The Adsorption of the 2,2 Dichlorovinylphosfate on Raw and Modified Bentonites

[1]Vahap Yonten and [2]Senol Kubilay
[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

Abstract: This study aimed to investigate the adsorption of the 2,2 Dichlorovinylphosfate (DDVP) on raw and modified bentonite using High Pressure Liquid Chromatography (HPLC) and infrared spectroscopy (FT-IR). The modified bentonite were prepared by adding HNO_3 and Na_2CO_3. The Freundlich adsorption isotherm defines DDVP adsorption in aqueous and ethanol-aqueous solutions by raw and modified bentonite. The variables of temperature, time and pH were observed on adsorption of DDVP. Then maximum adsorption of DDVP capacity was measured on bentonite modified with HNO_3 in pH 3.0 and 40°C . The MBB clay used in experimental work played a major role on the adsorption of DDVP so MBB has better characteristics than other adsorbents and The Freundlich isotherms of MBB in aqueous ethanol solution was better than isotherms of aqueous solution for much better to adsorb of DDVP.

Key words: Adsorption, bentonite, insecticides, 2,2 Dichlorovinylphosfate, aqueous solutions, adsorbents, Turkey

INTRODUCTION

The environmental contamination associated with the presence and accumulation of poison and dangerous chemicals in soil as well as in surface and ground water may be considered. Chemicals that 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 (Goodrich et al., 1991; Kolpin et al., 1998; Kalkhoff et al., 1998).

The past few decades have seen increasing use of a widerange of pesticides in agriculture that finally find their way directly or indirectly into soils. The risk of these compounds entering the human food and drinking water has given rise to a need for extensive research into the fate and behavior of pesticides and other organic molecules. The organic molecules are not more dangerous as pesticides but they are found as degradation products of pesticides and can also act as model compounds in soil.

The fate and behaviour of the 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 soils depend strongly on their retention by the solid organo-mineral phase. Although, retention includes all the processes that prevent or retard movement of pesticides in soils, the primary means of retention is adsorption of pesticides on soil constituents. The most important soil constituents for adsorption are clay minerals and organic matter (Symonds et al., 2004; Barriga et al., 2002).

Many investigations have shown that clays are promising for environmental remediation, in particular for the removal of organic and inorganic pollutants from water (Barriga et al., 2002; Ulibarri et al., 2001; Houri et al., 1999; Kovanda et al., 1999; Seida and Nakano, 2002; Nomura et al., 2003). 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 (Hermosin and Cornejo, 1992; Pal and Vanjara, 2001; Yaron-Marcovich et al., 2004; Neitsch et al., 2006).

The present study was performed to investigate the adsorption of DDVP pesticides from aqueous solutions based on adsorption isotherms. Three different clays, Raw Bentonite (RB), Modified Bentonite prepared by HNO_3 (MBA) and Modified Bentonite prepared by Na_2CO_3 (MBB) were studied on adsorption of DDVP. The variables of temperature and pH were measured.

MATERIALS AND METHODS

About 2,2 Dichlorovinylphosfate were supplied from Fig. 1. These insecticide are widely used in agriculture and areas that people lives. Bentonite was
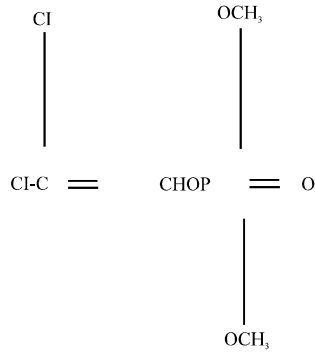

Fig. 1: The structure of 2,2 Dichlorovinylphosfate

Table 1: The capacity of cation enhance of raw and modified bentonite

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

Table 2: The per cent oxides of raw bentonite (Tubitak)

Oxides	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

obtained from The Department of Mine Technology (Tokat, Turkey). Percent of oxide on bentonite was shown in Table 1 and 2.

The other chemicals (HCl, Na_2CO_3, HNO_3, NaOH and aceto nitrile, etc.) used in this research were purchased from Merck (Darmstadt, Germany).

The preparation of RB, MBB and MBA: About 200 g of original bentonite was eliminated by 200-400 mesh sieves and stored at 100°C for 48 h. The procedure for the production of calcined bentonite was ended as stored in a desiccator prior for further uses. A total of 0.8 g Na_2CO_3 was solved in water for MBB. After the solution of 40 g clays were added to solution, it was centrifugated at 450 rpm for 1 h. The samples were taken into the oven at 800°C for 2 h.

The calcined bentonite was washed with 3% HCl and dried at room temperature and then stored to use in a desiccators. For the preparing of MBA, 0.75 molar HNO_3 and 25 g clay were mixture and boiled for 1 h with back fridge, it was centrifugated and heated for 1.5 h and then stored to use in a desiccators such other clays.

The capacity of cation enhance of RB, MBB and MBA: This method was based on adsorption of blue methylene on some particulars. The suspension of 1 g clays and 150 mL distil water were prepared in the laboratory. The pH of suspension was adjusted to 3.8 with H_2SO_4. The blue methylene was added to the suspension with 3

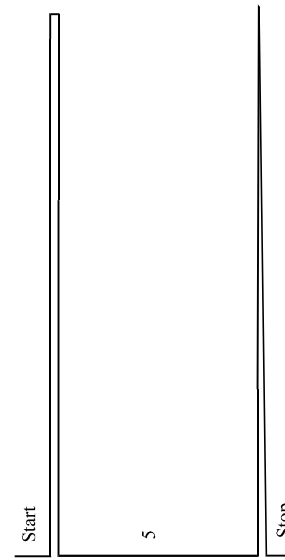
Fig. 2: The chromatogram of 2,2 Dichlorovinylphosfate on HPLC and UV detector

or 5 mL to shaker for 3 min. This process was ended when a clear blue was observed. The capacity of cation enhance of RB, MBB and MBA were calculated the same as this method shown in Eq. 1:

$$CCE = E\left(\frac{V}{W}\right) \tag{1}$$

Adsorption experiments: The change of adsorption on clays was performed in three ways; time, pH and temperature concentration dependent on adsorption. The suspensions were prepared with 1 g clays as a sorbent and 2.0, 4.0, 6.0, 8.0, 12, 14, 16, 18 and 20 μL pesticide solutions in aqueous solution.

They were shaken at 20, 25, 30, 35 and 40°C temperatures in pH 3.0, 4.0, 5.0, 7.0, 8.0 and 9.0 with 0.05 M HCl or NaOH. These suspensions were shaken for 24 h and centrifuged under the same conditions as the adsorption isotherm experiments. The equilibrium pH and DDVP concentrations were calculated for the supernatants in different times and temperature (Hsu *et al.*, 2000). A method used by Battal was modified to determine the amount of adsorbed pesticide on bentonite.

Specific insecticide was prepared in concentrations, the device can read the values in reference to the clay and the resulting supernatants were treated with HPLC. The chromato grams of these standarts were shown in Fig. 2. The column for insecticide during certain periods are expressed as transition periods. The researchers have carried out this study as taken a reference on this graph.
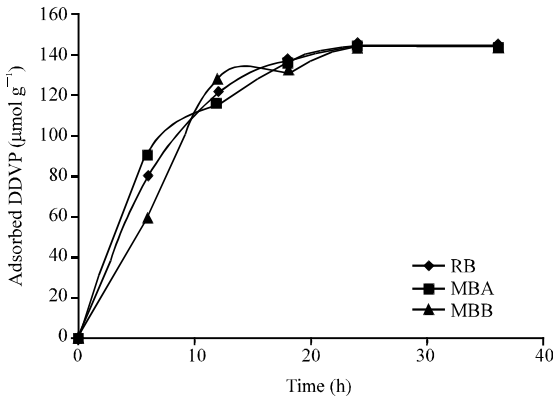
Fig. 3: Effect of time on adsorption of DDVP

After equilibration, 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 insecticide 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 (Japon, Kyoto) system with an µBondapak C18 column, 18% acetonitrile water at 1.5 mL min⁻¹ was used as an eluent, detection was made by UV and column temperature was fixed as 55°C. 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. Figure 3 shows the FT-IR spectra of origin and modified bentonites obtained in this study.

RESULTS AND DISCUSSION

IR Study: Infrared spectra of RB lattice absorption in the OH-stretching band in 3643 cm⁻¹ was shown in Fig. 4. The 3464 cm⁻¹ was also bound and zeolitic water OH-stretching absorption bands were shown in Fig. 5. The 2346 cm⁻¹ was the next spectrum of the RB and pruning were the property of Si-H bond. A 1667 cm⁻¹ in the RboH deformation of water shown in Fig. 5 when the spectrum at 1625 cm⁻¹ was treated with MBB, C = O bond was observed. Bentonite 476 cm⁻¹ and the other two Si-O bonds as the deformation has shown in Fig. 5.

The kinetic study: The interaction of insecticide with clays at the different concentrations was investigated as a contact period's function. The adsorbed insecticide for each clay and their times are shown in Fig. 3. It represented that maximum adsorption of DDVP reached
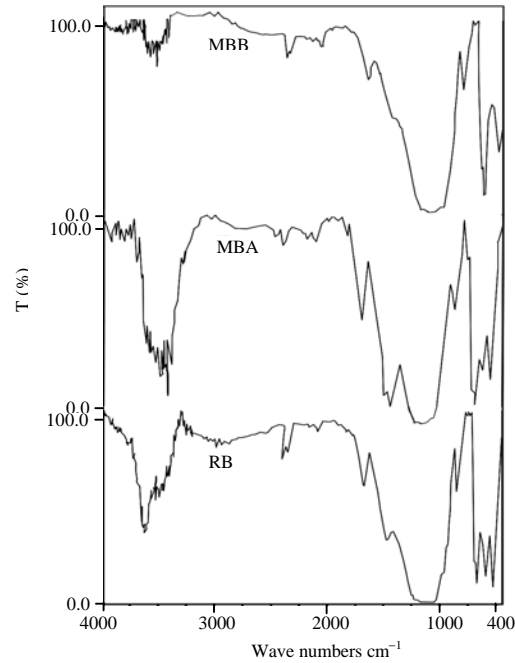

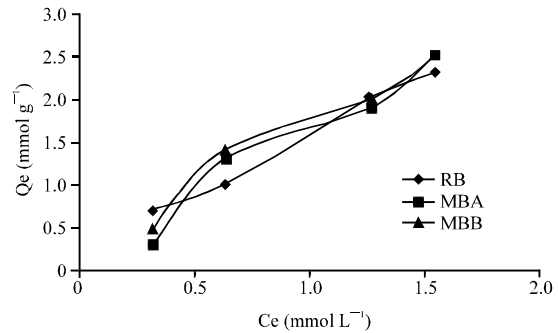Fig. 4: FT-IR graphic of RB, MBB and MBA

Fig. 5: The adsorption isotherms of DDVP on RB, MBA and MBB in aqueous

Table 3: Effect of pH on adsorption of DDVP by RB, MBA and MBB

pH	RB (µmol g⁻¹)	MBA (µmol g⁻¹)	MBB (µmol g⁻¹)
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

on 30th h. The adsorption of DDVP at distinct pH is shown in Table 3. The maximum adsorption of insecticide was observed at pH 3.0 by MBA. Adsorption of MCPA on clays at pH 5.0 had been observed at maximum levels (Inacio *et al.*, 2001).

The maximum capacity of adsorption of DDVP was studied at 40°C on raw and modified bentonite as shown in Fig. 6. When the temperature was increased, the capacity of adsorption was increased too. The increasing
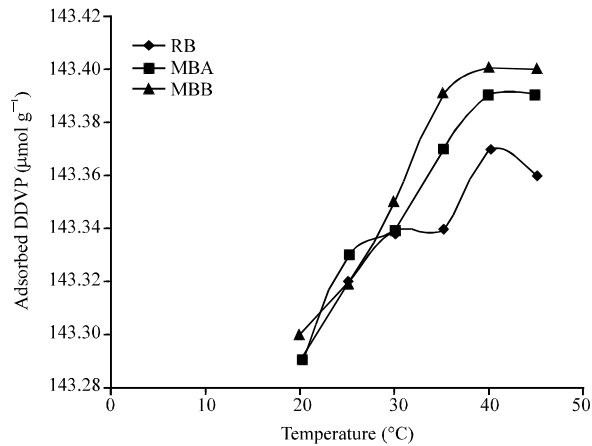
Fig. 6: Effect of temperature on adsorption of DDVP

Fig. 7: The adsorption isotherms of DDVP on RB, MBA and MBB in aqueous-ethanol solutions

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 (Symonds *et al.*, 2004). This figure showed that maximum adsorption was reach at 40°C by MBB. In this temperature, the maximum adsorption capacity of MBB was better than the maximum adsorption capacity of RB and MBA.

Adsorption isotherms of DDVP on RB, MBB and MBA:
The data at the equilibrium point is known as adsorption isotherms. Adsorption systems were set for main equipment. It has been explained due to the shapes isotherms as positive, smooth and concave. The amount of adsorbed DDVP increases with the equilibrium concentrations of DDVP.

Figure 5 shows adsorption isotherms of pesticide on raw and modified bentonite. It has been observed that the capacity of adsorption on MBB was better than the capacity of adsorption on RB and MBA. In Fig. 5, the maximum Q_e was measured 5.9, 5.4 and 5.0 mmol g^{-1} on MBB, MBA and RB, 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 (Inacio *et al.*, 2001). Some models were matured to describe adsorption condition. Owing to the shape of the isotherms, the sorption data were analyzed according to Freundlich Eq. 2:

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

Where:
K = The amount of pesticide per unit weight of the clay
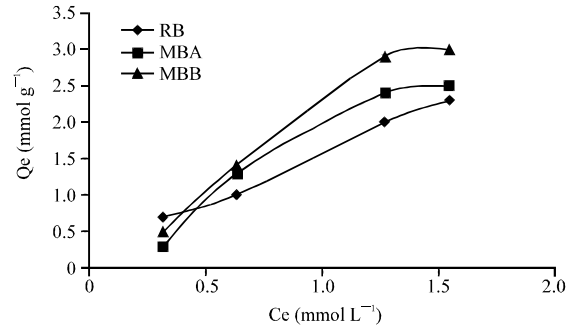C_e = The equilibrium concentration of the adsorbate

Table 4: Freundlich parameters for DDVP adsorption on RB, MBA and MBB

Adsorbent	Freundlich		
	K_f (mmol g^{-1})	n	R^2
RB	908.33	0.887	0.98
MBA	5628.61	1.327	0.99
BB	26.40	0.610	0.99

K and n = The constants that give estimates of the adsorption capacity and intensity, respectively (Inacio *et al.*, 2001)

The linear equation of isotherm is given by Eq. 3:

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

Constants of isotherm using the linear equation are shown in Table 4. Figure 7 showed that MBB used in this study with aqueous-ethanol solutions was better adsorption capacity than MBB, RB and MBA used in water solution.

CONCLUSION

The modified bentonite 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 DDVP adsorption. The adsorption of insecticide on MBB show higher adsorption on RB and MBA. The combination of the results from aqueous ethanol solutions employed to study headsorption of 2,2 Dichlorovinylphosfate on raw bentonite, modified bentonite with acid and modified bentonite with base samples leads to the following conclusions. The using ethanol in place of water is better than using water. So, the researchers can use a little ethanol with water while 2,2 Dichlorovinylphosfate 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 2,2 Dichlorovinylphosfate from aqueous. Research is needed to optimize the application of this compound as adsorbent of these herbicides from contaminated waters.

ACKNOWLEDGEMENT

NOMENCLATURE

C_e	=	The Concentration of pesticides on the equilibrium
CCE	=	The Capacity of Cation Enhance (meg/100 g clays)
E	=	The concentration of blue methylene (0.01 N)
MBB	=	Modified Bentonite with Na_2CO_3 (base)
MBA	=	Modified Bentonite with HNO_3 (acid)
RB	=	Raw Bentonite
Tubitak	=	The science academy of Turkey
V	=	The Volume of blue methylene which is consumed (mL)
W	=	The mass of clays (g)
Q_e	=	The mass of adsorption of pesticide on the equilibrium
DDVP	=	2,2 Dichlorovinylphosfate

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