Adsorption of benzyltrimethylammonium to montmorillonite: application to herbicide formulations
Adsorption du benzyltriméthylammonium sur la montmorillonite : application à la formulation des herbicides

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The increased threat of environmental pollution by pesticides and other organic pollutants promoted investigations on the use of organo-clays as sorbents for organic molecules (Boyd et al., 1988; Gerstl and Mingelgrin, 1979; Hermosin and Cornejo, 1993; Jaynes and Boyd, 1991; Lagaly, 1987; Mortland et al., 1986). Organo-clays can stabilize pesticides and reduce their volatilization and photodecomposition (Margulies et al. 1992,1994). Benzyltrimethylammonium (BTMA) is a quaternary amine monovalent cation that can be effective in modifying the surface of the clay for the enhanced adsorption of non-polar organic molecules from water. Alachlor is a pre-emergence herbicide widely used for selective weed control in various field and horticultural crops. Based on the combined effects of its adsorption and degradation in soils, alachlor was considered as highly potentially leaching herbicide (Yen et al, 1994) and its residues were detected in groundwater in North America and Europe (Ritter et al., 1996)

The objectives of this work have been: 1) to elucidate the mechanism of adsorption of BTMA on montmorillonite by combining the experimental adsorption results and model calculations; 2) to develop new controlled release formulations of alachlor which would reduce its leaching in soils.

MATERIALS AND METHODS

The clay mineral used was Wyoming Na-montmorillonite SWy-1 obtained from the Source Clays Repository (Clay Minerals Society, Columbia,MO). BTMA was purchased from Aldrich (Milwaukee, WI, USA). Analytical grade alachlor (Chem Service, West Chester, PA) was used for making the formulations, whereas a commercial formulation (EC) (Alanex, 480g ai/kg, Agan Chemical Manufactures LTD., Ashdod, Israel) was used as a standard formulation. The electrolytes used were: NaCl, LiCl, $NaClO_4$, Na_2SO_4, CsCl.

Adsorption isotherms.

The adsorption isotherms of BTMA were measured in the range of 0-4.1 mmol/g clay as described in Polubesova et al (1997). The concentrations of BTMA were determined by measuring the absorption at 262 nm using an HP8452A diode array UV-Vis spectrophotometer (Hewlett-Packard Co., Palo Alto, CA). Equilibrium was reached within one day. The concentrations in supernatants of exchangeable cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) replaced by the organic cations were determined by using an inductively coupled plasma atomic emission spectrometer (Spectra Co, Kleve, Germany). The organo-clay herbicide complexes were prepared as in Margulies et al. (1992). Alachlor adsorption isotherms were measured in the range of 0-700 ìmol alachlor/g of clay-organic complex with BTMA pre-adsorbed at 0.5 and 0.82 mmol/g clay (the CEC of the clay). Equilibrium was reached within 24 hours. The supernatant was separated by centrifugation at 20,000g for 1 hour. Alachlor was extracted using a solvent mixture of ethyl acetate-isooctane (1:9, V/V) and analyzed by GC.

Model calculations.

The model used in this study has been described in Nir (1986), Margulies et al. (1988), Nir et al. (1994a), Rytwo et al. (1995). The programs consider cation binding, the electrostatic Gouy-Chapman equations, and solve iteratively for the solution concentrations of all cations in a closed system. Cation adsorption is calculated by considering specific binding to surface sites and residence in the double layer region.

The binding coefficients of the inorganic cations in the system were taken from our previous studies (Nir et al., 1986; Rytwo et al., 1996). For BTMA the intrinsic binding coefficients K_i for formation of neutral complexes and K_i for charged complexes were determined from adsorption data. Alachlor adsorption was analyzed in terms of Scatchard plots as described in Nir et al. (1994b).

Leaching studies.

Sandy soil (Rehovot, 6% clay; 3.5% silt; 90% sand; <0.1% organic matter; pH 7.5) was used throughout the study. The study was performed as decribed in (El-Nahhal et al., 1997). Tin columns filled with soil were used. Alachlor formulations were sprayed (2.0 kg/ha) on the soil surface, then the column was irrigated (500m³/ha). Following 48 h of equilibration, the column was sliced along its length to form two similar parts, in which test plants, green foxtail (*Setaria viridis*) were sown. Plants were grown in the glass house under natural light conditions. Shoot height determined 16 days after treatment was used to estimate herbicide activity at different soil depths.

RESULTS AND DISCUSSION

Adsorption of BTMA.

The isotherm of BTMA adsorption is presented in Fig.1. When 3.3 mmol/g BTMA was added, adsorption of BTMA reached the CEC, and the ratio of the amounts of BTMA adsorbed to the sum of exchangeable cations displaced was equal to unity. In this range, the mechanism of BTMA adsorption appears to be primarily cation exchange. The adsorption model can adequately account for the adsorbed amounts of BTMA.
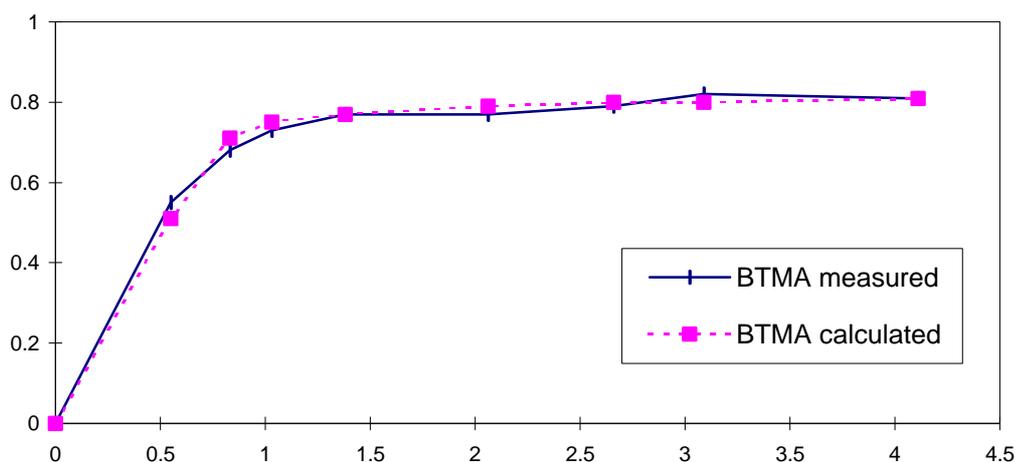

Fig1. Adsorption of BTMA on Na-montmorillonite

The increase of ionic strength of electrolyte solutions- LiCl, NaCl, $NaClO_4$, Na_2SO_4 and CsCl- resulted in reduced adsorbed amounts of the organic cations (Table 1). The reduction in the adsorbed amounts of BTMA was dependent on the inorganic cations according to the sequence: $Cs^+ > Na^+ > Li^+$ corresponding to the magnitude of their binding coefficients (Nir et al., 1986). The maximal reduction in the amounts adsorbed was found when 1.1 mmol/g BTMA was added: 5% reduction with 0.333M LiCl, 15% with 0.667M NaCl and 0.333M Na_2SO_4 and 75% reduction with 0.333 M CsCl.

Table 1. **Effect of inorganic cations (Na^+, Cs^+, Li^+) and concentration of electrolytes on adsorption of BTMA on Na-montmorillonite**

Salt added mmol/g		BTMA added mmol/g	BTMA adsorbed mmol/g	
			experimental	calculated
0		0.55	0.55	0.51
0		1.1	0.72	0.72
LiCl,	0.333M	0.55	0.52	0.45
		1.1	0.69	0.66
NaCl,	0.333M	0.55	0.52	0.44
		1.1	0.64	0.65
NaCl,	0.667M	0.55	0.50	0.40
		1.1	0.61	0.61
$NaClO_4$,	0.333M	0.55	0.50	0.44
		1.1	0.63	0.65
Na_2SO_4,	0.333M	0.55	0.52	0.40
		1.1	0.61	0.61
CsCl,	0.333M	0.55	0.14	0.05

The type of anion did not affect the adsorption of organic cations. For example, the adsorbed amounts of BTMA in the presence of 0.333M sodium chloride or perchlorate are very close for both cations. The adsorbed amounts in the presence of 0.667 M sodium chloride are similar to the results in the presence of 0.333M of sodium sulphate. The decrease in adsorption of BTMA with the increase of ionic strength was explained by the competition of inorganic cations with BTMA for the adsorption sites and reduction in the magnitude of the surface potential. The affinity of BTMA to the clay surface is higher than the affinity of the above inorganic cations: the binding coefficient K used for BTMA was 5000 M^{-1}, whereas the binding coefficients of Cs+, Na+, and Li+, were 200, 1.0 and 0.6 M^{-1}, respectively (Nir et al., 1986). The model calculations gave fair predictions for the adsorbed amounts of BTMA in the presence of electrolyte solutions (Table 1). The underestimation of the BTMA adsorption in the presence of 0.333M CsCl could be explained by its relatively loose hydration shell, that leads to the removal of water from the interlayer space, and by this way, promotes the adsorption of organic cations.

Alachlor adsorption.

The adsorption isotherms on clay and clay-BTMA complexes are shown in Fig. 2. Alachlor was poorly adsorbed on montmorillonite alone, whereas adsorption of the herbicide on the clay pre-adsorbed with BTMA significantly increased. Partial saturation of the clay with BTMA at a load 0.5 mmol/g clay resulted in better alachlor adsorption than at the BTMA load of 0.8 mmol/g (the CEC of the montmorillonite). The adsorption was modeled with very good fits, in fact, within experimental errors (R^2 = 0.99). The binding constants were : k = 50, 800, and 1000 M^{-1} for alachlor adsorption to the clay alone, or to the clay with BTMA at loads of 0.8 and 0.5 mmol/g, respectively. Model calculations with the binding coefficients for the formation of charged complexes K=20M^{-1} revealed that BTMA adsorption up to the CEC resulted in the formation of a

certain fraction of charged complexes. In these complexes the molecules of BTMA interacted among themselves, thus reducing the possibility for alachlor molecules to interact with the phenyl ring of BTMA molecules, which led to the decrease in alachlor adsorption. These data indicate that achieving maximal transformation of the clay surface from hydrophillic to hydrophobic, does not necessarily imply optimal interactions between the herbicide and the organo-clay complex.
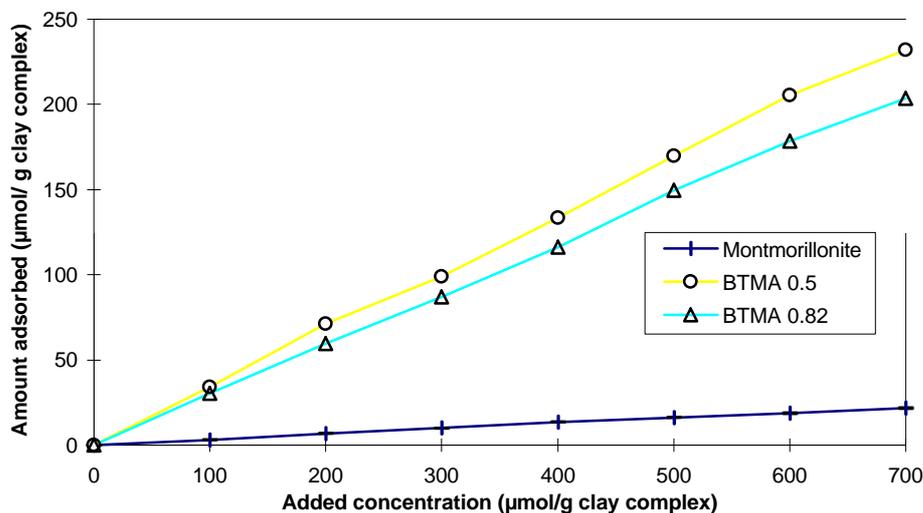

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Fig.2 Adsorption isotherms of alachlor on Na-montmorillonite, montmorillonite pre-adsorbed with BTMA 0.5 mmol/g clay (BTMA 0.5) and montmorillonite pre-adsorbed with BTMA 0.8 mmol/g clay (BTMA 0.8).
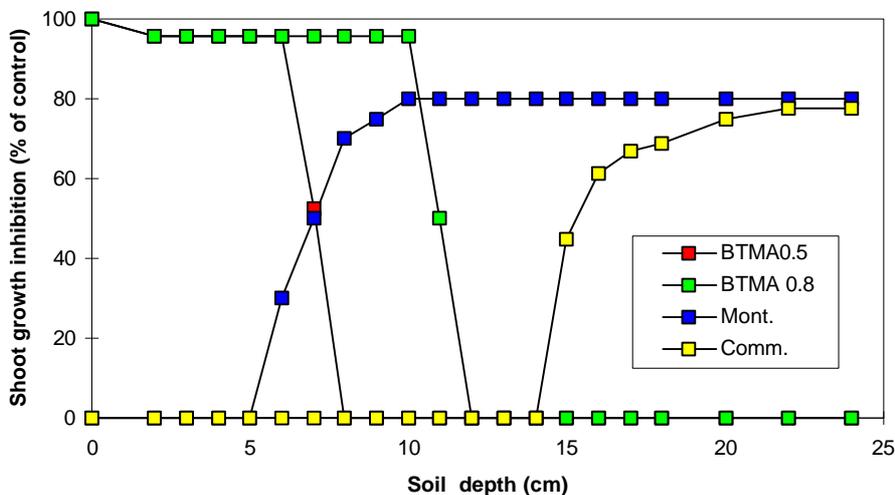

Fig 3. Leaching of alachlor in a soil column. Alachlor formulations were: commercial formulations (Comm.), alachlor on clay alone (Mont.), alachlor on clay, pre-adsorbed with BTMA 0.5 and 0.8 mmol/g clay.

Leaching studies.

The results of the leaching experiments are shown in Fig.3. Low herbicidal activity for commercial alachlor was detected only at soil depth of 15-24cm, indicating that most of the herbicide applied leached out from the column. Adsorption of alachlor

to montmorillonite reduced somewhat the leaching of herbicide in the soil. Alachlor formulated on BTMA-clay complexes resulted in excellent herbicidal activity confined to the top 8 and 10 cm of the soil column for BTMA 0.5 and 0.8 mmol/g clay, respectively. This data further support the results, presented in the Fig. 2, demonstrating the relative difference in adsorption of alachlor to above tested organo-clay complexes. The results also indicate, that although the herbicide is strongly bound to the organo-clay complexes, the released amount is sufficient to provide adequate weed control.

CONCLUSIONS

1. Adsorption of BTMA to montmorillonite, mainly by ionic exchange mechanism, was adequately simulated by the applied adsorption model.
2. The increase of the concentration of electrolyte solutions resulted in reduced adsorbed amounts of BTMA. The reduction was dependent on the binding coefficients of the inorganic cations corresponding to the sequence: Cs>Na>Li.
3. Alachlor adsorbed significantly to the BTMA-montmorillonite complexes. BTMA-clay formulations of alachlor may provide effective weed control, reduce herbicide leaching and decrease the threat imposed by alachlor to the environment.

ACKNOWLEDGMENTS

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