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Adsorption–desorption characteristics and pollution behavior of reactive X-3B red dye in four Chinese typical soils

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Abstract

Purpose Organic dyes have been turned into an important emerging type of chemical pollutants with the development of rural textiles, synthetic dye, printing, and dyeing industries and the continuous release from washing fabrics and clothes in recent decades. In order to assess ecological risk of reactive X-3B red dye as a typical dye, the adsorptive and desorptive traits of the dye in soils were investigated and the environmental factors influencing those processes were examined and discussed.

Materials and methods Adsorptive and desorptive isotherms and dynamics of reactive X-3B red dye as a typical emerging pollutant were investigated by the standard batch experiments using four typical soils in China including relatively clean brown earth (burozem), drab soil (cinnamon soil), paddy soil (aquorizem), and red soil (krasnozem) and calculated by mathematical models using the Microsoft Excel software.

Results and discussion It was suggested that the adsorptive behavior of reactive X-3B red dye by the four soils can basically be described using the Langmuir equation, and their maximum adsorbing capacity was in the sequence paddy soil > red soil > brown earth > drab soil. The adsorption could be divided into four stages including high-speed adsorption, slowdown adsorption, tardiness adsorption, and zero-approaching adsorption. It was also indicated that the adsorption ability of the dye decreased with the reduction in soil organic matter or air temperature and under neutral, runny, or unwatered conditions. The increase of desorption was observed with the decrease of soil organic matter and the increase of air temperature or soil moisture, while desorption was inhibited by the acidification or basification of soils. The comparative study validated that the basic adsorption–desorption laws of the dye at high concentrations were basically consistent with those at low concentrations.

Conclusions It could be concluded that reactive X-3B red dye has the potential properties of persistent organic pollutants with high ecological risk, and its release from contaminated soils and uptake by crops can be disturbed and changed by human activities.

Keywords Adsorption · Chemical dynamics · Desorption · Emerging pollutant · Environmental factor · Organic dye · Soil pollution

1 Introduction

Since the synthesis of the first organic dye named “mauveine” from coal tar chemicals by the English chemist William Henry Perkin (1838–1907) in 1856, various synthetic organic dyes have ceaselessly and increasingly entered into chemical industry and textile community and played more and more important roles in

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our daily life (Brightman 1956; Waring and Hallas 1990; MCI-China 1995). The continuously extended syntheses and production of organic dyes subsequently engender environmental problems of organic dye pollution and result in their adverse effects on human health in the world (Kanekar and Sarnaik 1991; Sun et al. 2001; Zhou and Huang 2001; Allègre et al. 2006). Nowadays, organic dyes have been turned into an important emerging type of chemical pollutants with the development of textiles, synthetic dye, printing, and dyeing industries and the continuous release from washing fabrics and clothes in recent decades (Zhou and Wang 1997; Zhou 2001). Environmental pollution of water–soil–plant systems by organic dyes and their adverse effects on human health by way of food chain is increasingly concerned, which has greatly gone beyond the previous prediction and its prime mover (Zhou and Wang 2006). Particularly in Chinese coasting areas, the concentration of organic dyes in soil was very high because of its long-term accumulation. According to the previous investigation (Zhou 2001), organic dye concentration in soil nearby a printing and dyeing plant in Dailian, Shaoxing, and Guangzhou (China) was up to 134.4–1130.2, 25.3–3114.0 and 23.2–1238.1 mg kg^{-1}, respectively. Moreover, organic dye concentration in ponds and rivers nearby a printing and dyeing plant, Guangzhou (China) was up to 269–706 mg l^{-1}. Thus, doing research on environmental behavior and ecological effects of reactive X-3B red dye at high concentrations is of great significance in practice.

According to some available research reports (McLaren 1983; Willetts et al. 2000; Ong et al. 2005; Mohan et al. 2007; Sirianuntapiboon et al. 2007), treatment of wastewater from textiles, synthetic dye, printing, and dyeing industries has been extensively investigated and explored from different angles. There is a large literature about the decolorization of wastewater containing organic dyes (Hao et al. 2000; Kang et al. 2000; Panswad and Luangdilok 2000; Park et al. 2007). Sonolysis, chemical oxidation, photocatalytic degradation, aerobic and anaerobic biodegradation, and biosorption of organic dyes were also examined and discussed extensively (Stock et al. 2000; Jonnalagadda and Nadupalli 2004; Gupta et al. 2006). However, research on traits and dynamics of soils adsorbing organic dyes as emerging pollutants has not been involved basically. The chemical behavior of organic dyes in the environment and their ecological effects, including environmental fate of organic dyes released into waters, desorption from soils, and transport and transformation between water and soil, still remain unclear (Zhou and Huang 2001; Crini 2006).

On the basis of our previous investigation (Zhou 2001; Cheng and Zhou 2002), reactive X-3B red dye was chosen to do further research as a typical emerging organic pollutant which has extensively occurred in the soil environment of Chinese coastal areas and other countries in the world. Through analyzing adsorptive and desorptive traits of the dye in soil environment and discussing environmental factors influencing the adsorption and desorption of the dye in soil environment, this work aims at providing basic data for the safe assessment of agricultural and food production and industrial syntheses of organic dyes with low ecological risk and providing a scientific foundation for the control of soil pollution by organic dyes at high concentrations.

2 Materials and methods

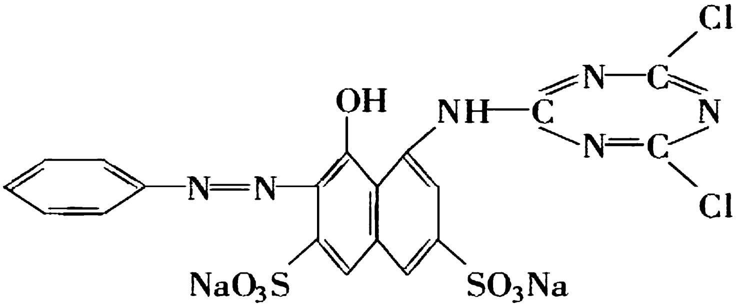
2.1 Tested soils and reactive X-3B red dye

As the representative types of soils distributed in the Chinese coastal areas with flourishing printing, dyeing, textile, and synthetic dye enterprises, four soils including relatively clean brown earth (burozem), drab soil (cinnamon soil), paddy soil (aquorizem), and red soil (krasnozem) were systematically sampled. The soil samples were taken from 0- to 20-cm depth. Each type of soil samples from four sites was mixed, air-dried, sieved through 2 mm, and stored in a refrigerator. Basic physical and chemical properties of these tested soils are listed in Table 1.

Table 1 Physical and chemical properties of the tested soils

Soil type	pH (H_2O)	Organic matter (%)	Total N, N%	Total P, P_2O_5%	CEC, meq·(100g soil)$^{-1}$	Clay content (%)	
						<0.001mm	<0.01mm
Brown soil	6.5	2.31	0.10	0.08	12.05	10.3	18.0
Drab soil	7.8	1.38	0.08	0.13	25.23	14.5	20.3
Paddy soil	6.8	2.97	0.15	0.13	19.67	24.1	38.6
Red soil	5.3	2.37	0.09	0.06	8.71	17.2	32.7

The corresponding compound of reactive X-3B red dye was supplied from the Lin-an Synthetic Dye Plant through the Hangzhou Silk-Dyeing Plant, Zhejiang Province, China. The purity and solubility of this compound is 96.7% and 80.0 g l^{-1} (20°C), respectively. The solubility of the dye increases with an increase in temperature (MCI-China 1995). The chemical structure is depicted as follows:



It contains azo group (–N=N–), hydroxy (–OH), and sulfonic acid group (–HSO_3) in its structure.

2.2 Adsorptive isotherms

The chemical was carefully weighed, and 20.48, 40.96, 61.44, 81.92, 122.88, and 245.76 mg of reactive X-3B red dye was respectively placed into 250 ml of measuring flasks with 10.0 g of surface soil samples. Then the flasks were filled with deionized water to their scale, tightly covered with caps, and the samples shaken for 24 h on a reciprocating shaker at 150 rpm and 25±1°C. The suspensions were filtered and the filtrates were analyzed for reactive X-3B red dye using the gas chromatography method (Santos-Delgado et al. 2000; Nagaraju and Huang 2007). Each treatment was replicated four times. At the same time, the control experiment for each type of soils was carried out. The amount of the dye adsorbed on the soil particles was calculated using the subtraction method (He et al. 1998).

2.3 Adsorptive dynamics and determination of adsorptive velocity

Subsequently, 10.00 g of soil samples and 81.92 mg of the organic dye were placed into 250 ml of measuring flasks. The flasks were filled with deionized water to their scale and tightly covered with caps. The samples were shaken for 0.25, 0.50, 0.75, 1, 2, 4, 6, 8, 12, 16, 20, and 24 h on a reciprocating shaker at 150 rpm and 25±1°C, respectively. The suspensions were filtered through a 0.45-μm pore size membrane filter and the filtrates were analyzed for reactive X-3B red dye using the gas chromatography method (Santos-Delgado et al. 2000; Nagaraju and Huang 2007). Each treatment was replicated four times. The adsorptive velocity of the dye on soils was calculated according to changes of the dye in the process of adsorption (Zhou 1995; He et al. 1998).

2.4 Desorptive dynamics and determination of desorptive velocity

The above soils adsorbing the dye were taken back to the flasks and shaken in 250 ml of deionized water for 1, 2, 4, 8, 16, 32, and 64 h on a reciprocating shaker at 150 rpm and 25±1°C, respectively. The suspensions were filtered and the filtrates were analyzed for reactive X-3B red dye using the gas chromatography method (Santos-Delgado et al. 2000; Nagaraju and Huang 2007). Each treatment was replicated four times.

2.5 Influences of added dye concentrations and environmental factors on dye adsorption and desorption

In the subsequent experiment on adsorptive isotherms, 0.0200 and 0.1000 mg of reactive X-3B red dye were carefully placed into 250 ml of measuring flasks with 10.0 g of surface soil samples, respectively. In the subsequent experiment on adsorptive dynamics and determination of adsorptive velocity, 10.00 g of soil samples and 0.1000 mg of the organic dye were carefully placed into 250 ml of measuring flasks. Similarly, the subsequent experiment on desorptive dynamics and determination of desorptive velocity was also carried out using the soils adsorbing the dye at 0.1000 mg of the organic dye and 10.00 g of soil samples. All the other procedures were unchangeable as mentioned above.

Temperature, solution-to-soil ratio to denote soil moisture, soil organic matter, and pH were changed, respectively, when adsorption and desorption velocities were determined according to the above procedure where 122.88 mg of the dye was placed in the flasks. The changed temperature was 10±1°C, 15±1°C, 20±1°C, 25±1°C, 30±1°C, and 35±1°C, and the tested solution-to-soil ratio (*V*/*W*) was 5:1, 10:1, 15:1, 20:1, 25:1, 30:1, 35:1, 40:1, and 45:1, respectively, according to the field humidity of the four soils. The content of organic matter in the soils was cut down through firing air-dried soils 2, 4, 6, 8, and 10 min in an oven set at 100°C (He et al. 1998), and the inner temperature in the oven was about 109°C, 117°C, 123°C, 127°C, and 131°C, respectively, after firing 2, 4, 6, 8, and 10 min. In the meantime, the H_2O_2 method (Hyeong and Capuano 2000) for the removal of organic matter was also adopted and compared with the firing method. In order to keep at the constant pH in the suspension, $CaCl_2$ was added for dye adsorption and desorption when changes in temperature, solution-to-soil ratio (*V*/*W*), and soil organic matter because adding $CaCl_2$ can buffer pH value in soil solution. Soil pH was adjusted using thin HCl and NaOH solution. Each treatment was replicated six times.

2.6 Data processing and statistical analysis

The average of four or six replicates for each treatment was calculated on a computer using Microsoft Excel software. Regression equations between the amount of reactive X-3B red dye adsorbed on soils or desorbed from soils and the content of soil organic matter, air temperature, soil pH, and solution-to-soil ratio (*V*/*W*) were also analyzed statistically.

3 Results and discussion

3.1 Adsorptive isotherms and maximum adsorbing capacity

Like most organic pollutants, the adsorptive characteristics of reactive X-3B red dye on soil particles can be described using mathematical methods such as the Freundlich equation, the Elovich equation, the Langmuir equation, the Temkin equation, and the Henry model. When the concentration of the dye in adsorption equilibrium solutions at 25±1°C is set as C (mg l^{-1}), the amount of the dye adsorbed on soils is q_e (mg kg^{-1}), and the isotherms of the dye adsorbing on the four soils could well conform to the Langmuir equation (Eq. 1) and the Freundlich equation (Eq. 2; He et al. 1998; Uludag-Demirer and Bowers 2000; Koleli et al. 2007), namely,

$$q_e = \frac{q_m a C_e}{1 + a C_e} \tag{1}$$

and

$$q_e = K_f C_e^n \tag{2}$$

where q_e is the amount adsorbed on soil (mg kg^{-1}), C_e is the equilibrium concentration of the dye in treatment supernatant (mg l^{-1}), a (l mg^{-1}) is a Langmuir constant related to the energy of adsorption, q_m (mg kg^{-1}) is the maximum adsorption capacity of the sample, and K_f is the Freundlich sorption coefficient and provides with an index of sorption capacity.

According to Fig. 1, it was indicated that the Langmuir equation was a more appropriate adsorptive isotherm than the Freundlich equation in describing adsorptive characteristics of the dye on the soils. As indicated in Fig. 1 and Table 2, the maximum dye-adsorbing capacity on the soils was in the sequence paddy soil (1,603.6 mg kg^{-1}) > red soil (1,254.4 mg kg^{-1}) > brown soil (1,207.4 mg kg^{-1}) > drab soil (971.3 mg kg^{-1}), and the adsorption capacity based on the Langmuir adsorption coefficient of the four soils was in the sequence brown soil (50.7) > paddy soil (48.2) > drab soil (41.9) > red soil (36.4). Obviously, the dye-adsorbing ability of these soils is very strong, perhaps because the dye contains azo group (–N=N–), hydroxy (–OH), and sulfonic acid group (–HSO_3) in its structure; in particular, sulfonic acid groups are significant when coupling to soils which act as ion exchangers. It could thus be deduced that the dye could be largely accumulated in these soils and possibly considered as a persistent organic pollutant with high ecological risk, thereby polluting soil environment, harming agricultural crops, and endangering human health if wastewater containing the dye is discharged into farmland and used as agricultural irrigation water. There are indications by toxicity toward various crops which, however, might also be due to some secondary product formed from reactive X-3B red dye after contacting with soil, e.g., by hydrolysis.

3.2 Dynamics and velocity of the dye adsorbing on soils

As shown in Fig. 2 and Table 3, adsorbing dynamics of reactive X-3B red dye by the four soils can be intuitively depicted by the Elovich model (Eq. 3), the first-order kinetic model (Eq. 4), and the second-order kinetic model (Eq. 5), namely,

$$q_t = \left(\frac{1}{Y}\right)\ln(XY) + \left(\frac{1}{Y}\right)\ln t \tag{3}$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

and

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \tag{5}$$

where q_e and q_t are the amount of reactive X-3B red dye adsorbed on soil (mg kg^{-1}) at equilibrium and at time t (h), respectively; k_1 (1/h) is the pseudo-first-order rate constant,

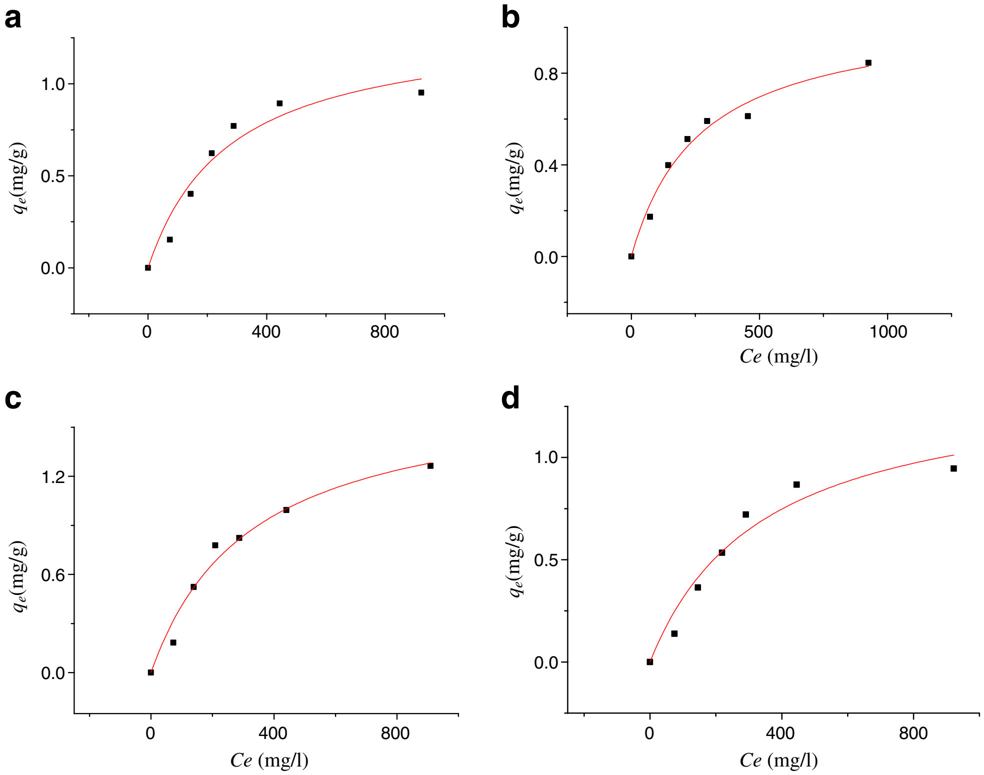


Fig. 1 Adsorption isotherms of brown soil (**a**), drab soil (**b**), paddy soil (**c**), and red soil (**d**) and their Langmuir fits

and k_2 (kg mg^{-1}h^{-1}) is the pseudo-second-order rate constant of adsorption.

The fitting of the Elovich model indicates that the adsorption dynamics of reactive X-3B red dye was a heterogeneous diffusion process. The maximum sorption amount (q_e) and the apparent adsorption rate constant (k) can be determined from the fittings of pseudo-first-order and pseudo-second-order kinetic models. The apparent adsorption rate constant was the velocity change when the sorption reached its equilibrium. Thus, the greater is the rate constant, the more easily is the equilibrium reached. As shown in Table 3, the maximum sorption amount and the apparent adsorption rate of paddy soil was the greatest among the four soils. Also, as shown in Fig. 2, the maximum adsorption of the dye by the soils took place within 1.0 h after the adsorption experiment began; in particular, paddy soil adsorbed 91.9% of the amount of the dye at equilibrium (q_e). Within 6.0 h after the adsorption experiment began, all the soils could adsorb more than 96.0% of the maximum adsorbing capacity. However, when the adsorption experiment was ongoing from 1.0 to 6.0 h, the increment in the adsorption of the dye by the soils decreased with time gradually. After the adsorption experiment was carried out through 20.0 h, the amount of the dye adsorbed on the soils was no more increased with time. At that time, the adsorption reached its equilibrium state.

As shown in Fig. 2, the adsorption of the dye by the soils could be divided into four stages: (1) the high-speed adsorption stage (0–1.0 h): The velocity of the dye adsorbing on the soils increased with time and was very high during this stage; (2) the slowdown adsorption stage (1.0–6.0 h): The velocity of the dye adsorbing on the soils decreased with time during this stage; (3) the tardiness adsorption stage (6.0–20.0 h): The velocity of the dye adsorbing on the soils was slow; and (4) the zero-approaching adsorption stage at an established adsorption equilibrium (20.0–24.0 h): The velocity of the dye

Table 2 Fitting parameters (average ± standard deviation) obtained from the Freundlich and Langmuir models

Soil	Langmuir			Freundlich		
	q_m	a	R^2	K_f	n	R^2
Brown soil	1,207.4±213.9	0.003±0.001	0.895	50.7±38.27	0.45±0.12	0.756
Drab soil	971.3±103.4	0.003±8.5E−4	0.953	41.9±18.3	0.44±0.07	0.899
Paddy soil	1,603.6±206.7	0.003±8.1E−4	0.950	48.2±26.7	0.49±0.09	0.874
Red soil	1,254.4±230.8	0.003±0.001	0.915	36.4±26.9	0.49±0.12	0.802

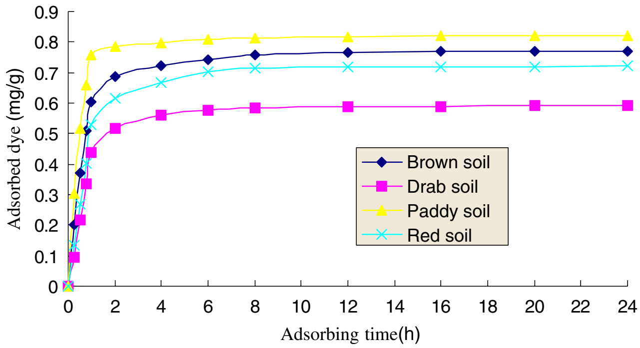


Fig. 2 Curves of reactive X-3B red dye adsorption dynamics

adsorbing on the soils tended to zero. At the first stage, the adsorption velocity was in the sequence paddy soil > brown soil > red soil > drab soil. At the second stage, the velocity was in the sequence red soil > brown soil = drab soil > paddy soil. At the third stage, the adsorption velocity was in the sequence brown soil > paddy soil = red soil > drab soil.

3.3 Dynamics and velocity of the dye desorbing from soils

The desorption dynamics of reactive X-3B red dye from the four soils can be described by the Elovich model, the first-order kinetic model, and the second-order kinetic model (Fig. 3 and Table 4). The total amount of the dye desorbed from the soils increased with time (see Fig. 3). During the 64.0-h desorption experiment, the total amount of the dye desorbed from the soils accounted for 42.5% (drab soil)–60.8% (paddy soil) of the dye previously adsorbed by the soils. However, the maximum desorbing capacity of the dye from the soils took place within 1.0 h after the desorption experiment began. The increment of the dye desorbed from the soils decreased with time; in particular, only 0.005–0.019 mg g^{-1} when the desorption experiment was carried out from 32.0 to 64.0 h. Correspondingly, the desorptive velocity of the dye from the soils reduced with time gradually (Fig. 4). This phenomenon showed that the dye adsorbed on the soils could ceaselessly release through its desorption and be gradually utilized by crops and other living organisms, thus resulting in inconspicuous chronic toxicity to crops such as wheat (*Triticum aestivum*), cabbage (*Brassica chinensis*), and rice (*Oryza sativa*). This mechanism can give a compelling answer to a riddle which explains the results of our previous work (Zhou 2001; Cheng and Zhou 2002).

3.4 Influences of added dye concentrations and environmental factors on adsorption

It was shown by the subsequent experiment on adsorptive isotherms that the adsorptive characteristics of reactive X-3B red dye at the low concentrations on soil particles can be also described more appropriately using the Langmuir equation (Eq. 1) than the Freundlich equation (Eq. 2). The sequence of the dye adsorption capacity for the four soils at the low concentrations was consistent with that at the aforementioned high concentrations, namely, brown soil > paddy soil > drab soil > red soil. Similarly, adsorbing dynamics of reactive X-3B red dye at the low concentration by the four soils were also consistent with those at the high concentrations. Within 6.0 h after the subsequent adsorption experiment began, all the soils could adsorb more than 94.5% of the maximum adsorbing capacity. When the subsequent adsorption experiment was ongoing from 1.0 to 6.0 h, the increment in the adsorption of the dye at the low concentration by the soils decreased with time gradually. After the subsequent adsorption experiment was carried out through 20.0 h, the amount of the dye at the low concentration adsorbed on the soils was no more increased with time. In particular, the adsorption of the dye at the low concentration by the soils could be also divided into the four stages mentioned above.

The content of organic matter in the soils was cut down through having fired the soils (He et al. 1998) and had an important influence on the amount of dye adsorbed on the soils. In other words, the amount of dye adsorbed on the soils was being decreased with the reduction in soil organic matter (Fig. 5). There were significantly ($p<0.001$) positive correlations between the two which can be described using the regression equations (Eqs. 6–9) in Table 5 where C_{org} is

Table 3 Sorption kinetic models constants and correlation coefficients for adsorption of the dye in the tested soils

Soil type	Elovich model			First-order kinetic model			Second-order kinetic model		
	$(1/Y)\ln(X{\cdot}Y)$ (μgg^{-1})	$1/Y$	R^2	q_e (mgkg^{-1})	k_1 (kgmg^{-1} h^{-1})	R^2	q_e (mgg^{-1})	k_2 (kgmg^{-1} h^{-1})	R^2
Brown soil	503±30.9	109±15.9	0.807	756±7.48	1.42±0.06	0.988	804±16.3	0.003±3.22E−4	0.962
Drab soil	349±27.8	99.4±14.3	0.812	586±9.10	1.09±0.07	0.979	631±19.3	0.002±4.13E−4	0.945
Paddy soil	619±35.5	86.4±18.3	0.660	816±6.73	2.09±0.08	0.986	854±19.9	0.004±6.84E−4	0.914
Red soil	426±30.9	120±15.9	0.835	711±9.93	1.09±0.06	0.983	766±19.9	0.002±2.89E−4	0.958

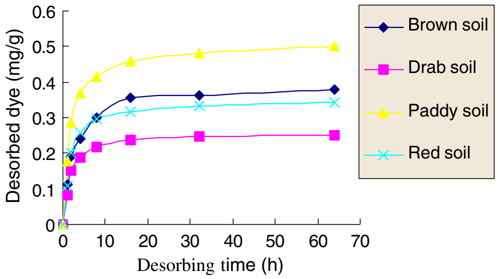


Fig. 3 Curves of reactive X-3B red dye desorption dynamics

the content of organic matter in soils (%) and Q_1, Q_2, Q_3, and Q_4 denote the amount of the dye adsorbed on paddy soil, brown soil, drab soil, and red soil, respectively. It can be deduced from Eqs. 6–9 in Table 5 that the reduction in soil organic matter could inhibit the accumulation of the organic dye in the soils, thereby mitigating its ecological harmfulness and adverse effects on human health due to the less accumulation.

In the meantime, the content of organic matter in the soils was also cut down using the H_2O_2 method (Hyeong and Capuano 2000). A further study showed that the basic adsorption laws of reactive X-3B red dye using the mild peroxide method were consistent with those using the firing method because some traits of the soils may be consentaneously destroyed when firing the soil. In other words, the basic adsorption laws of reactive X-3B red dye could be not affected by various methods to cut down organic matter because organic matter is the main influencing factor and other soil traits are not the main influencing factors in the adsorption experiments with changing organic matter in soils.

According to the experimental data obtained in this work, the elevated temperature promoted the adsorption of the dye on the soils to a certain extent. The changing trend is in concordance with the results that temperature increased Cd^{2+} adsorption in both the Cd^{2+} and Cd^{2+} + phenol treatments for the unmodified soil (Meng et al. 2008), and 9.6 % more imazapyr had been adsorbed by the soil at 35°C than at 15°C after 8 h (Jenkins et al. 2000), which might be explained by the fact that influences of temperature on the adsorption of the dye on the soils would be related to the structure of the dye; in particular, the solubility of the dye increases with an increase in temperature (Kabanova et al. 1980; McLaren 1983; MCI-China 1995; Zhou and Huang 2001). The positive correlation between the amount of the dye adsorbed on the soils and temperature under the experimental conditions was significant ($p<0.01$). Let temperature be t (°C); there were corresponding regression equations (Eqs. 10–13). According to Eqs. 10–13, the dye adsorption by soils distributed in southern China under high-temperature climate conditions should be stronger than that in northern China under low-temperature climate conditions. In other words, the dye is easily accumulated in soils of southern China, thereby likely resulting in the pollution of soil–crop systems in this area. It could also be deduced according to the coefficients of the independent variable in regression equations (Eqs. 10–13) that the influencing intensity of temperature was smaller than that of soil organic matter. However, some researchers concluded that adsorption of some organic pollutants such as diuron and phenol decreased as temperature increased. They thought that phenol adsorption in this soil was mainly due to physical adsorption (Meng et al. 2008), and lower tendency of diuron adsorption in the soils is responsible for the exothermic adsorption of diuron on soil that the adsorbate–adsorbent bonds were weakened with increasing temperature (Liu et al. 2010).

Influences of soil pH on the dye adsorption were complex, similar to the result by Liu et al. (2010) that the adsorption of diuron on the selected soils was rather high at low pH values and decreased with the increasing pH values of the suspension. In this work, neutral, slightly acidic, and alkaline soils had the lowest dye-adsorptive capacity, and the relationship between the adsorption of the dye on the soils and soil pH can be described using upward parabolas (see Fig. 5). When soils became acidified or basified, the amount of the dye adsorbed by the soils could increase. In particular, there was a great increasing extent in acidified soils. The changing trend is likely attributed to the hydroxy (–OH) and sulfonic acid groups ($-HSO_3$) in the structure of

Table 4 Desorption kinetic models constants and correlation coefficients for adsorption of the dye in the tested soils

Soil type	Elovich model			First-order kinetic model			Second-order kinetic model		
	$(1/Y)\ln(X\cdot Y)$ ($\mu g g^{-1}$)	$1/Y$	R^2	q_e ($mg kg^{-1}$)	k_1 (h^{-1})	R^2	q_e ($mg g^{-1}$)	k_2 ($kg mg^{-1} h^{-1}$)	R^2
Brown soil	0.155±0.022	0.053±0.009	0.850	0.358±0.012	0.317±0.039	0.955	0.358±0.012	0.317±0.039	0.955
Drab soil	0.118±0.016	0.038±0.006	0.846	0.240±0.006	0.439±0.043	0.965	0.240±0.006	0.439±0.043	0.965
Paddy soil	0.229±0.025	0.074±0.010	0.897	0.468±0.014	0.435±0.051	0.950	0.468±0.014	0.435±0.051	0.950
Red soil	0.155±0.022	0.053±0.009	0.850	0.326±0.007	0.421±0.039	0.972	0.326±0.007	0.421±0.039	0.972

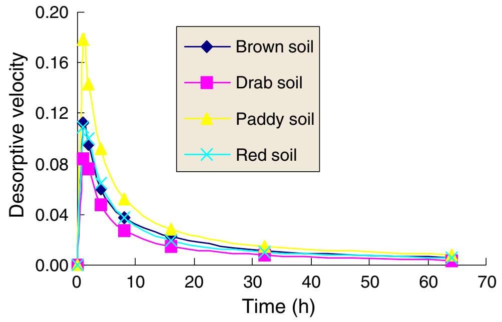


Fig. 4 Desorptive velocity of the dye from the soils

the dye. According to Eqs. 14–17 in Table 5, it also makes knowing that the soils do not easily accumulate the dye and there is low dye pollution possibility of soil–crop systems under neutral conditions.

Solution-to-soil ratio could obviously affect the adsorption of the dye on the soils. As shown by Fest et al. (2008), the concentrations of dissolved organic matter increased almost linearly with solution-to-soil ratio for both extraction solutions. Chang and Wang (2002) also pointed out that the adsorption constant K_f decreases from 34.1 to 23.2 l/kg when soil-to-water ratio of the batch system increases from 0.1 to 2.0 g/ml. In this work, there was a maximum adsorptive capacity of the dye by the soils when solution-to-soil ratio was equal to 20–35. When solution-to-soil ratio was higher than 35, the amount of the dye adsorbed on the soils decreased with an increase in solution-to-soil ratio. However, when solution-to-soil ratio was lower than 20, the amount of the dye adsorbed on the soils decreased with a decrease in solution-to-soil ratio. Influences of solution-to-soil ratio on the dye adsorbed on the soils can be depicted using a series of downward parabolas. Their correlations can be expressed using the regression equations (Eqs. 18–21) in Table 5. Thus, it can be deduced that adsorption of the dye by the soils can be inhibited when the soil become waterlogged or in drought.

3.5 Influences of added dye concentrations and environmental factors on desorption

Similarly, the desorption dynamics of reactive X-3B red dye from the four soils at the low concentrations were consistent with those at the high concentrations. The total amount of the dye desorbed from the soils increased with time when the initial concentration of the dye was low, and the maximum desorbing capacity of the dye from the soils took place within 1.0 h after the subsequent desorption experiment began.

Under various field conditions, any organic pollutant occurring in soils can be desorbed. Temperature and soil organic matter had a certain influence on desorption of the dye from the four soils. When temperature was going up,

Fig. 5 Influences of environmental factors on adsorption of reactive X-3B red dye on soils

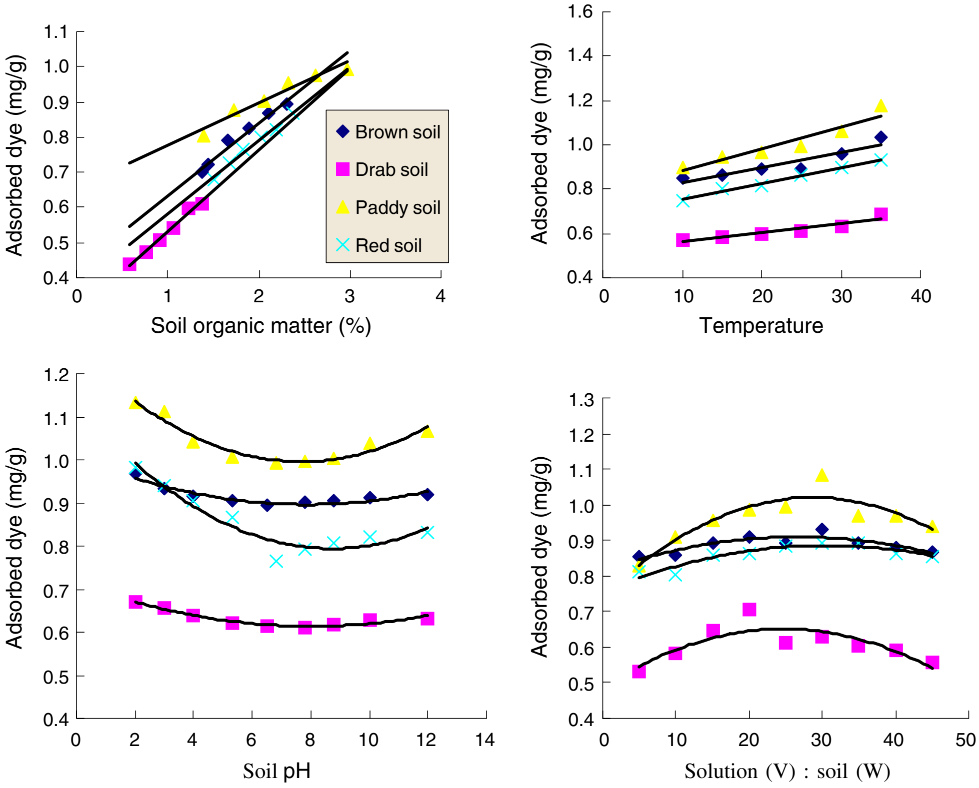


Table 5 Influences of environmental factors on adsorption of reactive X-3B red dye

Influencing factor	Soil type	Regression equation	R^2	*n*	*P*	Sequence number
Organic matter	Paddy soil	$Q_1 = 0.120C_{\mathrm{org}} + 0.655$	0.952	6	<0.005	(6)
	Brown soil	$Q_2 = 0.207C_{\mathrm{org}} + 0.427$	0.975	6	<0.005	(7)
	Drab soil	$Q_3 = 0.231C_{\mathrm{org}} + 0.301$	0.986	6	<0.005	(8)
	Red soil	$Q_4 = 0.207C_{\mathrm{org}} + 0.376$	0.985	6	<0.005	(9)
Temperature	Paddy soil	$Q_1 = 0.0100t + 0.782$	0.898	6	<0.005	(10)
	Brown soil	$Q_2 = 0.0069t + 0.758$	0.870	6	<0.005	(11)
	Drab soil	$Q_3 = 0.0042t + 0.520$	0.890	6	<0.005	(12)
	Red soil	$Q_4 = 0.0073t + 0.680$	0.992	6	<0.005	(13)
Soil pH	Paddy soil	$Q_1 = 0.0043(\mathrm{pH})^2 - 0.0666\mathrm{pH} + 1.25$	0.940	9	<0.005	(14)
	Brown soil	$Q_2 = 0.0018(\mathrm{pH})^2 - 0.0279\mathrm{pH} + 1.01$	0.890	9	<0.005	(15)
	Drab soil	$Q_3 = 0.0015(\mathrm{pH})^2 - 0.0248\mathrm{pH} + 0.71$	0.948	9	<0.005	(16)
	Red soil	$Q_4 = 0.0044(\mathrm{pH})^2 - 0.0765\mathrm{pH} + 1.13$	0.919	9	<0.005	(17)
Ratio of solution (*V*) to soil (*W*)	Paddy soil	$Q_1 = -0.0003(V/W)^2 + 0.0195(V/W) + 0.74$	0.837	9	<0.005	(18)
	Brown soil	$Q_2 = -0.0001(V/W)^2 + 0.0072(V/W) + 0.81$	0.756	9	<0.005	(19)
	Drab soil	$Q_3 = -0.0003(V/W)^2 + 0.0133(V/W) + 0.49$	0.676	9	<0.005	(20)
	Red soil	$Q_4 = -0.0001(V/W)^2 + 0.0086(V/W) + 0.76$	0.857	9	<0.005	(21)

the total amount of the dye desorbed from the soils increased gradually (Fig. 6). The significantly positive correlation can be expressed using the regression equations (Eqs. 22–25) in Table 6, where Q_1', Q_2', Q_3', and Q_4' are the amount of the dye desorbed from paddy soil, brown soil, drab soil and red soil, respectively. The trend of temperature affecting desorption of the dye is basically consistent with Kaiser et al. (2001) about the relationship between the release of dissolved organic carbon (DOC) and temperature. They also pointed out that increasing temperature had a stronger effect on the release of hydrophilic than of hydrophobic DOC, which may have resulted from enhanced solubility of hydrophilic substances such as reactive X-3B red dye at higher temperatures compared to hydro-

Fig. 6 Influences of environmental factors on desorption of reactive X-3B red dye from soils

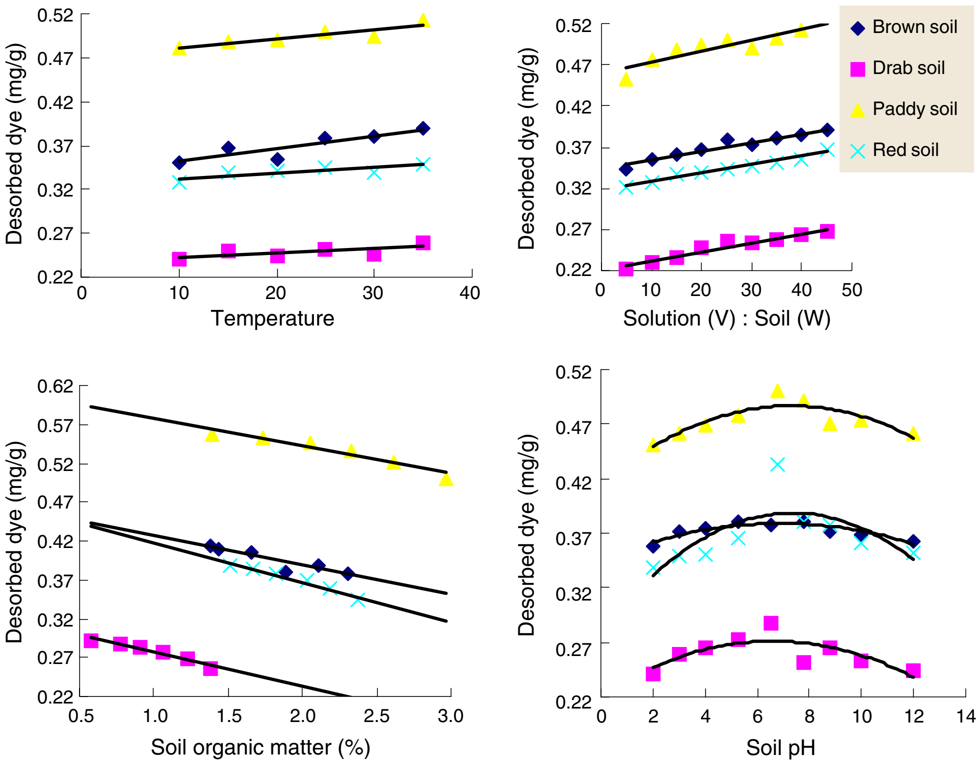


Table 6 Influences of environmental factors on desorption of reactive X-3B red dye

Influencing factor	Soil type	Regression equation	R^2	N	P	Sequence number
Temperature	Paddy soil	$Q_1 = 0.0010t + 0.472$	0.786	6	<0.005	(22)
	Brown soil	$Q_2 = 0.0014t + 0.338$	0.799	6	<0.005	(23)
	Drab soil	$Q_3 = 0.0005t + 0.237$	0.605	6	0.018	(24)
	Red soil	$\mathrm{Q}_4 = 0.0006\mathrm{t} + 0.326$	0.725	6	0.008	(25)
Organic matter	Paddy soil	$Q_1 = -0.0353C_{\mathrm{org}} + 0.612$	0.915	6	<0.005	(26)
	Brown soil	$Q_2 = -0.0379C_{\mathrm{org}} + 0.851$	0.851	6	<0.005	(27)
	Drab soil	$Q_3 = -0.0436C_{\mathrm{org}} + 0.937$	0.937	6	<0.005	(28)
	Red soil	$Q_4 = -0.0513C_{\mathrm{org}} + 0.973$	0.973	6	<0.005	(29)
Ratio of solution (V) to soil (W)	Paddy soil	$Q_1 = 0.0013(V/W) + 0.460$	0.847	9	<0.005	(30)
	Brown soil	$Q_2 = 0.0011(V/W) + 0.343$	0.942	9	<0.005	(31)
	Drab soil	$Q_3 = 0.0011(V/W) + 0.220$	0.935	9	<0.005	(32)
	Red soil	$Q_4 = 0.0010(V/W) + 0.318$	0.966	9	<0.005	(33)
Soil pH	Paddy soil	$Q_1 = -0.0013(\mathrm{pH})^2 - 0.0194\mathrm{pH} + 0.416$	0.776	9	<0.005	(34)
	Brown soil	$Q_2 = -0.0007(\mathrm{pH})^2 - 0.0099\mathrm{pH} + 0.345$	0.840	9	<0.005	(35)
	Drab soil	$Q_3 = -0.0011(\mathrm{pH})^2 - 0.0149\mathrm{pH} + 0.222$	0.572	9	<0.005	(36)
	Red soil	$Q_4 = -0.0020(\mathrm{pH})^2 - 0.0294\mathrm{pH} + 0.281$	0.545	9	0.010	(37)

phobic organic matter. In other words, the desorption of the dye from soil increased with an increase in temperature due to the enhanced solubility. This is also dependent on the fact that the adsorption and desorption of the dye is a reversible process. However, when the content of organic matter in the soils decreased, the total amount of the dye desorbed from the soils increased. There were significantly negative correlation relationships between the two, which are expressed using the regression equations (Eqs. 26–29) in Table 6. A further study using the H_2O_2 method showed that the basic desorption laws of reactive X-3B red dye using the mild method were basically consistent with those using the firing method, like the influences of organic matter on adsorption of the dye on the soils. Thus, a lot of current agricultural activities can promote the release of the dye adsorbed on soils because they are continuously consuming organic matter in soils.

There was an obvious influence of solution-to-soil ratio on the total amount of the dye desorbed from the soils, but were not different from those on the total amount of the dye adsorbed on the soils. The correlation relationships can be described using the first-order linear equations (Eqs. 30–33) in Table 6. The changing trend is also in concordance with the linear relationship between the release of indigenous DOC (on mass base) and solution-to-soil ratio, as suggested by Kaiser et al. (2001). Thus, the release of the dye from the soils could be promoted when farmland was inundated.

Influences of soil pH on desorption of the dye from the soils were still complex, like the influences of soil pH on adsorption of the dye. Their relationships can be expressed by quadratic equations with one unknown quantity, including Eqs. 34–37 in Table 6. The expressions pointed out that the maximum desorption of the dye from the soils took place when soil pH was at the neutral conditions. The bioavailability of the dye in soils is controlled by soil pH to a certain extent. Thus, release of the dye from contaminated soil and uptake by crops can be changed by human activities (Willetts et al. 2000; Zhou and Huang 2001).

4 Conclusions

The study on the adsorption of reactive X-3B red dye on the four Chinese typical soils showed that the adsorptive behavior of the dye by these tested soils can be basically described using the Langmuir equation. The calculation on the basis of the adsorptive isotherms indicated that the maximum adsorbing capacity based on the Langmuir adsorption coefficient of the dye by the soils was in the sequence paddy soil > red soil > brown earth > drab soil. According to the dynamics and the velocity of soil adsorbing and desorbing the dye, the adsorption of the dye by the soils could be divided into the four stages including high-speed adsorption, slowdown adsorption, tardiness adsorption, and zero-approaching adsorption at an established adsorption equilibrium. There was a great difference in adsorbing velocity between various soil types during these different stages. The total amount of the dye desorbed from the soils increased with time, but the velocity of the dye desorbing from the soils decreased with time. The comparative study showed that the basic adsorption–desorption laws of reactive X-3B red dye at high concentrations were basically consistent with those at low concentrations. Environmental factors influencing this adsorption and desorption, including contents of organic matter and water in soils (in the form of solution-to-soil ratio), soil pH, and air temperature were also analyzed. It was indicated that the adsorption of the dye on soils decreased, thereby inhibiting the accumulation of the dye in soil environment when soil organic matter or air temperature reduced and under neutral, runny, or unwatered conditions. The decrease in organic matter in the soils and the increase in air temperature or soil moisture could promote desorption of the dye from the soils. When soil became acidified or basified, desorption of the dye from the soils would be also inhibited.

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