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Bentonite for controlled release formulation of linuron

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ABSTRACT

This study aims to define the various factors that influence the adsorption-desorption of linuron on organo-bentonite for develop controlled release formulations. Ca^{+2}-bentonite surfaces were activated for the adsorption of linuron by simple ion exchange reaction using hexadecyl tributyl phosphonium ($HDTBP^{+}$) or trimethybenzyl ammonium (BTMA) salts. The results show that HDTBP is a very good adsorbent for linuron. Release studies show that 32 % of linuron was released after 96h followed by a steady state release up to 21 days. No further release was observed. These results suggest that $HDTBP^{+}$-Bentonite is a promising porous material for controlling linuron release. The application of these materials may improve the herbicidal activity of linuron, reduces the frequency of application and protects the ground water.

Key Words: Linuron, bentonite; $HDTBP^{+}$, adsorbent.

INTRODUCTION

Linuron, 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea, is a herbicide widely used in agriculture for weed control on soybean, carrots, cotton, potatoes, carrots, and celery. Its application may result in water, and soil contamination, for instance linuron residues were found in drinking water wells in the USA (Smith *et al.,* 1999), and in potatoes, carrots, and mixed vegetables in Italy (Sannino, 1998), and in Canada (Worobey and Shields, 1991). Movement by leaching is greatest in sandy soil. Adsorption in soil is an important factor in evaluating the fate of linuron. Soils of high fractions of clay and organic matter contents may adsorb large amount of linuron. Consequently leaching may be reduced.

Berglof *et.al.,* (2000) studied linuron sorption-desorption in field-moist soils. They found that both soil water content and temperature influenced

sorption and K(d) values increased with increased water content, and decreased with increased temperature. Sanchez-Camazano *et al.,* (2000) studied the adsorption and mobility of linuron in soils as influenced by soil properties, organic amendments, and surfactants. They found that the adsorption isotherms conformed to the Freundlich adsorption equation, and the Freundlich constant, K, and the distribution coefficient, K(d), were highly correlated with the OM content of soils.

Iglesias-Jimenez *et al.,* (1997) studied the sorption of linuron by a sandy loam soil modified with different exogenous organic materials, and found that the isotherms in all cases, fitted the Freundlich sorption equation. Effect of the non-ionic surfactant, Triton X-100, (Rodriguez-Cruz., *et al.,* 2004 and 2006) and anionic surfactant, sodium dodecyl sulphate (SDS) (Sanchez-Martin *et al.,* 2003) on the desorption of linuron adsorbed on soils with different organic matter (OM) and clay contents were carefully studied. The results obtained indicate the enhancement of linuron desorption by the addition of SDS surfactant to soil-water system.

Bahadir and Pfister (1985) studied the release rates of linuron, from three different types of formulations to control aquatic weeds in running waters. They found that the migration of active ingredients (a,i.) from conventional wettable powder formulations was complete within 1 day, while the migration from ethylene-vinyl acetate co-polymeric matrix lasted significantly longer due to low diffusion coefficient of monomeric pesticides in polymeric matrices. Release duration of active ingredients from calcium alginate beads lasted 2 weeks. Tunceli *et al.,* (2001) investigated the effect of pH and other parameters, that influence the retention of pesticides on *Saccharomyces cerevisiae* immobilized on sepiolite. They showed that it was possible to achieve quantitative analysis when the sample pH was in the range of 4-8 for linuron.

Little attempts in the literature were made to develop friendly linuron formulations. Therefore, the present study was evaluated the effect of different factors on the adsorption of linuron on activated bentonite for the purpose of development environmentally friendly formulation for controlled release.

MATERIALS AND METHODS

Materials: Ca^{2+}-bentonite clay used in this investigation was provided by Prof G. Lagaly, Department of Inorganic Chemistry Kiel University. The bentonite was modified with benzyltrimethyl ammonium (BTMA), phenyltrimethyl ammonium (PTMA), N-dodecyl pyridinium (|NDDP) or N-hexadecyl tributylphosphonium bromide ($HTDTP^{+}Br^{-}$) salts (purchased from Sigma Chemical Comp.,Gemrmany). Technical grade of linuron with purity ≥ 94 % , molecular weight 249.11, was purchased from Fluka (Germany). It is a hydrophobic herbicide with an octanol / water partitioning coefficient Kow = 3.0043 (USDA, 1998) and weakly soluble in water (63.8 mg / L). The volatility is low (vapor pressure at room temperature is 2 mPa).

Preparation of the organo-bentonite complexes: The organo-bentonite complexes were prepared by addition of 5 mmol of the solid organic salt to 1 L of 1 % (w / v) aqueous dispersion of Ca^{+2}- bentonite under stirring for 3 days (EL-Nahhal, 2003a). The organo-bentonite was separated by centrifugation (4000 g, 30 min), washed three times with distilled water, freeze-dried, and ground to < 50-µm arrogates. The amount of organic cation bound to Ca^{+2}-bentonite was calculated from the carbon content (CNSHO analyzer, Euro EA 3000 Elemental Analyzer), and related to gram silicate.

Adsorption experiments: A stock solution of linuron was prepared by dissolving 30 mg in 2-3 mL methanol and diluting to 1 L with deionized water. The low concentration of methanol in the adsorption experiments had no influence on linuron adsorption. Adsorption kinetic was measured at 2, 4, 24, 48 and 96 h to evaluate the equilibrium. In this experiment 5 ml of the stock solution of linuron was diluted with 20 ml of deionized water and added to 5 mg organo-bentonite and shaked for the periods mentioned above. Concentration of linuron in the equilibrium solution was determined by HPLC as described below.

Influence of the temperature on the adsorption isotherms of linuron on the organo-bentonite was measured at various temperature (278, 303, 313 ± 2 ºk). Appropriate aliquots of the aqueous solution of linuron were diluted with water to 25 mL and added to 5 mg organo-bentonite in 30-mL

centrifuge tubes. The concentration of linuron ranged between 1.2 and 31 mg / L. The final concentration of the organo-bentonite was 0.2 g / L. The dispersions were kept under continuous rotary agitation at 303 and manual shaking for the cases 278 and 313 ºK during 48 hours. The supernatant was separated by centrifugation at 20 000 g for 0.5 h. The concentrations of linuron in the supernatant were determined by Waters 717 HPLC equipped with UV detector (detection wavelength 254 nm). A Nova-Pak C_{18} analytical column (inner diameter 3.9 mm, length 150 mm) was used. The mobile phase was methanol / water 51/49 (v / v) with flow rate at 1 ml /min. The amount of linuron adsorbed was calculated from the depletion of the linuron concentration by adsorption as recently described (EL-Nahhal and Lagaly, 2005). For each isotherm a reference solution with an intermediate concentration was stirred without organo-bentonite to evaluate adsorption on the glass or other losses.

Analysis showed that linuron was not adsorbed on the glass of the centrifuge tubes. All adsorption experiments were made in duplicate. Influence of pH range (3-8) on the adsorption isotherms of linuron was tested at room temperature. The acidic and alkaline pH values were adjusted by addition of few drops of concentrated acetic acid or ammonium hydroxide, respectively. Influence of NaCl at concentrations of (4-40 g / L) on the adsorption isotherm of linuron was studied at room temperature at a concentration range of 1.2-31 mg / L.

Preparation of the organo-bentonite-linuron formulations: The organo-bentonite-linuron formulations were prepared by dissolving appropriate amounts of linuron (w / w) of organo-bentonite in acetone and adding it to the suspended powdered bentonite, or organo-bentonite in the same solvent with a total volume of 50 ml. The solvent was evaporated under reduced pressure as previously described (EL-Nahhal *et al.,* 1998).

Release experiments: A set of release experiments were designed to investigate if the adsorption process of linuron is truly reversible and slow. In this procedure:

1. A 10 mg organo-bentonite-linuron formulation containing 1 mg ai linuron was suspended in 100 ml of deionized water under continuous stirring. At a certain periods (1, 2, 4, 8, 24, 48, 72, and 96 h) 600 µL samples were collected and centrifuged at 20,000 *g* for 30 min. The supernatant was transferred to HPLC tubes and the remaining solid materials (organo-

bentonite-linuron) was shaked with another 600 µL deionized water and transferred back to the stirring flask to maintain the volume to the constant value of the starting points. Linuron concentrations in each tube were determined as described before by HPLC.

2. Funnel experiments:The procedure described recently by EL-Nahhal et al., (2005) was modified and used, a 20 mg organo-bentonite-linuron formulation was mixed with 50 g oven dried sandy soil in a glass baker using glass rod to ensure homogenized distribution of the formulation. Each sample was placed in a Buchner funnel containing a tissue paper. The funnel was shaked manually to insure homogenization and thickness. Each Buchner sand sample was washed with 500 ml of distilled water added dropwise at a rate of 10 ml / 15 min. The water was collected in 50 ml sample, 600 µl of each sample was centrifuged at 20 000 g for 30 min and analyzed by HPLC.

RESULTS AND DISSCUSSION

Preparation of the organo-bentonite complexes: The cationic quatenanry ammonium or phosphonium ions used in this study as surface-active agent (surfactant) are solid at room temperature, they have a non-polar hydrocarbon group and an ionic, polar component. The molecular structure of BTMA, and PTMA includes three methyl groups and a phenyl ring, whereas the molecular structure of HDTBP neither includes phenyl ring nor quaternary ammonium cation. The amounts adsorbed of organic cation are below the cation adsorption capacity of the bentonite.

The detector response was found to be linear in the entire concentrations encountered 0.03-6 mg / l. Regression analysis showed a correlation coefficient (R^2) of 0.9995 indicating a strong positive dependence. This indicates validity and suitability of the used method and allows for direct measurement of linuron in the supernatants.

Adsorption of linuron on Ca^{+2} – bentonite is poor due to the hydrophobic nature of linuron, Kow=3.0043, (USDA, 1998) and hydrophilic nature of Ca^{+2} –bentonite (EL-Nahhal and Lagaly, 2005). Partial modification of Ca^{+2}–bentonite surfaces with quaternary aromatic cations (PTMA, BTMA) does not appreciably increase the adsorbed amount of

linuron above that obtained on Ca^{+2}–bentonite without surface modification (Figure 1). Using larger quaternary ammonium cation (NDDP) to modify the bentonite surfaces significantly increased the adsorbed amount of linuron. The explanation of these results is that modification of Ca^{+2}–bentonite with larger quaternary ammonium cation (NDDP) generates hydrophobic environment on the bentonite surfaces. This environment may enhance the partitioning of the organic molecules on the clay surfaces (Boyd *et al.,* 1988) and/or the physical interaction with surfaces (El-Nahhal, 2003b). Beside the fact that modification of bentonite surfaces with PTMA, BTMA may not generate suitable adsorption sites for linuron, as it does for chloroacetanilde herbicides (EL-Nahhal *et al.*, 2000). However, the presence of 2 N-atoms in the chemical structure of linuron may result in

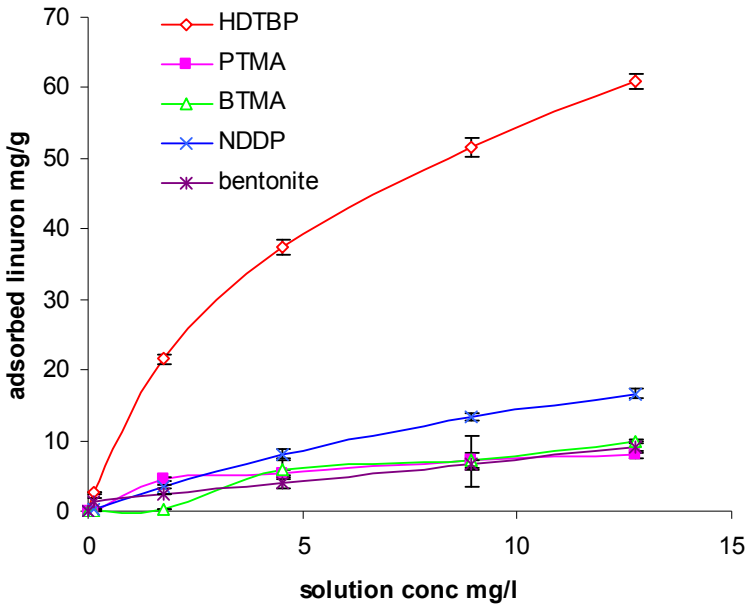

Fig. (1): Adsorption isotherm of linuron on bentonite alone (bentonite) or modified with NDDP, BTMA, PTMA or HDTBP ion. Bars represent standard error.

repulsion with the N atom in PTMA / BTMA or NDDP which attached to the bentonite surfaces. Beside, the fact that the molecular size of linuron is larger than PTMA or BTMA molecular size. Consequently, the physical interaction between linuron and PTMA or BTMA molecules on bentonite surfaces may not be optimized. EL-Nahhal *et al.* (2000) emphasized the importance of the chemical structure of the organic cations pre-adsorbed to clay in the adsorption of herbicides. In contrast, modification of bentonite with $HDTBP^+$, a quaternary phosphonium cation, dramatically increased the adsorbed amount of linuron above that obtained by using quaternary ammonium cation (PTMA, BTMA or NDDP) to modify the bentonite surfaces (Fig.1). These results suggest that pre-adsorbing the bentonite surfaces with $HDTBP^+$, may provide suitable adsorption sites for linuron beside the fact that the geometry and / or the molecular size of $HDTBP^+$ may optimize interaction between the C-N groups of linuron and C-P group of the phosphonium. EL-Nahhal (2003a) obtained similar results for acetochlor.

The rate of linuron adsorption on $HDTBP^+$-bentonite was determined at various temperatures and times. The results given in Figure 2 show that adsorption appears to be completed within 2 hours, but the amount of linuron adsorbed continued to change up to 96 h. About 78 - 96 % of the added amount was adsorbed after 2 h at high and low temperature respectively, (Figure 2). The adsorbed amounts at both temperatures reached (80.43 %) after 24 h. The adsorbed amount further decreased after 48 h, no further decrease was observed after 96 h. This suggests that adsorption process was fast and reached the maximum after 24 h, then a slow diffusion was occurred. Furthermore, the amount adsorbed at lower temperature was a little higher than at high temperature, but the differences are not significant. This may be attributed to the decrease in the diffusion at high temperature. Beside the fact that raising the temperature may enhance the loss due to evaporation although the adsorption tubes cap were covered with plastic para-film. In another investigation, Berglof *et al.* (2000), reported that soil temperature influenced sorption and K(d) values decreased with increased temperature.

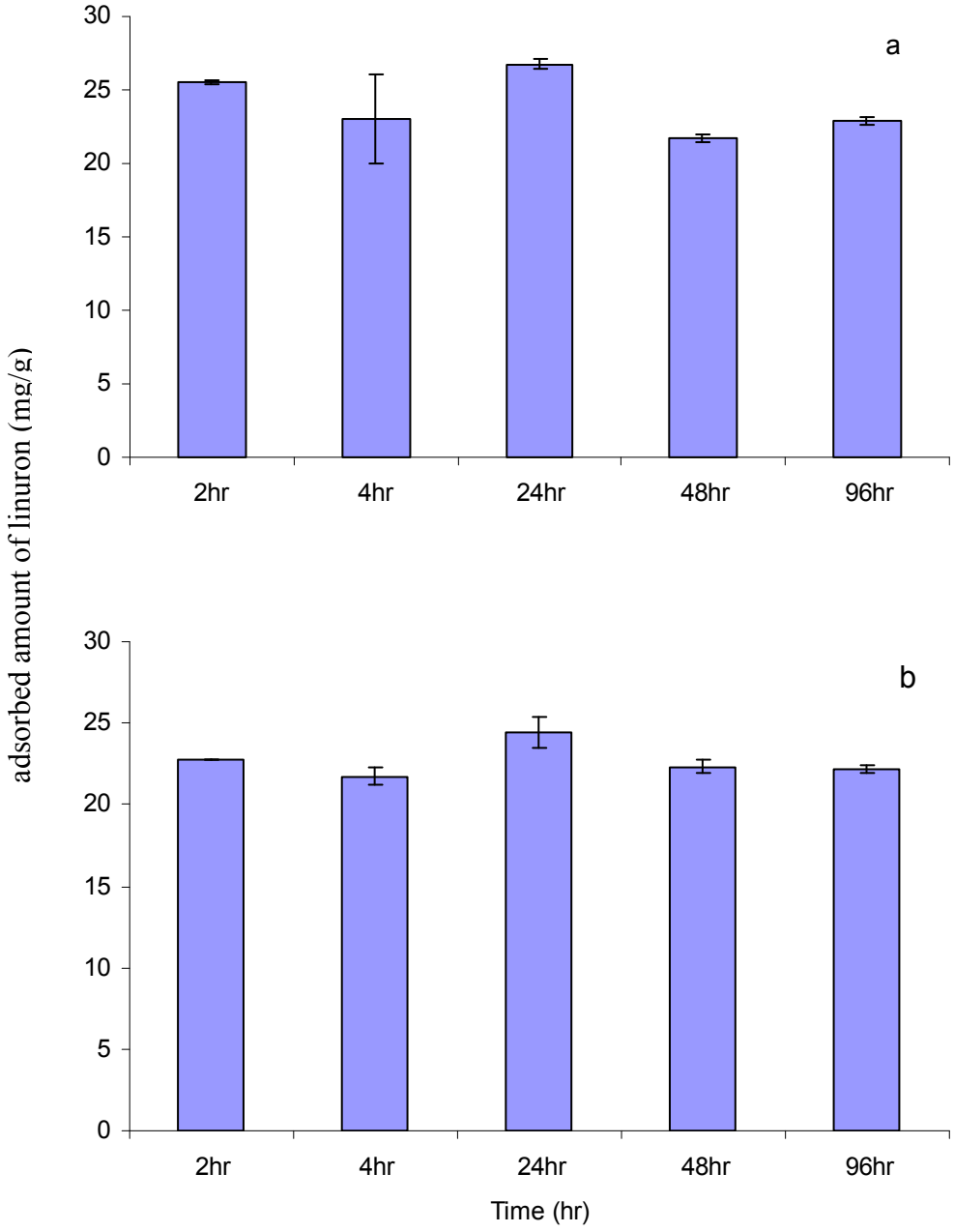

Fig. (2): Adsorption kinetics of linuron on HDTBP0.15-bentonite at 5 ^{o}C (a) and 40 ^{o}C (b). Bars represent standard deviation.

Influence of various factors on the Adsorption of linuron on bentonite:
Organic load on bentonite: Adsorption of linuron as a function of organic load pre-adsorbed to bentonite are shown in Figure 3. The general conclusion is that the amount of linuron adsorbed (mg / g) increased as the pre-adsorbed amount of $HDTBP^+$ increased on the bentonite surfaces.

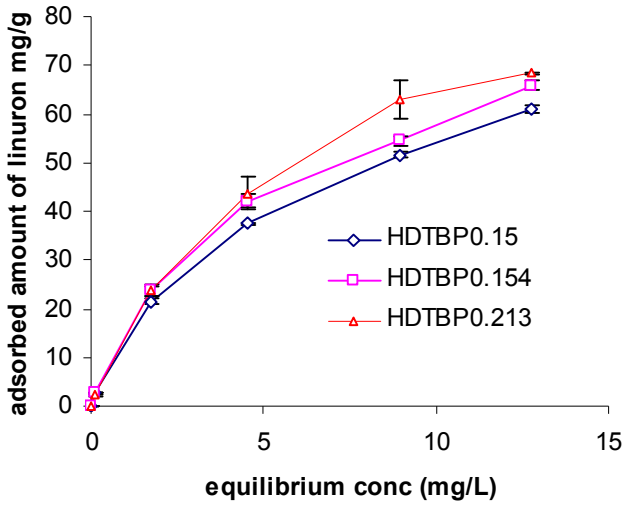

Fig. (3): Adsorption isotherms of linuron on bentonite modified with HDTBP ions at various loadings. The numbers in the legend represent the amount of HDTBP adsorbed in mmol/g bentonite. Bars represent standard deviation**.**

Temperature: The experimental results of adsorption isotherms of linuron on the $HDTBP^+$-bentonite at different temperatures are shown in Figure 4. The amount of linuron adsorbed increased with decreased temperature. The statistical analysis does not discriminate significant difference as shown by the overlapping of the error bars.

pH values: A range of pH from 3 to 8 does not influence the adsorption of linuron on bentonite modified with $HDTBP^+$ (Data not shown).

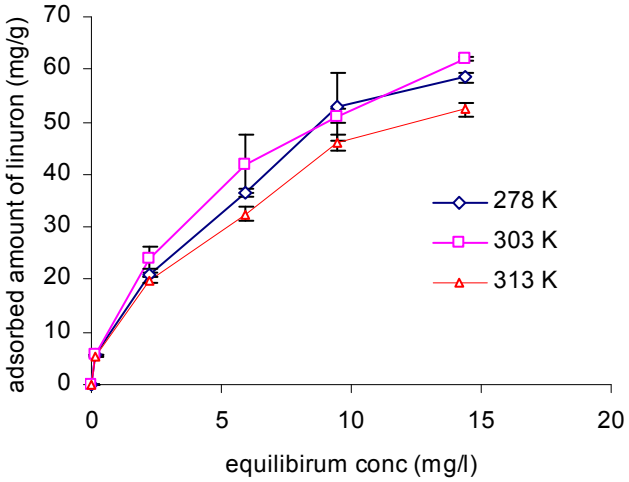

Fig. (4): Adsorption isotherms on linuron at HDTBP0.15-bentonite at different temperatures. Bars represent standard deviation.

NaCL concentration: The experimental results presented in Figure 5 show that the adsorption isotherms of linuron are more pronounced from solutions containing high NaCl concentration (40 g / L). The maximum adsorbed amounts were 76.95±3.3 and 95.6±7.2 mg linuron / g on $HDTBP^{+}$-bentonite at 4 and 40 g NaCl / L, respectively.

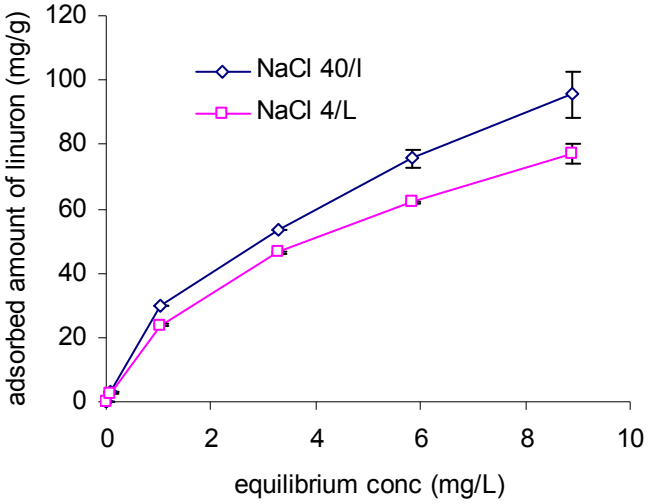

Fig. (5): Adsorption isotherms of linuron on HDTBP0.15 bentonite in the presence of NaCl at various concentrations. Bars represent standard deviation

General characteristics of the adsorption isotherms: The general shape of the adsorption isotherms of linuron on PTMA-/BTMA-/NDDP-/or HDTBP-bentonite shows a steep rise and then a flat top in which the amount of linuron adsorbed per unit gram of $HDTBP^{+}$-bentonite does not change appreciably with increasing solution concentration. This adsorption phenomenon may suggest that linuron interact with the hydrophobic adsorption sites $HDTBP^{+}$-bentonite by attachment to number of adsorption sites on the surface.

These isotherms can be classified as C-type, in this case the availability of the adsorption sites remains constant at all concentrations up to saturation. This signifies that the initial curvature shows that as more sites in the $HDTBP^{+}$-bentonite are filled with linuron molecule. It becomes increasingly difficult for a free linuron molecule to find a vacant site available. This implies either that the adsorbed linuron molecule is not vertically oriented or there is no strong competition from the solvent. Accordingly, the presented figures may be characterized by one of the following features: 1) the adsorbed linuron molecules are most likely to be adsorbed flat, or 2) if adsorbed end-on, linuron molecules suffer little solvent competition. Beside, the intermolecular attraction may not be high between linuron molecules and surfaces of $HDTBP^{+}$-bentonite.

Release of linuron: The experimental results presented in Figure 6 show a fast release of linuron from bentonite (M48). About 90 % of linuron released in the first hour. then release was not appreciably increased even after 96 hour.

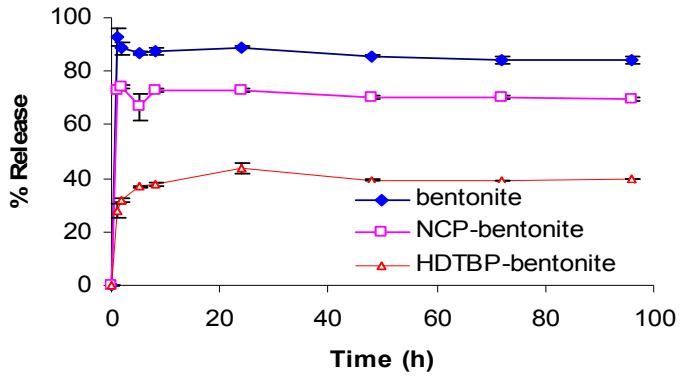

Fig. (6): Release of linuron from different formulations at different periods in closed system. Bars represent standard errors.

The released fraction of linuron from $HDTBP^{+}$-bentonite was lower than from NCP-bentonite and was below 40 % even after 96 h. The adsorption release mechanism indicates the reversibility of the process. An interesting outcome of these experiments is that the release of linuron from $HDTBP^{+}$-bentonite does not increase above 35 % even after 120 h. On the other hand, the released fraction as a function of water quantity used are presented in Figure 7. It can be seen that less than 15 % of linuron was released from $HDTBP^{+}$-bentonite even after washing with large volume of water 500 mL. These results are in accord with the adsorption results (Fig. 1). About 58 % of linuron was released from bentonite in the first washing (50 ml) and the released fraction appreciably increased as the washing volume increased. Relatively, above 70 % of linuron was released from bentonite at the end of the experiment. On the other hand, released fraction of linuron from NCP-bentonite formulation was significantly slow. Statistical analysis of the results indicate significant difference at the level of 0.05.

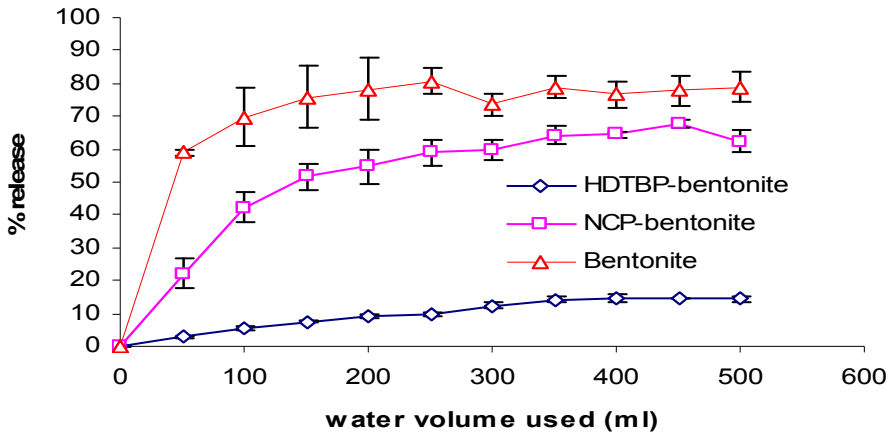

Fig. (7): Release of linuron from different organo-bentobite formulations at various amount of water using funnel technique. Legend indicates type of linuron formulation. Bars represent standard deviation.

Concluding remarks: This study reveals the adsorption behavior of linuron on different organo-bentonite complexes. The findings show that the adsorbed amounts of linuron obtained at bentonite partially modified with smaller quaternary ammonium cation ($BTMA^{+}$, $PTMA^{+}$) were very low and nearly equal to that obtained at Ca^{+2}-bentonite. Using larger quaternary ammonium cation (NDDP) significantly increased the adsorbed amount

(Fig.1). In addition using quaternary phosphonium cation ($HDTBP^+$) dramatically increased the adsorbed amounts of linuron above all organo-bentonites used in this study (Fig. 1). Increasing the load of $HDTBP^+$ on bentonite further enhanced the adsorption of linuron (Fig. 3). The rational of this work is that adsorption of linuron on bentonite may be enhanced by the modifying the bentonite with phosphonium cations. Increased temperature further increased the adsorption of linuron beyond that obtained at low temperature (Fig. 4). Release of linuron follows this order: Ca+-bentonite> NCP^+-bentonite>> $HDTPP^+$-bentonite. These finding may provide valuable information for preparation of linuron formulation.

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