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Mechanism of Diazinon Adsorption on Iron Modified Montmorillonite

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ABSTRACT

The study was carried out with the objective of developing suitable and sustainable low cost adsorbent materials for diazinon, an organophosphate pollutant used as a pesticide. Montmorillonite modified with iron was used. Two different types of iron-montmorillonite, each having different contents of iron and synthesized with different pH and levels of Fe hydrolysis were used. One was denoted "Fe-modified" and the other denoted as "FeOH-modified". The color of the samples changed from greyish green to light-reddish brown after the modification. X-ray diffraction and physical observations were used for characterization of the samples. The d-spacing of the samples was greater than 15 Å, indicating the formation of iron hydroxides in the interlayer space of montmorillonite. The amount of adsorption was calculated from the difference between the initial and the final concentration of diazinon. The adsorption data were analyzed using the Langmuir adsorption isotherms. The amounts of diazinon adsorbed were 58.8 and 54.1 mmol·kg^{-1} for Fe-modified and FeOH-modified respectively. The steep rise in their adsorption isotherms indicated the possibility of adsorption for low level of diazinon in polluted water.

KEYWORDS

Pesticide; Diazinon; Adsorption

1. Introduction

The contamination of soil, ground water and surface water by pesticides is currently a significant concern throughout the world because many of these compounds are detrimental to both human health and the environment. Increasing use of pesticides in agriculture, and domestic activities for controlling pests are polluting water resources day by day. Pesticides form a strong class of water pollutants as they are mostly nonbiodegradable. Moreover, most pesticides are carcinogenic. Modern agriculture relies increasingly on the use of pesticides to meet the ever-growing need for food and fiber. While pesticides are indispensable to increase the quantity and quality of food commodities and to safe guard society through better health and higher living standards, their off-site migration and detrimental effects on surface wa-

ter and groundwater quality are of environmental concern. Among newly developed pesticides, organophosphate pesticides are most commonly used [1]. This is due to their reduced persistence and shorter half-life as compared to organochlorine pesticides whose use is banned in many countries.

Diazinon is a broad spectrum organophosphorous insecticide classified by the World Health Organization (WHO) as "moderately hazardous" Class II [2]. It is used as a control for sucking and chewing insects and mites. It is also an active ingredient of some veterinary ectoparasiticides to control mange mites, ticks, lice, keds, biting flies, blowflies on sheep, cows, pigs, goats as well as horses [3]. It is relatively water soluble, moderately mobile and persistent in soil, hence it is a concern for ground and surface water derived drinking water. Toxic effects of diazinon are attributed to its inhibition of the enzyme acetylcholinesterase. It is also associated with

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toxicity to aquatic organisms at concentrations of 350 ng·l^{-1} with an LC50 of 4.4 mg·l^{-1} in killifish (48 h). Fatal human doses were found to be in the range of 90 to 440 mg·kg^{-1} [4]. Over 13 million lbs. of diazinon are applied annually in the United States alone. All residential uses in the US were banned starting December 31, 2004 [5]. In many developing countries, however, diazinon is still being used for multiple uses including indoor uses.

Various adsorbents have been used for the removal of diazinon from the environment through adsorption and they include the use of agricultural soil [6], use of surfactant modified agricultural soil [7] and Organo-Zeolites [8]. Adsorption provides one of the most efficient methods for the removal of pollutants from the environment. It is a means of limiting mobility of pollutants to a wider area once they get adsorbed. Owing to their adsorbent properties, clay minerals have often been used in different industrial and technological processes [9]. In recent years, much attention has been paid to the development of modified clays with improved sorption capacities.

Montmorillonite is one type of clay minerals and has been used as an adsorbent for a long time. It is a 2:1 clay mineral, characterized by its interlayer spacing and external surface. It is particularly suitable for many reactions, such as adsorption of heavy metal ions and organic compounds [10]. Its surface reactions are used to control different organic chemicals [11] such as azinfhosmethyl [12], atrazine [13], paraquat and diquat [14], triasulfuron [15] and triphenylmethane dyes [16]. The modification of expandable phyllosilicates with Fe to form materials that could be used as adsorbents has also been explored for a long time. These materials have shown important potential application as catalysts and adsorbents for inorganic pollutants. However, little is known about their application as adsorbents for organic pollutants such as organophosphate pollutants.

In the present study, adsorption of organophosphate pesticide diazinon was done using Fe-modified montmorillonite as a low cost adsorbent. The abundance of montmorillonite in nature, its expansion abilities and large interlayer space qualifies these phyllosilicates as useful adsorbents for such pollutants with generally large molecular size.

2. Materials and Methods

2.1. Description of Adsorbate

Diazinon was supplied by Dr. Ehrenstorfer-Schäfers laboratory. **Figure 1** shows its chemical structure. It is a colorless liquid pesticide with a faint ester like smell. It has a molecular weight of 304.35, water solubility of 40 mg·l^{-1} at 25˚C and log Kow of 3.81.

2.2. Iron Modification Procedure

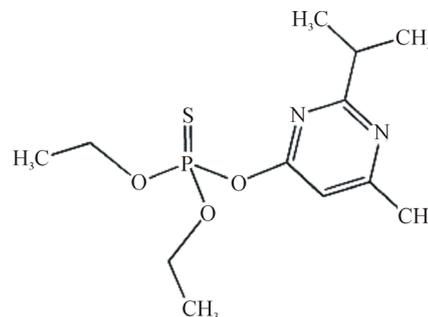Montmorillonite supplied by the Japan Clay Science So-

Figure 1. Chemical structure of diazinon.

ciety was used for making the Fe modified samples. Montmorillonite was initially saturated with Ca^{2+} by washing with 0.5 M CaCl$_2$. After the CaCl$_2$ washing, the samples were washed thrice with water and once with acetone. Finally, the samples were dried for 48 hours at 40˚C. After drying the samples were ground, sieved and stored in clean, dry jars. These were called Ca-montmorillonite.

Fe (NO$_3$)$_3$ purchased from Nacalay Tesque was used for iron modification. Two types of Fe modified samples were synthesized at different pH and NaOH hydrolysis. To Ca-montmorillonite, 0.01 M Fe (NO$_3$)$_3$ was added and shaken for 1 hour, centrifuged and decanted. This addition and centrifugation was done thrice. The samples were then washed thrice with water and once with acetone. Samples were then dried for 48 hours at 40˚C. After drying the samples were also ground, sieved and stored in clean, dry jars. These were called Fe-modified samples. For the second sample, dubbed FeOH-modified, the 0.01 M Fe (NO$_3$)$_3$ was pre hydrolyzed with NaOH to achieve and OH/Fe ratio of 2. The hydrolyzed solution was then added to Ca-montmorillonite samples and a similar procedure to the one used for the Fe modified sample was followed.

2.3. Sample Characterization

The three samples (Ca-montmorillonite, Fe-modified montmorillonite and FeOH-modified montmorillonite) were subjected to physical Characterisation by X-ray diffraction using a Rigaku Ultima IV X-ray Diffractometer and physical observations.

2.4. Water Adsorption Experiment

Water adsorption was measured by putting each 0.5 g of sample into glass weighing bottles and heat drying at 105˚C for 24 h. The samples were then kept in desiccators containing silica gel for cooling. After cooling, the samples were placed in desiccators containing saturated solutions of various salts at temperatures of 20˚C ± 1˚C. Samples were maintained at these humidity levels for 3 weeks with weighing at intervals. The equilibrium mass

of each sample was measured and the amount of water adsorbed was calculated from the difference between the equilibrium mass and mass of sample dried at 105°C for 24 h. Saturated solutions of salts with various relative humidities (RH) that were used were: LiCl (RH = 0.15), CH_3COOK (RH = 0.20), $CaCl_2$ (RH = 0.31), KNO_2 (RH = 0.45), $Na_2Cr_2O_7$ (RH = 0.52), $NaNO_2$ (RH = 0.66), $NaClO_3$ (RH = 0.75), $(NH_4)_2SO_4$ (RH = 0.81), Pb $(NO_3)_2$ (RH = 0.98).

2.5. Determination of Total Iron Content

The total Fe content in samples was measured with extraction by 1 M HCl. To 0.1 g of iron modified sample, 20 ml of 1 M HCL was added and shaken in a reciprocal shaker for 1 h after which the sample was centrifuged and decanted. This was repeated until the samples were free from Iron evidenced by a change in color to greyish green, the original color of unmodified montmorillonite. Iron analysis was done using Atomic Absorption Spectrophotometry (AAS) with a Hitachi Z-5000 spectrophotometer.

2.6. Diazinon Adsorption Experiment

Diazinon (97.5%) purity was purchased from Dr. Ehrenstorfer-Schäfers laboratory, German. HPLC grade distilled water was purchased from Nacalay Tesque and acetonitrile from Kanto Chemical Co., INC. The concentrations of diazinon in solution were determined by a Jasco PU-2089 plus HPLC equipped with an Inertsil ODS-4 5 µm 4.6 × 150 mm column, 1.0 mL/Min Flow rate, UV detection at 246 and an Injection volume of 100 µL. A Jasco UV-2075 plus intelligent UV-Vis detector was used and results were obtained from a Hitachi D-2500 Chromato-integrator.

Diazinon adsorption experiments were conducted in glass tubes with screw caps lined with Teflon. All experiments were conducted in the tubes covered with aluminium foil at pH of 4. Concentrations ranging from 0 to 128 µmol/L were used. To 0.05 g sample of montmorillonite, 30 ml of pesticide solution were added. Samples were shaken in a reciprocal shaker for an equilibration time of 24 hours under room temperature. The amount of sample (0.05 g), shaking time (24 hours) and the initial pH of the solution (4) were all determined during preliminary experiments. Adsorption was calculated from the difference between the initial and equilibrium concentrations.

3. Results and Discussion

3.1. Characterization of Final Product

Visual observations indicated that, with Fe-modification, the color of the sample had changed from greyish green

(Ca-montmorillonite) to light-reddish brown (Fe-modified montmorillonite) and Dark-reddish brown (FeOH-modified montmorillonite). This indicated that Fe was present in the Fe modified samples. **Figure 2** shows the X-ray diffraction patterns of the three samples, Ca-montmorillonite, Fe-modified montmorillonite and FeOH-modified montmorillonite.

The XRD pattern for Ca-montmorillonite is typical for Calcium exchanged montmorillonite [17] with a d-spacing of 15.27 Å. With iron modification, the d-spacing changed to 15.33 Å for FeOH-modified and 15.38 Å for Fe-modified. This indicated that some iron was successfully intercalated into the interlayer space with some iron on the outer surfaces of the samples as well. The d-spacing values are obviously smaller than those of Fe-pillared clays in previous reports (2.5 ± 0.5 nm) [18]. However, they are similar to those reported in the other literature (about 1.54 nm) [19] as it is considered that hydrolyzates of iron ion are difficult to form stable and consistent structures.

3.2. Determination of Total Fe Content of Samples

The amount of Fe ions contained in the prepared sample was slightly higher than the CEC of the host montmorillonite. **Table 1** indicates the total iron results for the samples. It was clear that the Fe-modified sample had a higher total Fe of 140.7 Cmol/Kg in comparison to the FeOH-modified sample which had a total Fe of 128 Cmol/Kg. This was, to a large extent influenced by the level of hydrolysis which the Fe solution used during the modification had undergone. The Fe $(NO_3)_3$ solution that was used for the Fe-modified montmorillonite sample had gone through lesser hydrolysis with a preparation pH of 3.30. For the FeOH-modified sample, prior hydrolysis with NaOH to a pH of 5.34 may have resulted into a larger molecular size of Fe hence less possibility of penetrating into the interlayer space.

3.3. Adsorption Experiments

Adsorption experiments are useful to evaluate adsorption capacities of adsorbents and thermodynamic parameters like the energy of adsorption. Adsorption isotherms of water vapour on Ca-montmorillonite, Fe-modified montmorillonite and FeOH-modified montmorillonite at constant temperature of 20°C ± 1°C are shown in **Figure 3**. The isotherms indicate that the amount of water adsorbed by the montmorillonite samples increased with increasing RH. The water adsorption isotherms were Type II (S-shaped) sigmoidal function curves as commonly found for the sorption of water by clay [20]. However, the water adsorption was higher for the Fe modified than the rest of the samples. For all the samples adsorption
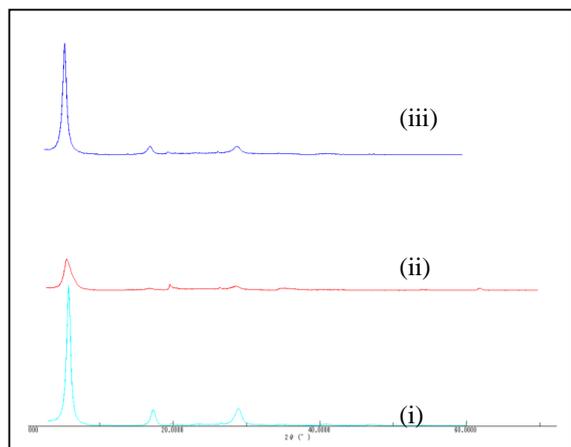
Figure 2. XRD patterns for (i) Ca-montmorillonite; (ii) Fe-modified and (iii) FeOH-modified montmorillonite.
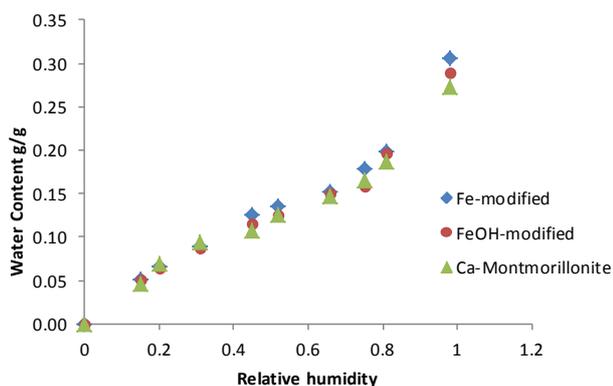

Figure 3. Water adsorption isotherm for Fe-modified, FeOH-modified and Ca-modified montmorillonite.

Table 1. Total iron content for Fe modified montmorillonite and FeOH modified montmorillonite.

SAMPLE	Fe (Cmol/Kg)
Fe-modified	140.7
FeOH-modified	128.0

increased rapidly until RH = 0.31. Then it increased gradually from 0.31 - 0.66 and again increased rapidly till RH = 0.98.

The isotherm was subjected to Langmuir analysis. The Xm values for the RH = 0.15 - 0.66 region were calculated for the Fe-modified, FeOH-modified and Ca-montmorillonite samples respectively. The maximum adsorption (Xm) so calculated were as 0.3947 g·g^{-1} and 0.3514 g·g^{-1} and 0.3326 g·g^{-1} for Fe-modified and FeOH-modified and Ca-montmorillonite samples respectively. The specific surface areas for the samples obtained through monolayer adsorption were 789 m^2·g^{-1}, 702 m^2·g^{-1} and 665 m^2·g^{-1} for the Fe-modified, FeOH-modified and Ca-montmorillonite respectively. These SSA results especially for the Fe-montmorillonite samples are in close

agreement with those reported by Marco-Brown [21]. **Figures 4-6** indicate the linear langmuir plots for the three samples. There was strong correlation of the samples to the Langmuir theorem as evidenced by the strong correlation efficiency values of the samples.

Figure 7 shows the adsorption isotherms of Diazinon on Fe-modified, FeOH-modified and Ca-montmorillonite. The results indicate that Fe modified montmorillonite had the highest potential to adsorb diazinon pesticide in comparison to FeOH-modified and Ca-montmorillonite. The chromatogram of diazinon before and after the adsorption experiments did not significantly change except for the intensity which was an indication that diazinon remained intact. There was generally strong adsorption of diazinon on both Fe samples as evidenced by the adsorption isotherm. The content of iron in the Fe modified sample was high which resulted into the sample having a higher adsorptive capacity. Since Fe has high affinity to Sulphur which is present in the molecular structure of diazinon, the presence of iron meant that diazinon could adhere to the adsorbent. In general, during the preparation of the Fe modified samples, the adsorbed Fe ions would be transformed into different chemical and physical forms (including oxidation state) depending upon the surrounding conditions, such as pH since the existence of iron species is pH dependent [22]. These iron chemical species, which include Fe^{2+} and Fe^{3+} ions, were the ones responsible for the removal of diazinon. They would, in effect alter the migration behaviour of pollutants in montmorillonite by redox reactions, adsorption, and change in swelling behaviour of the montmorillonite. However, the prepared samples may have contained other iron species since Fe ions are likely to transform into various chemical and physical forms [23-26]. The iron content of all the samples was slightly higher than the CEC of raw montmorillonite. The slight similarity of the amount of iron contained in the samples to the CEC of the samples indicated that the cation exchange sites of both samples were completely saturated with the iron species available.

The adsorption data have been subjected to the Langmuir adsorption isotherm analysis with the following linearized form:

$$C/X = 1/XmK + C/Xm \qquad (1)$$

where:
C—the equilibrium concentration (µmol·L^{-1});
X—the amount adsorbed (µmol·g^{-1});
Xm—the maximum adsorption (µmol·g^{-1});
K—a constant related to binding energy (unitless).

Table 2 indicates the Langmuir analysis results for the three samples. The Langmuir's adsorption capacities so calculated were 58.8, 54.1 and 31.3 µmol·g^{-1} for Fe-modified, FeOH-modified and Ca-montmorillonite re-

Fe-Modified

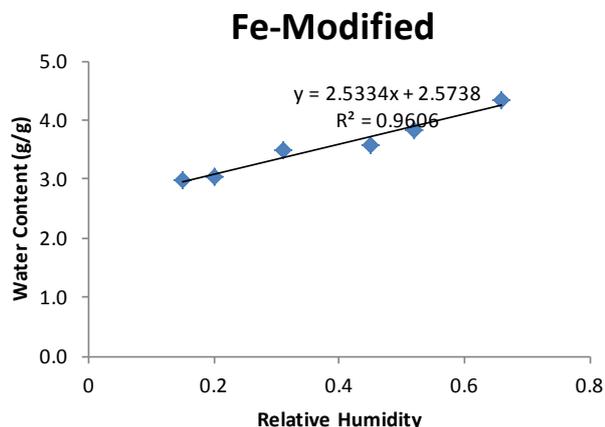$y = 2.5334x + 2.5738$
$R^2 = 0.9606$

Figure 4. Langmuir plot for Fe-modified sample.

FeOH Modified

$y = 2.8452x + 2.5911$
$R^2 = 0.9849$
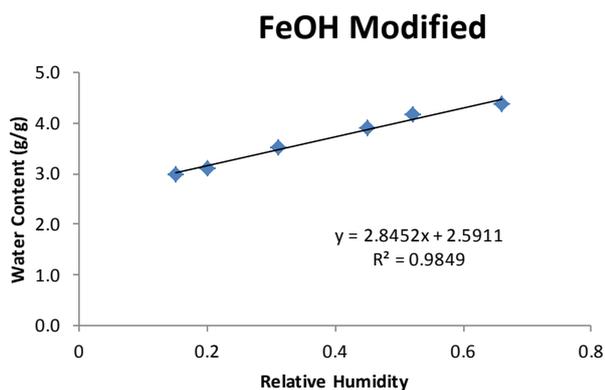
Figure 5. Langmuir plot for FeOH-modified sample.

Ca-Montmorillonite

$y = 3.007x + 2.5704$
$R^2 = 0.8592$

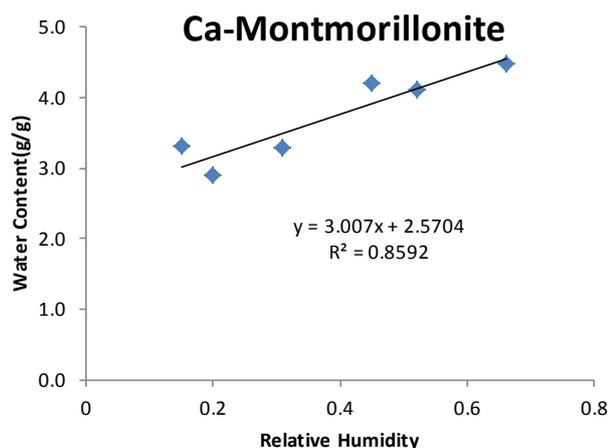**Figure 6. Langmuir plot for Ca-montmorillonite sample.**

spectively. Langmuir's K values related to binding energy on the samples were 1.52, 0.75 and 0.04 for Fe-modified, FeOH-modified and Ca-montmorillonite respectively. This indicated that the Fe modified sample apart from having high adsorptive capacity also has a high Langmuir binging energy constant, implying that diazinon was strongly bound to the sample unlike with the FeOH-modified and Ca-montmorillonite. Using this sam-
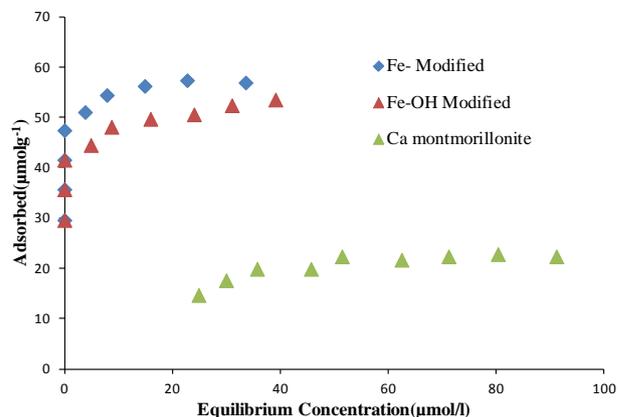

Figure 7. Adsorption isotherms of diazinon on Fe-modified, FeOH-modified and Ca-montmorillonite.

Table 2. Maximum adsorption and Langmuir K-constant for Ca-montmorillonite, FeOH-modified montmorillonite and Fe-modified montmorillonite.

Sample	Maximum Adsorption	Langmuir K-Constant
Ca-montmorillonite	31.3	0.04
FeOH-modified	54.1	0.75
Fe-modified	58.8	1.52

ple to remove diazinon as a water pollutant would therefore result into Diazinon being strongly bound to the adsorbent and its mobility would be greatly reduced.

The degree of polymerization had a significant contribution to the adsorptive properties of the samples. **Figures 8(a)** and **(b)** are illustrations of the mechanism for diazinon adsorption.

The Fe-modified sample, which was prepared at a lower pH than the FeOH-modified sample was less polymerized and had a comparatively larger available room within its structure for diazinon adsorption. On the contrary, the FeOH-modified sample whose preparation pH was slightly higher, had a higher degree of polymerization. This implied that the available room for adsorption of diazinon was less hence lower adsorption. In other studies, FeOH-montmorillonite prepared at OH/Fe = 2 (similar to current study), practically all original exchangeable cations in the montmorillonite sample were replaced by ferric ions with a majority of the total present outside the interlayer space [27]. This was due to the large size of the polymerized Fe species which could into easily penetrate into the interlayer space. This is unlike the Fe-modified sample whose Fe species could easily penetrate the interlayer space.

4. Conclusion

The use of iron modified montmorillonite as an adsorbent for pollutants such as diazinon is an effective means

FeOH-modified sample

(a)

Fe-Modified Sample

Montmorillonite sheet   FeOH
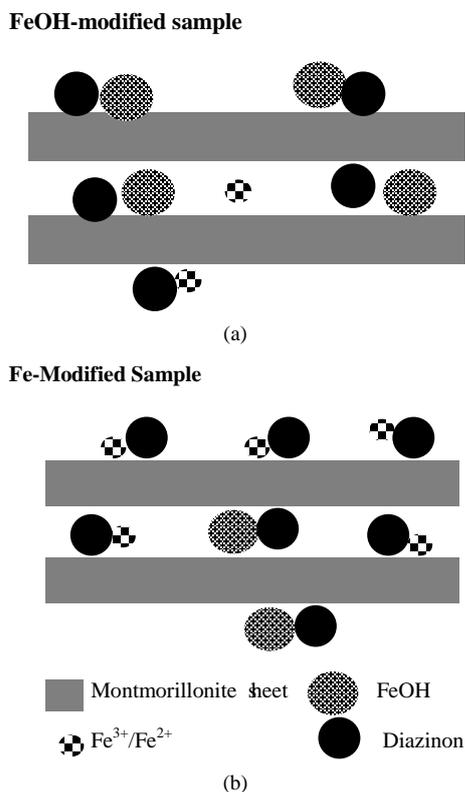
Fe^{3+}/Fe^{2+} Diazinon

(b)

Figure 8. (a) Mechanism for diazinon adsorption on FeOH-modifies sample; (b) Mechanism for diazinon adsorption on Fe-modified sample.

of environmental pollution clean-up. Iron modified montmorillonite is a low cost adsorbent due to the abundance of montmorillonite in nature as well as that of iron. Its application is not only diazinon but also other Sulphurs containing Organophosphate pollutants. At environmental concentrations of diazinon (<3 $\mu mol \cdot L^{-1}$ in many countries), iron modified montmorillonite would be very effective in pollution control. The mechanism for adsorption of diazinon on iron modified montmorillonite shows that diazinon can be adsorbed in the interlayer space of montmorillonite as well as its surface. The size of iron due to polymerization greatly determines its adsorptive abilities.

Acknowledgements

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