Adsorption–desorption behavior of atrazine on agricultural soils in China

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ABSTRACT

Adsorption and desorption are important processes that affect atrazine transport, transformation, and bioavailability in soils. In this study, the adsorption–desorption characteristics of atrazine in three soils (laterite, paddy soil and alluvial soil) were evaluated using the batch equilibrium method. The results showed that the kinetics of atrazine in soils was completed in two steps: a "fast" adsorption and a "slow" adsorption and could be well described by pseudo-second-order model. In addition, the adsorption equilibrium isotherms were nonlinear and were well fitted by Freundlich and Langmuir models. It was found that the adsorption data on laterite, and paddy soil were better fitted by the Freundlich model; as for alluvial soil, the Langmuir model described it better. The maximum atrazine sorption capacities ranked as follows: paddy soil > alluvial soil > laterite. Results of thermodynamic calculations indicated that atrazine adsorption on three tested soils was spontaneous and endothermic. The desorption data showed that negative hysteresis occurred. Furthermore, lower solution pH value was conducive to the adsorption of atrazine in soils. The atrazine adsorption in these three tested soils was controlled by physical adsorption, including partition and surface adsorption. At lower equilibrium concentration, the atrazine adsorption process in soils was dominated by surface adsorption; while with the increase of equilibrium concentration, partition was predominant.

Introduction

The herbicide atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) is widely used to control certain annual broadleaf and grass weeds, primarily in corn, but also in sugarcane, sorghum, other crops, and landscape vegetation to some extent. Atrazine was developed from research on derivatives of symmetrical triazines begun in 1952 (Knuesli, 1970). Atrazine has been a main herbicide worldwide since 1958, when atrazine was patented in Switzerland and then registered for commercial use in the United States (U.S. Environmental Protection Agency, 1994). Up to now, atrazine has been registered in more than 70 countries worldwide (Kauffmann et al., 2000; Zhang et al., 2004). In China, current annual atrazine usage is estimated at 10–15 million kg (Deng et al., 2005). However, widespread atrazine use is associated with increasing incidence of contamination in drinking water, with atrazine concentrations above the maximum contaminant level of 0.1 ppb (Guzzella et al., 2006). Atrazine and its degradation products, deethylatrazine and deisopropylatrazine, have been frequently detected in soils (Chung and Alexander, 2002), sediments (Jantunen et al., 2008), surface water (Al-Degs et al., 2009) and

groundwater (Hildebrandt et al., 2008) in many countries. Many recent studies have reported that atrazine and its metabolites are endocrine-disrupting chemicals and may pose potential risks to human health (Geng et al., 2013).

Atrazine accumulates in the soil due to its low chemical reactivity, leading to contamination of groundwater (Frank and Sirons, 1985). The environmental behavior of atrazine in a soil depends upon several factors, including adsorption by soil components, absorption by plants, transportation through runoff and leaching, volatilization, biodegradation, and chemical degradation (Deng et al., 2010). Adsorption and desorption of herbicides by soils play an important role in influencing the fate of herbicides in soil environments (Lesan and Bhandari, 2003; Wu et al., 2011). Close relationship exists between the adsorption–desorption behaviors of herbicides and the characteristics of soils (Wu et al., 2009), such as clay content and type, ionic strength (Ureña-Amate et al., 2005), soil pH (McGlamery and Slife, 1996), soil organic matter content (Seol and Lee, 2000), soil porous structure (Wang and Keller, 2008) and particles' specific surface area (Tang et al., 1998). Organic matter has been frequently reported to be the most important factor that influences adsorption of atrazine in soil, sediments or in solution (Lesan and Bhandari, 2003). Kulikova and Perminova (2002) reported that atrazine adsorption to soil humic substances was closely correlated to the aromaticity of the soil organic matter. It was showed that the quality of the soil organic matter plays an important role in the atrazine adsorption processes and hysteresis (Kempf and Brusseau, 2009). Most previous studies were conducted to study adsorption of atrazine on humic substances (Sun et al., 2010). Additionally, atrazine adsorption behaviors on biochars (Cornelissen et al., 2005), clays (Laird et al., 1992) and oxyhydroxides (Barriuso et al., 1994) were also investigated. Desorption and adsorption are of equal importance in determining the fate of atrazine in soils (Moreau and Mouvet, 1997), however, the adsorption and desorption of atrazine in different types of soils are poorly documented. Therefore, adsorption–desorption behavior of atrazine in soils is required to be further explored.

Various physical and chemical mechanisms are involved in herbicides adsorption in absorbents. They may act separately or together. Hydrogen bonds, Van der Waals forces and hydrophobic bondings are common mechanisms (Moreau and Mouvet, 1998). Senesi (1992) suggested that atrazine can also be adsorbed by ionic bonding on humic acid. Barriuso et al. (1994) showed that smectites absorbed atrazine primarily through relatively weak Van der Waals forces or hydrogen bonds. Píccolo et al. (1992) reported that charge transfer is a specific mechanism for atrazine

adsorption to humic acids. However, little is known about the mechanisms involved in atrazine adsorption on soils.

The objective of the present study was to understand the sorption and desorption characteristics of atrazine in three agricultural soils and to reveal the adsorption and desorption mechanisms, so as to provide a scientific basis for environmental risk assessment and ecological restoration of atrazine-contaminated soils and theoretical support for agricultural product quality and safety.

1. Materials and methods

1.1. Chemicals

Standard atrazine with >99.9% purity was purchased from Dr. Ehrenstorfer, Germany. The water solubility of atrazine is 33 mg/L, and the pK_a is 1.7 (Chefetz et al., 2004). Methanol used in this study was high-performance liquid chromatography (HPLC) grade from Sinopharm Chemical Reagent Co. Ltd., China. Deionized water (18.25 MΩ) was obtained from a Spring-S60i + S60i + PALL system. All other reagents were analytically leveled.

1.2. Soil characterization

The laterite and paddy soil used in sorption experiments were collected from Danzhou and Qiongzhong respectively in Hainan Province, China. Alluvial soil came from the Sixth Ring Road, Beijing, China. The soil samples were taken from 0 to 20 cm soil layers and were air-dried. All samples were sieved through a 1-mm mesh and sealed in a container for later use. The basic properties of the soils are summarized in Table 1.

1.3. Adsorption and desorption experiments

An atrazine adsorption experiment was carried out using a batch procedure (Chefetz et al., 2004). An appropriate amount of soil was transferred to 50-mL centrifuge tubes, and 10 mL of atrazine solution (in background solution of 0.01 mol/L $CaCl_2$ to maintain a constant ionic strength and 0.2 g/L of NaN_3 to inhibit microbial activity, with pH 7) was added at initial atrazine concentrations of 0.5, 1, 5, 10, and 20 mg/L. All tubes were immediately sealed and then mechanically shaken for 24 hr in a thermostatic oscillation incubator at 25°C, except for the thermodynamic experiments, in which temperatures of 15 and 35°C were adjusted and then the suspensions were

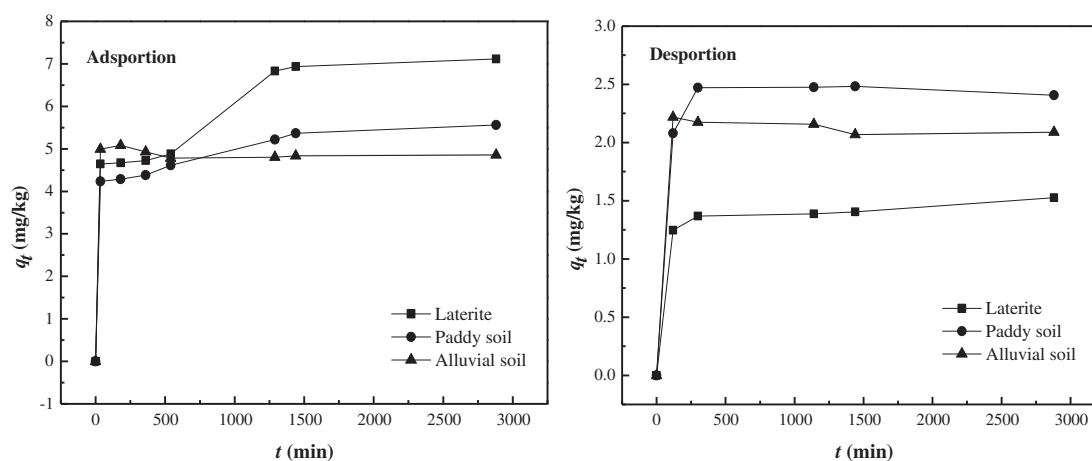| Table 1 – Physical and chemical properties of three agricultural soils.			
Property	Soil sample		
	Laterite	Paddy soil	Alluvial soil
pH ($CaCl_2$)	4.19 ± 0.01	5.21 ± 0.01	7.50 ± 0.01
Organic matter (%)	3.23 ± 0.02	4.19 ± 0.03	6.37 ± 0.03
Cation exchange capacity (cmol/kg)	7.47 ± 0.08	7.16 ± 0.15	7.24 ± 0.10
Sand (%)	34.12 ± 0.40	42.09 ± 0.29	24.50 ± 0.18
Silt (%)	40.19 ± 0.61	23.92 ± 0.72	59.27 ± 0.55
Clay (%)	25.68 ± 0.30	33.99 ± 0.18	16.23 ± 0.21

Fig. 1 – Adsorption and desorption equilibration curves of atrazine sorption in soils. The initial atrazine concentration was 5 mg/L, and the volume of the solution was 10 mL.

centrifuged at 5000 r/min for 5 min. A 2-mL supernatant was filtered through the membrane with a pore size of 0.45 μm and was then analyzed by HPLC. Each processing sets three repetitions. A blank (no soil) was prepared for each initial atrazine concentration. Atrazine loss during adsorption and filtration was negligible. The sorption kinetics of atrazine was evaluated at an initial atrazine concentration of 5 mg/L in all soils. To determine the contact time required to achieve sorption equilibrium, the suspensions were sampled at 35, 180, 360, 540, 1290, 1440, and 2880 min. The amount of atrazine sorbed was calculated by Eq. (1):

$$q_e = C_0 - C_e V/m \qquad (1)$$

where q_e (mg/g) is the amount of atrazine absorbed; C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium aqueous concentrations respectively; V (mL) is the solution volume; and m (g) is the mass of soil in the centrifuge tubes.

After adsorption experiments, desorption experiments were immediately conducted by replacing 10 mL supernatant with atrazine-free background solution. The tubes were agitated (200 r/min) for 24 hr and then centrifuged at 4000 r/min for 15 min. The supernatants were filtered through 0.45-μm syringe filters and analyzed by HPLC. To analyze the desorption kinetics, sampling times of 120, 300, 1140, 1440, and 2880 min were used.

Atrazine concentrations in the liquid phase were measured using a HPLC (Waters Alliance 2695) equipped with a Gemini C$_{18}$ analytical column (150 × 4.0 mm ID (Inner Diameter), 5 μm) and detected by UV (Ultraviolet) spectrophotometry. The operating conditions were: mobile phase 70/30 (V/V) of methanol/water, flow rate 1 mL/min, column temperature 35°C, and detector wavelength 220 nm. The retention time for atrazine was 4.8 min.

1.4. Data analysis

Pseudo-second-order kinetics (Eq. (2)) and the Elovich model (Eq. (3)) were used to stimulate the adsorption kinetics. The equations can be expressed as:

$$t/q_t = (1/k_2 q_e^2) + (1/q_e \times t) \qquad (2)$$

$$q_t = a + bt \qquad (3)$$

where q_t (mg/g) and q_e (mg/g) are the amount of atrazine adsorbed at time t (min) and under equilibrium conditions respectively and k_2 (g/(mg·min)) is the pseudo-second-order model rate constant for adsorption.

The Freundlich and Langmuir models were used to fit the adsorption and desorption isotherms. The Langmuir equation (Eq. (4)) is:

$$1/q_e = 1/q + (1/(K_L q))(1/C_e) \qquad (4)$$

where, q_e (mg/g) is the amount of atrazine adsorbed by a mass of soil and C_e (mg/L) is the equilibrium concentration in solution; q_{max} (mg/g) is the maximum adsorption capacity; and K_L (L/mg) represents the Langmuir constant related to the bonding force of sorption.

Sample	Pseudo-second-order model			Elovich equation		
	q_e (mg/g)	k_2 (g/(mg·min))	R^2	a	b	R^2
Laterite	0.009	0.395	0.984	1.635	774	0.821
Paddy soil	0.007	0.453	0.960	2.042	828	0.662
Alluvial soil	0.005	77.900	0.999	28.430	−4555	0.572

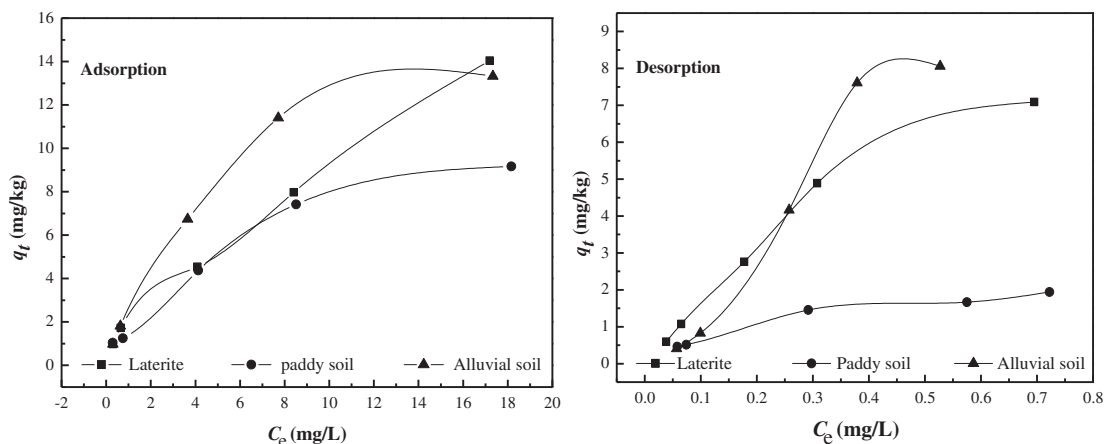Table 2 – Constants and coefficients of determination of pseudo-second-order kinetics and Elovich models of sorption.

Fig. 2 – Sorption and desorption isotherms for atrazine in soils.

The Freundlich equation (Eq. (5)) is:

$$\log q_e = \log K_F + (1/n) \log C_e \tag{5}$$

where q_e (mg/g) is the amount adsorbed by the soil mass, C_e (mg/L) is the equilibrium concentration of atrazine, K_F ((mg/g)(mg/L)$^{-n}$) is the adsorption equilibrium constant) representing the adsorption capacity, and n is a constant indicative of adsorption intensity.

The experiments were carried out at 288, 298, and 308 K. The thermodynamic parameters for the adsorption processes were obtained by the following equations:

$$\Delta G^o = -RT \ln K_F \tag{6}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{7}$$

where K_F is the Freundlich constant, T (K) is the absolute temperature, R is the gas constant (8.314 J/(mol·K), ΔS^o (kJ/(mol·K)) is the standard entropy change, and ΔH^o (kJ/mol) is the standard enthalpy change. ΔH^o and ΔS^o were obtained from the slopes and intercepts of a linear regression of $\ln K$ vs. $1/T$. ΔG^o (kJ/mol) is the standard Gibbs free energy.

The hysteresis coefficient (H) was calculated for the adsorption/desorption isotherms according to Eq. (8) (Barriuso et al., 1994):

$$H = (1/n_{des})/(1/n_{ads}) \tag{8}$$

where, $1/n$ is the Freundlich exponent for the desorption and sorption isotherms.

2. Results and discussion

2.1. Sorption kinetics

Adsorption kinetics is one of the most important characteristics governing solute uptake rate and represents adsorption efficiency. The sorption kinetics of atrazine in three kinds of soils is shown in Fig. 1. The atrazine adsorption process was similar among the three types of soils. The kinetics of atrazine in soils was completed in two steps: a "fast" adsorption and a "slow" adsorption. In the early stage, adsorption occurred as a rapid reaction, showing a sharp drop in solution concentration, but at 24 hr, the concentration increased slightly into balance. Therefore, it is apparent that the equilibrium time was approximately 24 hr. This phenomenon might be because that the adsorption of atrazine occurred on the surface of soil organic matter. With the increase of time, soil surface adsorption sites gradually saturated, causing the decrease of adsorption rate until reaching the equilibrium. The percentages of atrazine adsorbed at 24 hr were approximately 27.8%, 21.5%, and 19.3% for laterite, paddy soil, and alluvial soil, respectively. The results were consistent with the studies of Lesan and Bhandari (2003). The "fast" adsorption of organic compounds may be attributed to adsorption of organic compounds to mineral surfaces (Huang et al., 1996) or partitioning into a "rubbery" fraction of the soil organic matter (Xing and Pignatello, 1996), while the "slow" adsorption could be related to the gradual diffusion of organic compounds into soil micropores (Ball and Roberts, 1991) or into highly

Table 3 – Isotherm parameters for atrazine sorption in soils.								
Sample	Study	Freundlich model			Langmuir model			H
		$\log K_F$	$1/n$	R^2	K_L	q_{max} (mg/kg)	R^2	
Laterite	Adsorption	0.32	0.64	0.99	0.37	9.51	0.99	1.38
	Desorption	1.06	0.88	0.99	0.21	74.63	0.99	
Paddy soil	Adsorption	0.27	0.58	0.98	0.69	5.58	0.85	1.01
	Desorption	0.39	0.59	0.99	3.43	2.67	0.99	
Alluvial soil	Adsorption	0.39	0.68	0.98	0.21	15.90	1.00	2.14
	Desorption	1.41	1.45	0.99	−1.76	−3.73	0.99	

Table 4 – Thermodynamic parameters for atrazine adsorption in the three tested soils.

T (K)	K_F			$\triangle G^o$ (kJ/mol)			$\triangle H^o$ (kJ/mol)	$\triangle S^o$ (kJ/mol/K)
	288	298	308	288	298	308		
Laterite	1.153	2.103	3.646	−0.341	−1.842	−3.313	42.440	0.149
Paddy soil	1.415	1.855	2.592	−0.831	−1.531	−2.439	22.348	0.080
Alluvial soil	1.053	2.430	2.740	−0.124	−2.200	−2.581	34.979	0.123

cross-linked regions of soil organic matter (Karapanagioti et al., 2000). As shown in Fig. 1, atrazine desorption in soils was relatively slow, reaching desorption equilibrium at 5 hr. To reach an adequate desorption balance while remaining consistent with the adsorption reaction time, the balance time of the adsorption–desorption experiment was set at 24 hr.

Pseudo-second-order and Elovich models were used to study the atrazine adsorption mechanism (Table 2). Atrazine sorption kinetics were satisfactorily described by a pseudo-second-order model with coefficients of determination (R^2) ranging from 0.960 to 0.999, compared with R^2 values of 0.572–0.821 for the Elovich model. This well-fitting pseudo-second-order model indicated that the rate-limiting step was chemical adsorption, including electronic forces through sharing or exchange of electrons (Qiu et al., 2009). Moreover, it suggested that sorption was governed by the availability of sorption sites on the soil surfaces instead of by the atrazine concentration in solution (Liu, 2008).

2.2. Sorption isotherms

The adsorption isotherm was used for quantitative analysis of atrazine transport from liquid to solid phase and for understanding the nature of interactions between atrazine and the soil matrix (Kasozi et al., 2012). The sorption isotherms of atrazine in soils are plotted in Fig. 2. The results showed that the atrazine adsorption capacities of the three tested soils varied markedly due to their different physicochemical properties. With the increase of atrazine concentration, the adsorption quantity increased. At the low concentration of atrazine, adsorption capacity presented a relative linear increasing trend.

The Freundlich and Langmuir models are two common expressions used to describe atrazine adsorption (Chingombe et al., 2006). The isotherm parameters of the Freundlich and Langmuir models are listed in Table 3. The Freundlich isotherm is used mainly for adsorption surfaces with nonuniform energy distribution, whereas the Langmuir isotherm is used for monolayer adsorption on perfectly smooth and homogeneous surfaces (Yan et al., 2008). Based on the Freundlich and Langmuir equations, the adsorption parameters $\log K_F$, $1/n$, K_L, and q_{max} and the coefficient of determination (R^2) of atrazine in soils was obtained (Table 3). As shown in Table 3, the experimental soil atrazine data was fitted well using Freundlich and Langmuir models, respectively. According to the coefficients of determination (R^2), atrazine sorption data for laterite, paddy soil were better fitted by the Freundlich model, which assumes that atrazine sorption occurs on a heterogeneous surface with the possibility of sorption being multi-layered (Fuentes et al., 2014). This phenomenon has also been observed in humic acid and nanometer clay mineral (Wang and Si, 2009; Chang et al., 2010). All values of the affinity parameter ($1/n$, 0.581–0.676) were

less than 1, indicating sorption by heterogeneous media where high-energy sites are occupied first, followed by sorption at lower-energy sites (Sukul et al., 2008). The Freundlich sorption coefficient (K_F) reflected the adsorption capacity of soils for atrazine. The order of adsorption capacity was alluvial soil (K_F = 2.430 (mg/g)(mg/L)$^{-n}$) > laterite (K_F = 2.103 (mg/g)(mg/L)$^{-n}$) > paddy soil (K_F = 1.855 (mg/g)(mg/L)$^{-n}$). The low values of the Freundlich sorption coefficient indicate that atrazine is probably highly mobile in soil (Doretto and Rath, 2013).

Simultaneously, atrazine sorption data were well fitted by Langmuir model (Table 3), especially for alluvial soil (R^2 = 0.999), which indicated a homogenous distribution of active sites on the soil surface. The value of q_{max} in Langmuir model represents the maximum amount of atrazine that could be sorbed by the soil. Higher values of q_{max} were obtained for alluvial soil (15.898 mg/kg) and laterite (9.506 mg/kg), whereas lower values were obtained for paddy soil (5.577 mg/kg), a result that was consistent with the Freundlich model. The Freundlich constant (K_L), which is related to the binding energy of sorption, indicated the affinity of the soil surface for atrazine. K_L values for atrazine sorption on these soils ranged from 0.214 to 0.694 L/mg.

2.3. Sorption thermodynamics

To clarify the adsorption mechanisms, the thermodynamic parameters mentioned earlier were calculated and are presented in Table 4. Generally, the value of Gibbs free energy change ($\triangle G^o$) indicates the spontaneity of a chemical reaction. Therefore, it is possible to evaluate whether sorption is related to spontaneous interaction (Saha and Chowdhury, 2011). Negative values of $\triangle G^o$ (Table 4) indicated that the feasibility and spontaneous nature of the atrazine adsorption
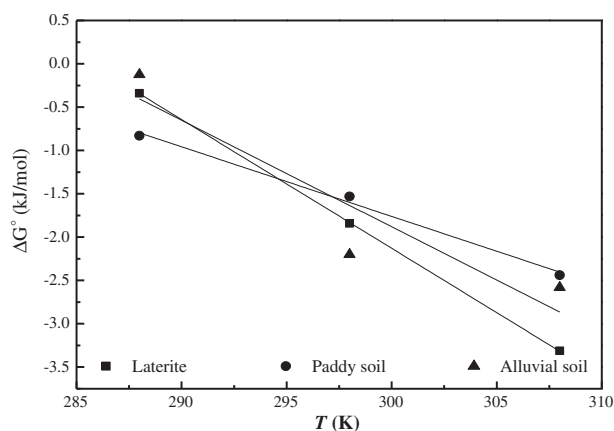
Fig. 3 – Effect of temperature on atrazine adsorption free energy in the three tested soils.

Table 5 – Energy of sorption by different forces (unit: kJ/mol).						
Van der Waals force	Hydrophobic interaction	H-bonding	Charge transfer	Ion exchange	Dipole bond force	Chemical bonding
4–10	≈5	2–40	Not available	≈40	2–29	>60

process in soils were obtained under the conditions and the temperature range (288–308 K) covered by this research. $\triangle G^o$ decreased with increasing temperature, $\triangle G^o_{288\ K} > \triangle G^o_{298\ K} > \triangle G^o_{308\ K}$ (Fig. 3), in agreement with the assumption of an endothermic adsorption process. This showed that atrazine sorption onto a soil surface is more favorable at higher temperatures (Guo et al., 2013). It was clear that the enthalpy changes ($\triangle H^o$) of the atrazine adsorption processes were positive, showing an endothermic heat of adsorption reaction for atrazine and suggesting that a large amount of heat was consumed to transfer atrazine from the aqueous into the solid phase. Increasing temperature was mostly favorable for atrazine sorption. All absolute values of $\triangle H^o$ for atrazine in the three tested soils were less than 40 kJ/mol, which was consistent with an assumption of physisorption (Kara et al., 2003; Von Oepen et al., 1991a, b). It has been reported that adsorption of organic pollutants in a solid–liquid interface is generally caused by a combination of various adsorption forces (Johannes, 2001; Picó and Andreu, 2007). Based on the magnitude of $\triangle H^o$, conclusions about the adsorption mechanism can be drawn. According to Von Oepen et al. (1991a, 1991b) (Table 5), hydrogen bonding and ion exchange may be regarded as the important interactions during the sorption process of atrazine on laterite ($\triangle H^o$ = 42.440 kJ/mol), whereas for paddy soil ($\triangle H^o$ = 22.348 kJ/mol), the atrazine sorption mechanism may be hydrogen bonding and dipole bond force. For alluvial soil, $\triangle H^o$ was 22.348 kJ/mol, indicating that atrazine adsorption in alluvial soil is probably caused only by hydrogen bonding. Moreover, the entropy values ($\triangle S^o$, Table 4) obtained for atrazine were positive, reflecting the affinity of the tested soils towards atrazine molecules. This also suggested an increase in randomness in the investigated soil/solution system, with some structural changes occurring in both the adsorbate and the adsorbent (Maszkowska et al., 2014).

2.4. Desorption

Pesticide desorption plays an important role in determining the release rate and the potential mobility of pesticides in soil (Deng et al., 2010). Desorption isotherms were determined based on the procedure used for adsorption isotherms. Desorption isotherms represent the amount of a compound that is still adsorbed as a function of the equilibrium concentration after one desorption cycle (Doretto et al., 2014). Desorption isotherms for atrazine in soils are presented in Fig. 2. Desorption data were fitted with Freundlich and Langmuir models for all soils, and the calculated parameters are summarized in Table 3. The desorption K_F values were consistently higher than those obtained for atrazine adsorption on the tested soils. The results indicated a lower desorption capacity and hence a low atrazine mobility in soils.

Hysteresis is a phenomenon indicating that desorption is strongly delayed or hindered relative to sorption (Lesan and

Bhandari, 2003). The hysteresis coefficient (H) measures the extent of hysteresis in the desorption step, and its value (Table 3) was evaluated using the Freundlich coefficients for sorption and desorption (Eq. (8)). Theoretically, if H is equal to 1, hysteresis is absent. However, when the Freundlich slope for the desorption isotherm ($1/n_{des}$) is less than the Freundlich slope for the adsorption isotherm ($1/n_{ads}$), a positive hysteresis is indicated ($H < 1$) because the molecule resists desorption from the soil. In contrast, when $1/n_{des}$ exceeds $1/n_{ads}$, negative hysteresis ($H > 1$) occurs, indicating that desorption is enhanced (Doretto et al., 2014). It is worth emphasizing that there is no consensus about an absolute value to indicate the presence of hysteresis in the literature and therefore the term is sometimes misused. Barriuso et al. (1994) defined that hysteresis is absent when $0.7 < H < 1$. This study presents hysteresis coefficients ranging from 1.01 to 2.14, suggesting negative hysteresis and indicating that atrazine desorption was favored on all soils evaluated. This phenomenon has been explained for sorption and desorption hysteresis by some authors as a result of: (1) sequestration or irreversible binding of organic carbon and/or clay minerals to soil aggregates (Bhandari et al., 1996) and (2) entrapment of sorbed molecules in meso- and microporous structures within the organic carbon matrix and the mineral structures of soil aggregates (Carroll et al., 1994; Farrell and Reinhard, 1994; Weber et al., 1998).

2.5. Effect of pH

The pH value is an important factor influencing the adsorption behavior, which can change the molecule charge, morphology and surface properties of adsorbent. To evaluate
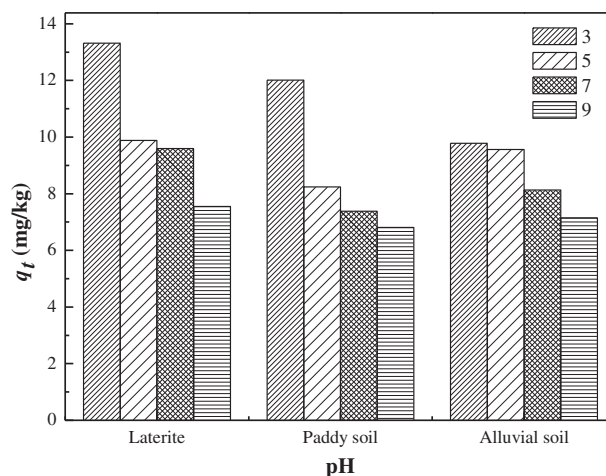
Fig. 4 – Effect of pH on atrazine adsorption in the three tested soils.

the effect of pH on atrazine adsorption in soils, the pH was varied from 3.0 to 9.0. The test results were presented in Fig. 4.

As shown in Fig. 4, the atrazine adsorption exhibited a similar tendency among all samples in the tested range of pH. For instance, the adsorption amount of atrazine in soils decreased with the increasing pH value. The results are consistent with Abate and Masini (2005) that lower pH provides more favorable conditions for atrazine adsorption. Several factors may be related to this phenomenon: Firstly, atrazine is weakly alkaline pesticide with the pK_a at 1.68 (Lima et al., 2010). When pH value is near the pK_a of atrazine, half of atrazine existed in the cationic form while the other half stayed in the non-ionic form. The increasing pH value could reduce the cationic fraction of atrazine in solution. The atrazine adsorption mechanism was mainly attributed to the molecular state and protonation of carboxyl group. With the pH value increase, the cationic state decreased and the protonation effect weakened, which reduced the adsorption quantity of atrazine (Tao and Tang, 2004). Secondly, the high pH value could promote the hydrolysis of carbonyl, hydroxyl and other functional groups on the surface of soil, resulting in the adsorption sites of atrazine decreased. Thirdly, alkaline condition could facilitate the dissolution of soil organic matter, then resulting in the reduction of the soil adsorption quantity of atrazine.

2.6. Mechanism analysis

After contaminants went into soils, its properties and molecular structure would affect the degree of adsorption. Chiou et al. (1979) reported that the organic content of soils played a major role in the adsorption of non-ionic pesticides, while the mineral components content had little effect. However, it was contrary to the ionic pesticides. Bailey and White (1964) showed that the adsorption behaviors of pesticides in soils could be affected by chemical properties, molecular structure, acidity and alkalinity (pK_a or pK_b), water solubility and other physical and chemical properties of pesticides.

According to Gibbs free energy change ($\triangle G^o$), the adsorption mechanism of atrazine in three tested soils can be obtained. Cater et al. (1995) concluded that the physical adsorption and partition were predominant, when the absolute value of $\triangle G^o$ exceed 40 kJ/mol. While the absolute value of $\triangle G^o$ was less than 40 kJ/mol, the surface adsorption was main. From Table 4, the Gibbs free energy ranged from −1.842 to 2.200 kJ/mol, which suggested that surface adsorption was the major adsorption behavior of atrazine in three tested soils.

Furthermore, Zhu and Chen (2000) had quantitatively described the contribution of partition and surface adsorption for the adsorption behavior of organic pollutants in soil/

sediment. In order to investigate the adsorption mechanism of atrazine in these soils, the adsorption quantity of atrazine in soils was calculated by following equations (Eqs. (9)–(11)). The results were showed in Table 6.

$$Q_T = Q_P + Q_A \qquad (9)$$
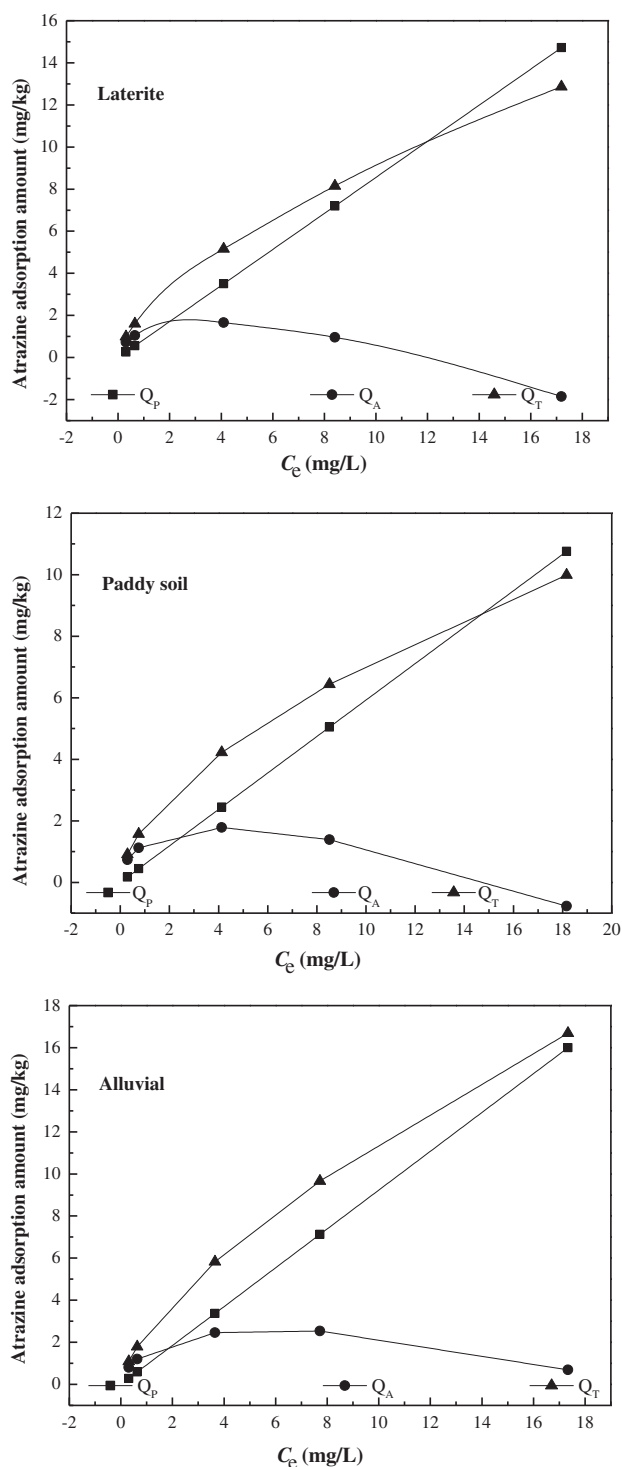$$Q_P = K_{oc} f_{oc} C_e \qquad (10)$$

Fig. 5 – The contribution of partition and surface adsorption to atrazine adsorption in three tested soils.

Table 6 – The contribution of surface adsorption and partition to atrazine adsorption in soils.

Soil samples	Partition	Surface adsorption
Laterite	$Q_P = 0.8561C_e$	$Q_A = 2.103C_e^{0.6366} - 0.8561C_e$
Paddy soil	$Q_P = 0.5924C_e$	$Q_A = 1.855C_e^{0.5808} - 0.5924C_e$
Alluvial	$Q_P = 0.9231C_e$	$Q_A = 2.430C_e^{0.6755} - 0.9231C_e$

$$Q_A = KC_e^n - K_{oc}f_{oc}C_e \qquad (11)$$

where, Q_T (mg/kg) is the total adsorption amount of atrazine; Q_p (mg/kg) is the atrazine adsorption amount generated by partition; Q_A (mg/kg) is the adsorption amount of atrazine generated by the surface adsorption; K_{oc} (L/kg) is the partition coefficient based on the equation $K_{oc}=K_d/f_{oc}$; f_{oc} is the organic carbon content of soils.

On the basis of Table 6, the relationship between Q_T, Q_p and Q_A with C_e could be presented in Fig. 5. It was found that the process of atrazine adsorption in three tested soils included surface adsorption and partition, however, the contribution was obviously different. At lower equilibrium concentration, the atrazine adsorption process in soils was dominated by surface adsorption; while with the increase of equilibrium concentration, surface adsorption reached saturation and the adsorption process was dominant by partition.

3. Conclusions

Atrazine adsorption and desorption on three tested soils were studied using a batch technique. The adsorption kinetics data were better modeled using pseudo-second-order kinetic equations, indicating that the rate-limiting step was chemical adsorption and that sorption was governed by availability of sorption sites on soil surfaces. Atrazine adsorption isotherms in soils were well correlated with both the Freundlich and Langmuir models. Experimental data demonstrated that the sorption capacity followed the sequence of alluvial soil > laterite > paddy soil based on K_F and q_{max}. Moreover, the calculated positive $\triangle H^o$ and negative $\triangle G^o$ values for adsorption indicated the spontaneous endothermic nature of atrazine adsorption in soils. Furthermore, desorption of atrazine in three tested soils exhibited negative hysteretic effects, indicating that atrazine desorption was favored. Acidic solutions are more conducive to the adsorption of atrazine in soils. The atrazine adsorption in these three tested soils belongs to physical adsorption, including surface adsorption and partition. At lower equilibrium concentration, the atrazine adsorption process in soils was dominated by surface adsorption; while with the increase of equilibrium concentration, surface adsorption reached saturation and the adsorption process was dominated by partition.

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