

Competitive Sorption between Imidacloprid and Imidacloprid-urea on Soil Clay Minerals and Humic Acids

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Soil organic matter and clay minerals are responsible for the adsorption of many pesticides. Adsorption and competitive sorption of imidacloprid on clay minerals and humic acids (HA) were determined using the batch equilibration method. The sorption coefficient of imidacloprid on humic acids was significantly higher than that on Ca-clay minerals, indicating that soil organic matter content was a more important property in influencing the adsorption of imidacloprid. Competitive sorption was investigated between imidacloprid and its main metabolite imidacloprid-urea on HA and Ca-clay minerals. The results showed that the sorption capacity of imidacloprid on clay minerals and HA was reduced in the presence of the metabolite, implying that imidacloprid-urea could occupy or block adsorption sites of imidacloprid on soil, potentially affecting the fate, transport, and bioavailability of imidacloprid in the environment. The interactions between a Ca-clay or HA-clay mixture and adsorption of imidacloprid and imidacloprid-urea were studied using IR differential spectra on thin films made of the adsorbent. The possible mechanisms were discussed from the shift of characteristic IR absorption bands of imidacloprid and imidacloprid-urea after sorption.

KEYWORDS: Imidacloprid; imidacloprid-urea; sorption; adsorption; competitive sorption; clay minerals; humic acids

Sorption of pesticides by soil significantly influences their environmental fate and bioavailability because many mechanisms, such as transport, microbial uptake, or metabolism, take place only with the fraction of nonsorbed molecules (1). Previous studies have shown that soil organic matter and clay minerals greatly contribute to the sorption of pesticides (2–4). In particular, soil organic matter (SOM) that consists of humic substances and partially decomposed biomass is considered to be a predominant sorbent for anthropogenic organic chemicals in soil and sediments (4–6). Some models have been proposed to describe the characteristics of the sorption process of organic chemicals in soil. Among these models, the Freundlich equation is commonly used to describe the nonlinearity of competitive sorption of low- or high-polarity organic compounds in soil.

Competitive sorption would be anticipated at the water–solid interface when there are only limited sorption sites on the surface of soil. Therefore, in dilute systems competitive sorption is characteristic of surface sorption rather than phase partitioning, such as partitioning between water and an immiscible organic solvent (7). Moreover, competitive sorption is also the result of overlap in the set of sites that can be occupied by nonidentical solutes (8). Due to the diversity and complexity of organic com-

pounds in the natural environment, competitive sorption may play an important role in the fate and transport of contaminants in soil.

Imidacloprid, 1-(6-chloro-3-pyridinylmethyl)-*N*-nitroimidazolidin-2-ylideneamine (**Figure 1a**), is a systemic insecticide that is used to control sucking pests such as aphids, white flies, plant bugs, planthoppers, thrips, and other harmful pest species (9). Owing to its low mammalian toxicity and high insecticidal effectiveness, imidacloprid has been used worldwide for soil and foliar application and seed treatment. Imidacloprid undergoes sorption and abiotic and biotic transformations in the environment. Extensive research has been done on imidacloprid in relation to its mobility and leaching potential in soils (10–13). A comparative examination of the kinetics and mechanism of the hydrolysis of imidacloprid has been reported (13), and the main hydrolysis product is imidacloprid-urea, 1-(6-chloro-3-pyridinylmethyl)-2-imidazolidinone (**Figure 1b**). Studies on the photochemical degradation of imidacloprid on leaf surfaces (14) and in aqueous solution (15, 16) also showed that imidacloprid-urea was the main metabolite. In a study carried out in a sugar beet field, imidacloprid-urea was again determined to be one of the metabolites (17, 18).

The objective of this study was to determine the sorption of imidacloprid and imidacloprid-urea and their competitive sorption on clay minerals and humic acids (HA). Possible interactions of imidacloprid or imidacloprid-urea with Ca-clay minerals

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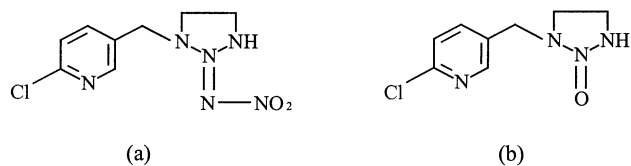


Figure 1. Structures of imidacloprid and imidacloprid-urea.

and HA were also investigated to understand the functional groups that may be involved in sorption.

MATERIALS AND METHODS

Materials. Imidacloprid was supplied by Linhua Chemical Co. (Zhejiang, China) as a colorless solid with 97.3% purity. Water and acetonitrile were of HPLC grade and were passed through a 0.45- μm filter before use. Hexane, dichloromethane, and other solvents were all of analytical grade.

Imidacloprid-urea was obtained according to a method reported elsewhere (13). Briefly, a solution of 1.0 g of imidacloprid in 200 mL of water containing 5% methanol was hydrolyzed under alkaline condition (pH 12) at 20 °C. When HPLC analysis showed that imidacloprid had completely disappeared, the solution was brought to pH 7.0 by the addition of 2 M hydrochloric acid and then extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate, and solvent was evaporated to dryness under vacuum. The hydrolysis product, imidacloprid-urea, was recrystallized using hexane and dichloromethane (3:4, v/v).

The clay was a montmorillonite and was collected from Linan (Zhejiang, China). The <2- μm fraction was obtained by sedimentation. Ca-clay (Ca²⁺-saturated clay) was prepared by repetitive treatment of the clay with a 0.1 M CaCl₂ solution. The prepared clay sample was centrifuged, washed repeatedly with deionized water until free of Cl⁻ as determined by titration with AgNO₃, and then ground to a fine powder after drying at room temperature. The pH measured from the supernatant of a 1:200 clay/0.01 M CaCl₂ mixture was 7.1. Cation-exchange capacity (CEC) was determined to be 72.3 (mequiv kg⁻¹).

Humic acids were prepared from a clay loam soil sampled from Anjie, Zhejiang Province, China. The organic matter content of the soil was 4.3%, and pH was 7.4. Briefly, 0.8 kg of air-dried soil was shaken with 3.0 L of 0.5 M NaOH solution under N₂ in a capped bottle for 24 h. The alkaline upper solution was centrifuged at 8500 rpm for 15 min, and the supernatant was acidified with 6 M HCl to pH 1, followed by standing for 24 h to permit coagulation of the HA fraction. The precipitated HAs were separated from the solution by centrifugation at 20000 rpm for 25 min and then redissolved in a small amount of 0.5 M NaOH solution under N₂. The NaOH dissolution and HCl precipitation of HAs were repeated two more times. Finally, HAs were dialyzed in distilled water under salt-free conditions and ground to a fine powder after being dried at 40 °C (19).

Sorption and Competitive Sorption Experiments. Sorption of imidacloprid was determined using the batch equilibrium method. Briefly, 5 mL of imidacloprid solutions with 10.0, 20.0, 30.0, 40.0, or 50.0 mg L⁻¹ herbicide concentration and 50 mg of Ca-clay or HA were placed in glass vials. The pesticide working solutions were prepared by diluting stock solutions with 0.01 M CaCl₂ that was used to maintain the solution ionic strength and to facilitate flocculation. Sealed vials were agitated on a reciprocal shaker at 25 \pm 2 °C for 24 h. After equilibration, the suspension was centrifuged at 13000 rpm for 15 min and 2 mL of the supernatant was filtered through a 0.45- μm membrane using a syringe. The filtrate was analyzed on HPLC as described below. The amount of pesticide sorbed to the soil was calculated from the difference between the initial and final concentrations of imidacloprid in the solution phase. A preliminary experiment showed that no sorption occurred on the glass wall of the vials, and loss due to degradation or volatilization was insignificant.

For competitive sorption, experiments were carried out in sealed vials in triplicates containing both imidacloprid and imidacloprid-urea. Five milliliters of the mixed solution was used, and the initial concentrations of imidacloprid were 0.20, 0.40, 0.60, 0.80, and 1.00 mg L⁻¹ for Ca-clay samples and 10.0, 20.0, 30.0, 40.0, and 50.0 mg

Table 1. Sorption Constants and Correlation Coefficients for Adsorption of Imidacloprid on Calcium Montmorillonite and Humic Acids

sorbent	K_f	$1/n$	R^2
Ca-clay (solid/solution = 1:200)	6.86	1.092	0.970
HA (solid/solution = 1:200)	247	0.960	0.997
HA (solid/solution = 1:100)	326	0.863	0.999

L⁻¹ for HA samples. The initial concentrations of imidacloprid-urea were 10 mg L⁻¹ for Ca-clay samples and 20 mg L⁻¹ for HA samples. The use of a higher initial concentration of imidacloprid for HA samples was to compensate for its greater adsorption capacity as compared with that of Ca-clay. Fifty milligrams of Ca-clay or 25 mg of HA was added into these vials and then shaken for 24 h to achieve equilibrium. The concentration of imidacloprid in the solution after centrifugation was determined by HPLC analysis.

Quantification of imidacloprid in the supernatant was conducted using a Septra Physics HPLC equipped with a 250 \times 4.6 mm C₁₈ analytical column (Yili Company, Dalian, China). A multiwavelength Spectra 100 UV-vis detector operating at 267 nm and a workstation UPPER were used for data acquisition and processing. The mobile phase (1.0 mL min⁻¹) was made of acetonitrile (20%) and water (80%) that was acidified to pH 4 with phosphoric acid. Calibration was made using external standards with linear regression analysis. The retention times of imidacloprid and imidacloprid-urea under the above conditions were 5.6 and 7.4 min, respectively.

Infrared Analysis. Infrared analysis of Ca-clay and HA-clay mixtures after pesticide sorption may provide information on the probable bond interactions between the pesticide and the sorbent. Thin self-supporting films were prepared using similar procedures as given by Liu et al. (19). Briefly, the films were prepared by evaporating 5 mL of a suspension that was prepared using 5 mL of water and 50 mg of homoionic clay or HA-clay mixture (the ratio of HA:Ca-clay was 1:20) by 24 h of mixing in a 5-cm (i.d.) ring on a polyethylene sheet at room temperature. After air-drying, the thin film was lifted off the plastic sheet and divided into halves. Half of the film was treated with imidacloprid or imidacloprid-urea by immersing the film in chloroform containing 2% of the pesticide for 24 h and then rinsed with clean chloroform to remove excess pesticide. The other half of the film was treated only with clean chloroform. Infrared spectra of these treated films were recorded at room temperature for the range of 4000–400 cm⁻¹ using an IR-470 spectrophotometer (Shimadzu, Kyoto, Japan). Differential spectra of adsorbed imidacloprid or imidacloprid-urea were obtained by subtracting the spectra of the pesticide-treated film from that of the pesticide-free film. The IR spectra of pure imidacloprid and its metabolite were obtained using KBr disks containing the respective chemical at ~2% (w/w).

RESULTS AND DISCUSSION

Sorption on Ca-Clay Mineral and Humic Acids. Sorption of imidacloprid on Ca-clay and HA may be described by the Freundlich equation

$$\log C_s = \log K_f + 1/n \log C_e$$

where C_s (mg kg⁻¹) is the concentration of pesticide sorbed by soil, C_e (mg L⁻¹) is the equilibrium concentration in solution, and $\log K_f$ and $1/n$ are empirical coefficients representing the intercept and slope of the linearized isotherm, respectively. The Freundlich constants K_f and $1/n$ obtained from the different treatments, together with the coefficient (R^2) for the linear fit, are given in Table 1. As shown in Table 1, the sorption capacity of HA for imidacloprid was significantly higher than that of Ca-clay. The K_f value of imidacloprid on HA was ~36 times greater than that on Ca-clay. This suggests that there might be more sorption sites for imidacloprid on HA than on Ca-clay due to the fact that HA may contain a large number of phenolic

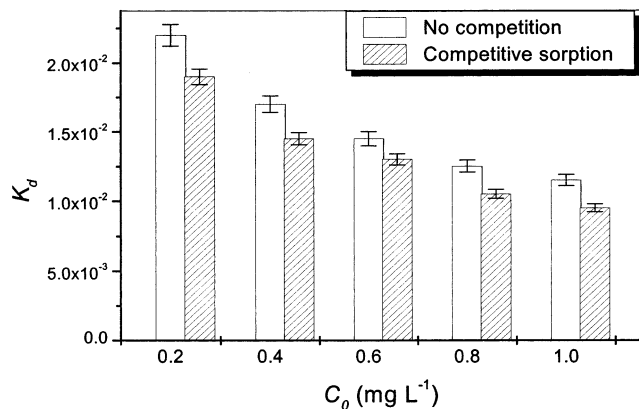


Figure 2. Competitive sorption between imidacloprid and imidacloprid-urea (10 mg L⁻¹) measured as the linear distribution coefficient K_d (L kg⁻¹) of imidacloprid at different initial concentrations of imidacloprid on Ca-montmorillonite.

hydroxyl and alcoholic hydroxyl groups. HA were one of the main components of organic matter in soil and play an important role in the sorption of many organic chemicals (20). Therefore, it could be postulated that organic matter can have an overwhelming contribution to imidacloprid sorption in soil.

When the sorption of imidacloprid on HA was measured using a solid/solution ratio of 1:200, K_f (Table 1) increased by 24% compared to when a 1:100 ratio was used. This implies that the small solid/solution ratio benefited imidacloprid sorption on HA, possibly due to greater dispersion of sorbent aggregates and greater exposure of the pesticide to sorbent surfaces.

Competitive Sorption on Ca-Clay. The sorption coefficients K_d of imidacloprid were significantly different with and without the presence of 10 mg L⁻¹ imidacloprid-urea in the system (Figure 2). On Ca-clay minerals, as the initial concentration of imidacloprid was increased, K_d generally decreased, which suggests that there might be a limited number of sites on the Ca-clay for the sorption of imidacloprid. The presence of imidacloprid-urea in the system consistently reduced the sorption of imidacloprid, with the reduction ranging from 12.8 to 17.8% for the concentration range of imidacloprid used. Therefore, imidacloprid-urea apparently competed for some of the same adsorptive sites used for imidacloprid sorption on the Ca-clay minerals. The sorption isotherms of imidacloprid on Ca-clay in the presence and absence of imidacloprid-urea are given in Figure 3. The isotherms apparently can be fitted to the Freundlich equation or a linear relationship. The sorption of imidacloprid was consistently less in the presence of imidacloprid than in the absence of the metabolite for the same initial concentrations of imidacloprid. Overall, the sorption capacity of imidacloprid on Ca-clay decreased ~15.8% in the presence of 10 mg L⁻¹ imidacloprid-urea, reflecting a decrease in K_f from 11.5 to 9.7.

Competitive Sorption on Humic Acids. The K_d values of imidacloprid sorption on HA with or without the presence of 20 mg L⁻¹ imidacloprid-urea are shown in Figure 4. Imidacloprid sorption on HA was somewhat similar to that on clay minerals. For instance, K_d of imidacloprid in HA suspension decreased as the initial imidacloprid concentration was increased when there was no imidacloprid-urea. The adsorption of imidacloprid was consistently greater in the absence of imidacloprid-urea than in the presence of the metabolite, indicating again competition for sorption sites between the two compounds. The overall reduction in imidacloprid sorption was greater on HA than on Ca-clay, ranging from 13.0 to 27.8%. This suggests

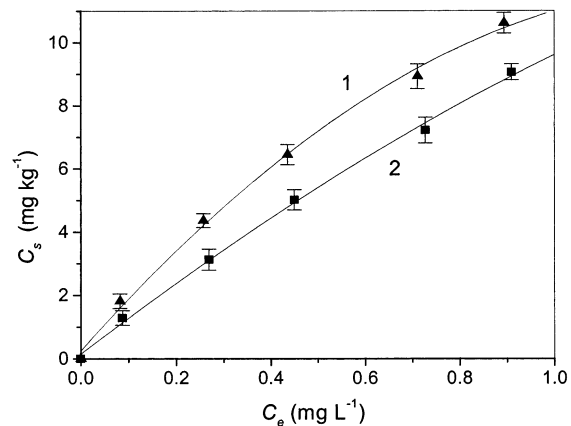


Figure 3. Sorption isotherms of imidacloprid on Ca-clay with (■) and without (▲) 10 mg L⁻¹ imidacloprid-urea.

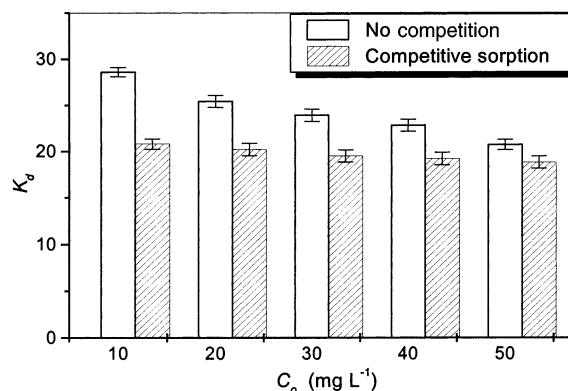


Figure 4. Competitive sorption between imidacloprid and imidacloprid-urea (20 mg L⁻¹) measured as the linear distribution coefficient K_d (L kg⁻¹) of imidacloprid at different initial concentrations of imidacloprid on humic acids.

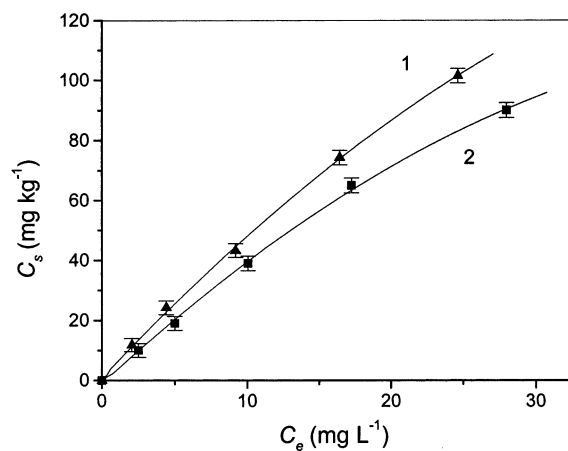


Figure 5. Sorption isotherms of imidacloprid on soil humic acids with (■) and without (▲) 20 mg L⁻¹ imidacloprid-urea.

that on HA, imidacloprid-urea may be able to compete for sorption sites more effectively than on clay minerals. The sorption isotherms of imidacloprid in HA suspensions are shown in Figure 5. In the presence of imidacloprid-urea, the sorption isotherms of imidacloprid consistently shifted lower compared to the isotherms in the single-solute system. Overall, the sorption capacity of imidacloprid on HA decreased ~25% in the presence of 20 mg L⁻¹ imidacloprid-urea, reflecting a decrease in K_f from 326 to 245. These results indicate that the leaching potential of

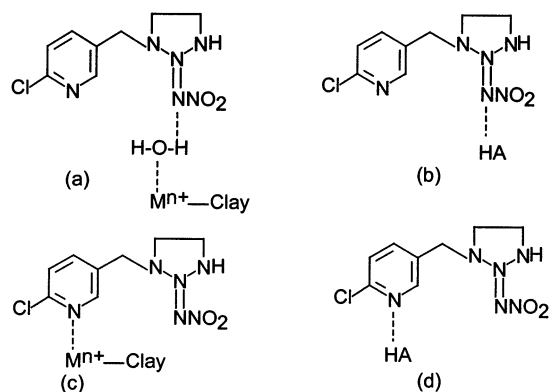


Figure 6. Possible interaction mechanisms of imidacloprid adsorbed on Ca-clay and humic acids.

Table 2. Shifts in Characteristic Vibration Bands (cm^{-1}) of Imidacloprid and Imidacloprid-urea after Sorption

assignment	imidacloprid			imidacloprid-urea	
	KBr	Ca-clay	HA-clay	KBr	HA-clay
$\nu_{\text{N}=\text{N}}$	1573	1565	1561		
$\nu_{\text{C}=\text{N}}$	1236	1254	1252	1264	1282
$\nu_{\text{N}=\text{O}}$				1683	1670

imidacloprid may be enhanced when its metabolite is formed in soil during degradation.

Sorption Mechanisms of Imidacloprid and Imidacloprid-urea. To understand the mechanisms of sorption of imidacloprid and imidacloprid-urea on soil components, differential IR spectra were obtained after sorption on Ca-clay or HA-clay mixtures. Some of the characteristic IR bands of Ca-clay or HA-clay complexes of imidacloprid and imidacloprid-urea are listed in **Table 2**.

The vibration band of $\text{N}=\text{N}$ in the imidazolidine ring of imidacloprid was shifted slightly from 1573 cm^{-1} for pure compound to 1565 cm^{-1} when it was adsorbed on Ca-clay or to 1561 cm^{-1} when it was adsorbed on HA-clay. The red shift on Ca-clay suggests that hydrogen bonds may have been formed between $\text{N}=\text{N}$ of imidacloprid and the hydrated cations of clay minerals (**Figure 6a**), which is in agreement with earlier reports for the sorption of $-\text{C}-\text{N}$ in chloroacetanilide herbicides on cation-saturated clays (19, 21). On HA, formation of a hydrogen bond between $\text{N}=\text{N}$ of imidacloprid and hydroxyl groups of HA may have occurred (**Figure 6b**). The vibration band of $\text{C}=\text{N}$ in the pyridine ring changed from 1236 cm^{-1} for the pure compound to 1254 cm^{-1} after sorption on Ca-clay and to 1252 cm^{-1} after sorption on HA-clay. These shifts may be attributed to the formation of a coordination bond between the $\text{C}=\text{N}$ group in pyridine and the exchangeable cation of clay (**Figure 6c**) and to the formation of a hydrogen bond between the $\text{C}=\text{N}$ group and a hydroxyl on the surface of HA (**Figure 6d**). These interactions are summarized in **Figure 6**.

Similar bonding mechanisms were visible for imidacloprid-urea. As shown in **Table 2**, the $\text{N}=\text{O}$ group stretch of imidacloprid-urea changed from 1683 cm^{-1} for the pure compound to 1670 cm^{-1} after sorption on HA-clay. The downward displacement of the carbonyl group was likely due to the decreasing double-bond nature of the $\text{N}=\text{O}$ group, which could be caused by the formation of a hydrogen bond between $\text{N}=\text{O}$ and hydrated cations of the clay surface (**Figure 7a**) or a hydrogen bond between the $\text{N}=\text{O}$ and a hydroxyl on the surface of HA (**Figure 7b**). A blue shift in the absorption band

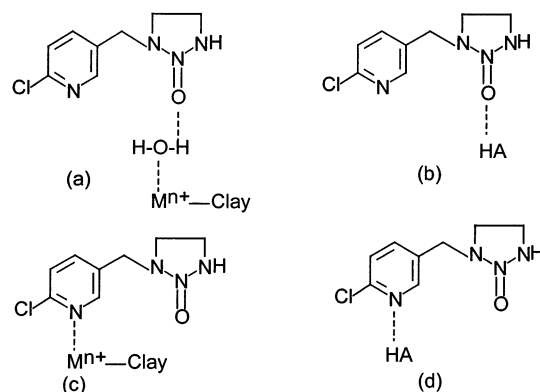


Figure 7. Possible interaction mechanisms of imidacloprid-urea adsorbed on Ca-clay and humic acids.

of $\text{C}=\text{N}$ in the pyridine ring after sorption suggests the formation of a coordination bond between the $\text{C}=\text{N}$ group in the pyridine ring with the exchangeable cation of the clay (**Figure 7c**) or the hydroxyl group on the surface of HA (**Figure 7d**). The potential mechanisms for sorption of imidacloprid-urea are illustrated in **Figure 7**.

Conclusions. Hydrolysis of imidacloprid in the environment produces imidacloprid-urea. The phenomena of competitive sorption between imidacloprid and imidacloprid-urea were studied using Ca-montmorillonite and humic acids that were extracted from a soil. Imidacloprid was moderately adsorbed to the Ca-clay and soil HA, and the linear distribution coefficient K_d of imidacloprid on HA was ~ 36 times greater than that on the Ca-clay. Sorption of imidacloprid was reduced by imidacloprid-urea in both Ca-clay and humic acids, indicating the occurrence of competitive sorption between these two compounds. The reduction in sorption caused by imidacloprid was more significant for HA than for the Ca-clay. From shifts in characteristic IR absorption bands of functional groups after sorption, a number of bonding interactions between imidacloprid or imidacloprid-urea and Ca-clay and HA were apparent. The primary interactions were proposed to be the formation of hydrogen bonds and coordination bonds between imidacloprid or its metabolite and soil components.

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