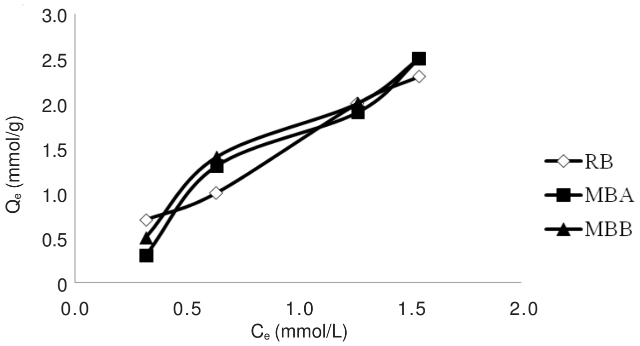

Fig. 5. Adsorption isotherms of 2,2-dichlorovinylphosphate on raw bentonite, modified bentonite with HNO_3 and modified bentonite with Na_2CO_3 in aqueous

K and n are constants that yield estimates of the adsorption capacity and intensity, respectively[16]. The linear equation of isotherm is presented below (3).

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

Isotherm constants using the linear equation are shown in Table-4. Fig. 6 showed that the modified bentonite with Na_2CO_3 used in this study with aqueous- ethanol solutions had a better adsorption capacity than modified bentonite with Na_2CO_3, raw bentonite and modified bentonite with HNO_3 used in water solution.

TABLE-4
FREUNDLICH PARAMETERS FOR 2,2-DICHLOROVINYL-PHOSPHATE ADSORPTION ON RAW BENTONITE (RB), MODIFIED BENTONITE WITH HNO_3 (MBA) AND MODIFIED BENTONITE WITH Na_2CO_3 (MBB)

	Freundlich		
Adsorbent	K_f (mmol/g)	n	R^2
RB	908.33	0.887	0.98
MBA	5628.61	1.327	0.99
MBB	26.40	0.610	0.99

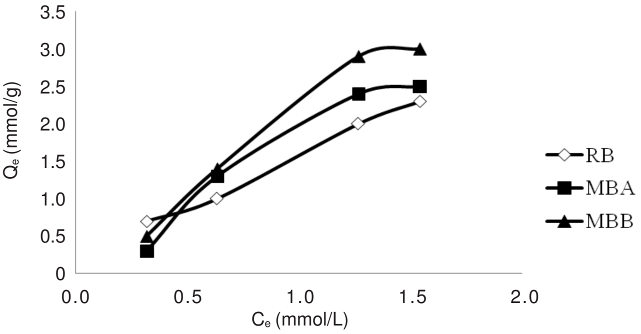

Fig. 6. Adsorption isotherms of 2,2-dichlorovinylphosphate on raw bentonite, modified bentonite with HNO_3 and modified bentonite with Na_2CO_3 in aqueous-ethanol solutions

Conclusion

The modified bentonite ensures a simple possibility 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 2,2-dichlorovinylphosphate adsorption. The adsorption of insecticide on modified bentonite with Na_2CO_3 displays a higher adsorption on raw bentonite and modified bentonite with HNO_3. Combination of the results from aqueous-ethanol solutions employed to study the adsorption of 2,2-dichlorovinylphosphate on raw bentonite, modified bentonite with acid and modified bentonite with base samples leads to the following conclusions. Utilization of ethanol instead of water is better. Therefore, we can use a little ethanol with water whereas 2,2-dichlorovinylphosphate is used in agricultural areas. Thus, the controls for removing hazardous pollutants were provided by modified bentonite with base, which are used in this study with aqueous ethanol solutions. The results illustrated that modified bentonite with base is quite a better adsorbent for 2,2-dichlorovinylphosphate than aqueous. Further research is needed to optimize the application of this compound as an adsorbent of these herbicides from contaminated waters.

ACKNOWLEDGEMENTS

The authors thank Yüzüncü Yil University for supplying laboratory facilities and funding.

REFERENCES

1. J.A. Goodrich, Jr. Lynkis 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. C. Barriga, M. Gaitan, I. Pavlovic, M.A. Ulibarri, M.C. Hermosin and J. Cornejo, *J. Mater. Chem.*, **12**, 1027 (2002).
5. M.A. Ulibarri, I. Pavlovic, C. Barriga, M.C. Hermosin and J. Cornejo, *Appl. Clay Sci.*, **18**, 17 (2001).
6. B. Houri, A. Legrouri, A. Barroug, C. Forano and J.P. Besse, *J. Chim. Phys.*, **96**, 455 (1999).
7. F. Kovanda, E. Kovacsova and D. Kolousek, *Coll. Czech. Chem. Commun.*, **64**, 1517 (1999).
8. Y. Seida and Y. Nakano, *Water Res.*, **36**, 1306 (2002).
9. R. Nomura, T. Mori, E. Kanezaki and T. Yaburani, *Int. J. Mod. Phys.*, **B17**, 1458 (2003).
10. M.C. Hermosín and J. Cornejo, *Chemosphere,* **24**, 1493 (1992).
11. O.R. Pal and A.K. Vanjara, *Sep. Purif. Technol.*, **24**, 167 (2001).
12. D. Yaron-Marcovich, S. Nir and Y. Chen, *Appl. Clay Sci.*, **24**, 167 (2004).
13. S.L. Neitsch, K.J. Mcinnes, S.A. Senseman, G.N. White and E.E. Simanek, *Chemosphere,* **64**, 704 (2006).
14. Y.H. Hsu, M.K. Wang, C.W. Pai and Y.S. Wang, *Appl. Clay Sci.*, **16**, 147 (2000).
15. H. Ceylan, P. Battal, S. Kubilay and T. Sahan, The Adsorption of Kinetin and Indol 3-Acetic Acid on Modified Bentonite, Ulusal Kromatografi Kongresi, Isparta, Turkey, p. 3 (2002).
16. C.J. Inacio, C. Taviot, C. Forano and J.P. Besse, *Appl. Clay Sci.*, **18**, 255, (2001).
17. H. Arnolds, *J. Phys. Chem.*, **B 108**, 14311 (2004).