

Feasibility of Using Drinking Water Treatment Residuals as a Novel Chlorpyrifos Adsorbent

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S Supporting Information

ABSTRACT: Recent efforts have increasingly focused on the development of low-cost adsorbents for pesticide retention. In this work, the novel reuse of drinking water treatment residuals (WTRs), a nonhazardous ubiquitous byproduct, as an adsorbent for chlorpyrifos was investigated. Results showed that the kinetics and isothermal processes of chlorpyrifos sorption to WTRs were better described by a pseudo-second-order model and by the Freundlich equation, respectively. Moreover, compared with paddy soil and other documented adsorbents, the WTRs exhibited a greater affinity for chlorpyrifos ($\log K_{oc} = 4.76\text{--}4.90$) and a higher chlorpyrifos sorption capacity ($K_F = 5967 \text{ mg}^{1-n} \cdot \text{L} \cdot \text{kg}^{-1}$) owing to the character and high content of organic matter. Further investigation demonstrated that the pH had a slight but statistically insignificant effect on chlorpyrifos sorption to WTRs; solution ionic strength and the presence of low molecular weight organic acids both resulted in concentration-dependent inhibition effects. Overall, these results confirmed the feasibility of using WTRs as a novel chlorpyrifos adsorbent.

KEYWORDS: chlorpyrifos sorption, kinetics, water treatment residuals, paddy soil, solution chemistry

INTRODUCTION

Chlorpyrifos is a broad spectrum organophosphate pesticide that is widely used for both agricultural and domestic pest control worldwide. The annual global use of chlorpyrifos between 2002 and 2006 was as much as 24.6 million kilograms of active ingredient (AI).¹ Its use has led to the detection of chlorpyrifos residues in the aquatic environment.^{2–4} Given the widespread use of chlorpyrifos, minimizing the movement of chlorpyrifos from fields into aquatic habitats is desirable to reduce potential detrimental effects.^{5–7} Recent research showed that phytoremediation and biodegradation were potential methods for chlorpyrifos removal.^{8,9} In addition, the use of enzymes with enhanced hydrolytic activities toward organophosphate pesticides, constructed wetlands, and some advanced oxidation processes have been reported to effectively remove chlorpyrifos from water.^{10–15} Sorption methods can also be used to minimize pesticide runoff from agricultural areas to the surrounding environment. Among the existing techniques for chlorpyrifos attenuation, sorption methods have advantages in terms of their simplicity, relatively low cost, and ease of application. Hence, increasing effort has been made to develop low-cost pesticide adsorbents.¹⁶

Drinking water treatment residuals (WTRs), a nonhazardous ubiquitous byproduct, are generated in enormous quantities from drinking water treatment facilities worldwide. In Europe alone, several million tons of WTRs are produced each year, and the quantity may double in coming decades.¹⁷ Due to the large volume of WTRs generated annually, disposal has become a public concern. Productive reuse of WTRs may provide an ideal solution to the issue of WTR disposal. WTRs principally contain iron and aluminum (Fe/Al) hydroxide minerals and humic materials, which are precipitated from raw water. Their high concentration of Fe/Al minerals and high specific surface

area have led numerous scholars to focus on the sorption of ionic pollutants by WTRs. It has been well documented that WTRs can be reused as cost-effective adsorbents for phosphorus, most metal ions, and some anions in soil and sediment remediation and in constructed wetland applications.^{18–22} Recent work has demonstrated effective sorption of ionic organic pollutants such as glyphosate and organic arsenic species by WTRs.^{23,24} However, few data are available on the sorption potential of WTRs for nonionic organic pollutants. Organic matter is the key factor in hydrophobic organic pollutant sorption when the organic matter content is $>0.1\%$.²⁵ Organic carbon, the chief element present in organic matter, is often used as an indicator of organic matter. The total organic carbon content of WTRs varies from 2.3 to 22.5%.²⁶ Thus, there may be potential for the productive reuse of WTRs as a novel adsorbent for nonionic pesticides such as chlorpyrifos.

To examine the feasibility of using WTRs as a novel adsorbent for chlorpyrifos, equilibrium batch experiments were used to investigate chlorpyrifos adsorption by WTRs. The adsorption capacity of WTRs was compared with that of paddy soil and other documented adsorbent materials. In addition, the solution pH, ionic strength, and presence of low molecular weight organic acids (LMWOAs) were evaluated to ascertain the effects of solution chemistry on chlorpyrifos adsorption by WTRs. The results of this study provide a useful reference for both the reuse of WTRs and the mitigation of pesticide pollution.

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MATERIALS AND METHODS

Sorbents and Sorbates. WTRs were collected from the Beijing City No. 9 Waterworks in China in April 2012. Soil was sampled from the surface (0–20 cm) layer of a rice paddy field in Changzhou, Jiangsu province (31° 33′ 40.4″ N, 119° 59′ 54.9″ E), in July 2012. Samples were air-dried, gently crumbled, and sieved through a 0.15 mm mesh screen. WTRs were digested with HNO₃, HCl, and H₂O₂ (U.S. EPA method 3050B) to detect primary elemental compounds using an inductively coupled plasma–atomic emission spectrometer (ICP-AES, ULTMA, JY, France). The organic matter contents of the WTRs and paddy soil were determined using the dichromate heat-of-dilution method,²⁷ and the organic matter fractions were extracted according to the method of Zbytniewski et al.²⁸ The Brunauer–Emmett–Teller (BET) surface area and porosity of the substrates were measured by nitrogen adsorption using a porosimeter (Nova Station D, Quantachrome Instruments, USA). The physicochemical properties of the WTRs and the paddy soil are summarized in Table 1,

Table 1. Characteristics of WTRs and Paddy Soil

sample	WTRs	soil
pH ^a	6.80	6.00
Fe (mg·g ⁻¹)	133	26
Al (mg·g ⁻¹)	98	45
Ca (mg·g ⁻¹)	21.0	3.7
Mg (mg·g ⁻¹)	1.8	2.7
Mn (mg·g ⁻¹)	2.6	0.3
TOM ^b (mg·g ⁻¹)	107	19
HA + FA ^c (mg·g ⁻¹)	17	8
HM ^d (mg·g ⁻¹)	90	11
BET surface area (m ² ·g ⁻¹)	78.5	18.3
total pore volume (cm ³ ·g ⁻¹)	0.0711	0.0193
average pore diameter (nm)	3.62	4.21

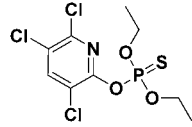
^apH was determined in slurries with a soil/water ratio of 1:2.5. ^bTOM, total organic matter. ^cHA + FA = total content of fulvic acid (FA) and humic acid (HA). ^dHM, humin.

and the micropore distributions of the substrates are provided in Figure S1 (see the Supporting Information). As shown in Table 1, the WTRs are mainly composed of iron and aluminum oxides/(oxy)hydroxides and organic matter (107 mg·g⁻¹), within which the content of humin is 90 mg·g⁻¹. Hydrophobic organic compounds (humin) are the predominant organic component of the WTRs. The WTRs have a larger BET surface area and total pore volume and smaller mean pore diameter than the rice paddy soil. With respect to the organic matter content (19 mg·g⁻¹), the rice paddy soil used in this study is representative of cultivated soils in southern China.

Chlorpyrifos of 98.6% purity was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Table 2 shows the structure and chemical properties of chlorpyrifos. Chlorpyrifos solubility in water is 1.12 mg·L⁻¹.^{29,30} A stock solution of chlorpyrifos (1 g·L⁻¹) was prepared in methanol solvent. The stock solution was diluted to specific concentrations using a solution containing 0.005 M CaCl₂ to maintain a constant ionic strength and 100 mg·L⁻¹ NaN₃ to inhibit biological activity. The methanol content of the dilution was maintained below 0.05% v/v to minimize the cosolvent effect. All solutions were filtered through a 0.45 μm membrane prior to use in the experiments.

Sorption Kinetics. A kinetic sorption study was carried out in 40 mL glass vials with PTFE-lined screw caps. An air-dried sample of 20 ± 0.01 mg WTRs or 1 ± 0.01 g paddy soil was placed in glass vials with 40 ± 0.5 mL of 0.28 mg·L⁻¹ chlorpyrifos solution. Headspace was kept to a minimum to reduce solute vapor loss. The mass of the sorbents used differed to achieve 25–85% sorption for ease and reliability of chlorpyrifos analytical detection. The glass vials containing the sorbent mixtures were agitated in the dark in a constant-temperature mixer at 150 rpm and 25 °C. Triplicate samples

Table 2. Structure and Chemical Properties of Chlorpyrifos^a

Common name	Chlorpyrifos
Name	O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate
CAS number	2921-88-2
Chemical family	Phosphorothioate esters
Structure	
MW ^b	350.6
log K _{ow} ^c	4.96
S _w ^d	1.12 mg·L ⁻¹
96 h LC 50 ^e	35 ng·L ⁻¹ (mysid shrimp)

^aData obtained from Gebremariam et al.³⁰ ^bMolecular weight. ^cOctanol/water partition coefficient at 20 °C. ^dSolubility in distilled water at 20 °C. ^eMedian lethal concentration for 96 h.

(10 mL) of the suspensions were collected at time intervals of 0.25, 0.5, 1, 2, 4, 6, 8, 10, 12, 18, 24, 36, and 72 h of shaking. The suspensions were centrifuged at 5200g (15 min) and then filtered through a 0.45 μm nylon membrane. Preliminary tests indicated that there was negligible loss of chlorpyrifos on the membrane filters during filtration. The chlorpyrifos concentrations in the supernatant were determined using high-performance liquid chromatography (HPLC). The adsorbed quantities of chlorpyrifos were calculated as the difference between chlorpyrifos concentrations in the initial solution and in the supernatant after centrifugation.

Sorption Isotherms. Batch equilibrium studies were conducted in 40 mL glass vials with PTFE-lined screw caps containing 40 ± 0.5 mL of chlorpyrifos solution at different initial concentrations ranging from 0.10 to 0.80 mg·L⁻¹. The initial solution pH was within the range of 6.65–6.85, and the pH of the suspensions after sorption was determined (Supporting Information, Table S1). The sorbent masses were the same as in the kinetic study. The glass vials were then agitated at 150 rpm and 25 °C. After equilibration, triplicate samples (10 mL) of the suspensions were centrifuged at 5200g (15 min) and filtered through a 0.45 μm nylon membrane. The 36 h equilibration time was determined using results from the sorption kinetics experiment. The initial and equilibrium concentrations of chlorpyrifos in solution were determined by HPLC. The adsorbed quantities of chlorpyrifos at equilibrium were calculated as the difference between the initial chlorpyrifos concentration and the supernatant concentration at equilibrium. Control groups without an added substrate were included in this experiment.

Effects of Solution Chemistry. Experiments similar to those described above were carried out to investigate the effects of solution chemistry including the pH, ionic strength, and addition of LMWOAs. Given the relatively rapid hydrolysis rate of chlorpyrifos in an alkaline environment, the effect of the solution pH was examined at pH 4.1, 5.1, 6.2, and 7.2. Calcium chloride was added at different concentrations, namely, 0.005, 0.01, 0.05, and 0.1 M, to test the effect of solution ionic strength. Two LMWOAs, malic acid (MA) and citric acid (CA), were selected to evaluate their effects on chlorpyrifos sorption to WTRs. Malic acid and CA are excreted by root systems, plant residues during decomposition, and microbes. Both are ubiquitous in the soil environment. To eliminate pH-induced variation, the stock solution of LMWOAs was adjusted to approximately pH 7 prior to the test. Sorption experiments were carried out with initial organic acid concentrations ranging from 0 to 10 mM.

Chlorpyrifos Determination. The chlorpyrifos concentration was analyzed at a wavelength of 288 nm using an HPLC (Waters 2695, USA) equipped with a UV detector (Waters 2489, USA) and a

Hypersil ODS column (250 mm × 4.6 mm × 5 μm, Thermo, USA). Acetonitrile and deionized water (95:5, v/v) comprised the mobile phase at a flow rate of 1 mL·min⁻¹. The injected sample volume was 20 μL, and the detection limit for chlorpyrifos (with a signal-to-noise ratio of 3:1) was 10 μg·L⁻¹.

Data Analysis. The kinetic sorption data were fitted using the nonlinear form of pseudo-first-order, the nonlinear form of pseudo-second-order, and the intraparticle diffusion models as shown in eqs 1–3, respectively:

$$Q_t = Q_e(1 - e^{-k_1t}) \quad (1)$$

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \quad (2)$$

$$Q_t = k_i t^{0.5} + C \quad (3)$$

k_1 and k_2 are the sorption rate constants, k_i is the intraparticle diffusion rate constant, C is the intercept and considered to be proportional to the boundary layer effect, and Q_t and Q_e are the adsorbed amounts of chlorpyrifos at time t and at equilibrium, respectively.

Freundlich and linear models were tested to describe the sorption isotherm experiment. Their expressions are given in eqs 4 and 5, respectively:

$$Q_e = K_D C_e \quad (4)$$

$$Q_e = K_F C_e^n \quad (5)$$

C_e (mg·L⁻¹) is the chlorpyrifos concentration in solution at equilibrium, K_D is the partition coefficient, and K_F and n are the coefficient of sorption capacity and the linearity index, respectively.

A single-point organic carbon-normalized distribution coefficient (K_{oc}) can be used to predict the affinity between the sorbate and organic matter at different concentration ranges (eq 6):

$$K_{oc} = K_F C_e^{n-1} / f_{oc} \quad (6)$$

f_{oc} is the percentage of organic carbon. K_{oc} was calculated at $C_e = 0.005S_w$, $0.05S_w$, and $0.5S_w$ in this study. S_w is chlorpyrifos solubility in water, 1.12 mg·L⁻¹.

The kinetic and isothermal curves were obtained using the Sigma Plot program 12.0 (Systat Software Inc., San Jose, CA, USA). Statistical analysis included a two-tailed t test using PASW Statistics package 18.0 (IBM, Chicago, IL, USA).

RESULTS AND DISCUSSION

Kinetics of Chlorpyrifos Sorption to WTRs and Paddy Soil. Kinetic plots for chlorpyrifos sorption to WTRs and paddy soil are presented in Figure 1. As shown in Figure 1a, within the initial 2 h, chlorpyrifos sorption to WTRs and paddy soil reached 50 and 88% of the observed maxima, respectively. Pseudo sorption equilibrium was achieved within 24 h in the WTRs and within 8 h in paddy soil. The equilibrium sorption capacities for WTRs and paddy soil were 445 and 8.2 mg·kg⁻¹, respectively.

Plots of kinetic sorption data fitted using the intraparticle diffusion model (Figure 1b) showed multilinearity. This indicates that two or three stages are involved in the sorption process.^{31,32} The positive intercept values for the linear portions of each plot were indicative of rapid adsorption to external sorbent surfaces. WTRs exhibited a longer period of intraparticle diffusion compared to paddy soil. This is likely due to differences in the total pore volumes and micropore distributions between the substrates (Table 1).

From the analysis of Figure 1 above, it could be concluded that there were two distinct stages for both the paddy soil and WTRs before sorption equilibrium reached. The two-phase

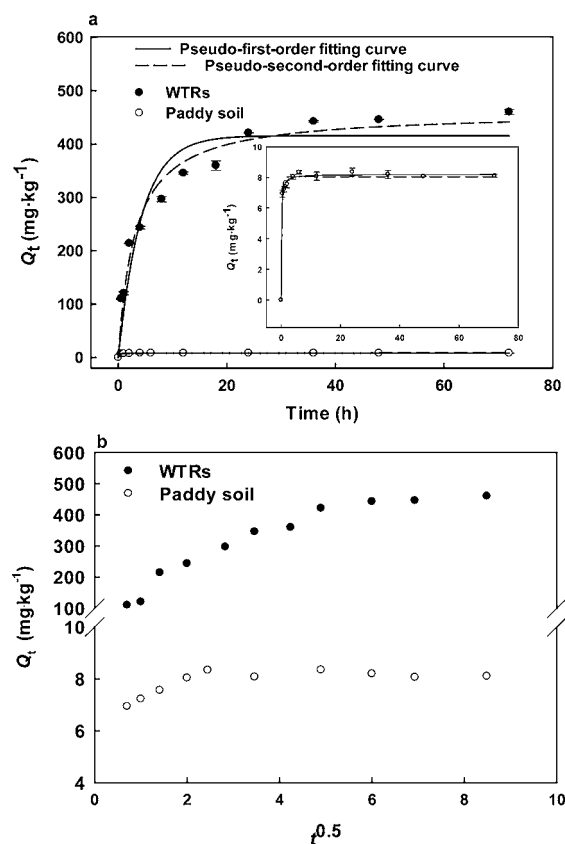


Figure 1. Kinetic plots for chlorpyrifos adsorption to WTRs and paddy soil at an initial chlorpyrifos concentration of 0.28 mg·L⁻¹. The kinetic sorption data were fitted by pseudo-first-order and pseudo-second-order models (a) and by the intraparticle diffusion model (b). Error bars represent the standard errors from triplicate samples.

sorption kinetics observed are likely due to rapid sorption of chlorpyrifos to external surface sites followed by slow migration and diffusion of chlorpyrifos into the organic matter matrix.³³ In comparison to the sorption process of paddy soil, the longer sorption period and the higher equilibrium chlorpyrifos sorption to WTRs may be attributed to the longer intraparticle diffusion process and the higher surface area and organic matter content,³⁴ respectively. The organophosphorus pesticides methyl parathion and endosulfan exhibit similar sorption trends in soils.^{35,36}

Pseudo-first-order and pseudo-second-order models were applied to further analyze the sorption processes. The fitting results are shown in Table 3 and Figure 1a. In comparison, the Q_e value from the pseudo-second-order equation was much closer to the experimental Q_{e-exp} value, and the pseudo-second-order equation yielded higher correlation coefficient values. Thus, the pseudo-second-order equation can better describe chlorpyrifos sorption. The rate constants (k_1 and k_2) for chlorpyrifos sorption to WTRs were relatively lower compared to the paddy soil. This finding is most likely associated with the smaller pore diameter and larger total pore volume of the WTRs. Meanwhile, according to the shape of the plots fitted using the intraparticle diffusion model, intraparticle diffusion plays an important role in the process of chlorpyrifos sorption by WTRs. Given that intraparticle diffusion is a relatively slow process, the greater quantities of chlorpyrifos sorbed by the WTRs may be attributable to the slower sorption rate. The greater quantities of chlorpyrifos adsorbed by the WTRs may

Table 3. Kinetic and Equilibrium Isotherm Parameters for Chlorpyrifos Sorption to Paddy Soil and WTRs

model	parameters	WTRs	paddy soil	
	Q_{e-exp}^a (mg·kg ⁻¹)	445	8.20	
pseudo-first-order	k_1 , h ⁻¹	0.23 ± 0.05	6.78 ± 0.17	
	Q_e , mg·kg ⁻¹	424.0 ± 23.8	7.9 ± 1.3	
	R^2	0.912	0.970	
pseudo-second-order	k_2^b , kg·(mg·h) ⁻¹	6.84 × 10 ^{-4c}	1.82 ^d	
	Q_e^b , mg·kg ⁻¹	465.0 ^e	8.1 ^d	
	R^2	0.964	0.989	
Freundlich	K_F , mg ¹⁻ⁿ ·L·kg ⁻¹	5967 ± 884	137 ± 21	
	n	0.93 ± 0.075	0.90 ± 0.061	
	R^2	0.992	0.980	
	log K_{oc}^e	0.005 S_w	4.90	4.08
		0.05 S_w	4.83	3.98
	0.5 S_w	4.76	3.88	
linear	K_D , L·kg ⁻¹	6837 ± 182	176 ± 5	
	R^2	0.990	0.973	

^aThe equilibrium adsorption capacities obtained from the experiments. ^b k_2 and Q_e are calculated by the values of k_2Q_e and $k_2Q_e^2$ obtained from the simulation results. ^c $k_2Q_e^2 = 148 ± 24.1$, $k_2Q_e = 0.318 ± 0.0616$. ^d $k_2Q_e^2 = 120 ± 23.2$; $k_2Q_e = 14.8 ± 2.98$. ^eThe calculated organic carbon (OC)-normalized sorption capacity coefficient.

adversely affect the molecular diffusion process, thereby resulting in a further decrease in the sorption rate (e.g., due to increasing steric hindrance with increased chlorpyrifos sorption to internal sorption sites). An inverse relationship between the sorption rate and sorption capacity has also been observed in the case of metalaxyl sorption by numerous soils.³⁷

Isotherms of Chlorpyrifos Sorption by WTRs and Paddy Soil. Figure 2 shows the sorption isotherms of chlorpyrifos in WTRs and paddy soil. Freundlich and linear models were employed to analyze the equilibrium data because the sorption isotherms of chlorpyrifos generally followed either model.³⁰ The parameters and correlation coefficients (R^2) for the models are given in Table 3. On the basis of the R^2 values, the Freundlich model fits the experimental data slightly better than the linear model. This result indicates that chlorpyrifos uptake occurred on the heterogeneous surfaces of the paddy soil and WTRs by multilayer sorption. Information about the sorption mechanisms can be obtained from the shape of sorption isotherms. According to the classification by Giles et al.,³⁸ the isotherms obtained in this study are of type L and close to type C ($n = 0.90, 0.93$). The observed sorption isotherm shape reveals that there is constant partitioning of solute between the solution and substrate at low sorbate concentrations, and the sorption rate will decrease with an increase of sorbate concentration due to the increasing difficulty of accessing the sorption sites.

The K_F and K_D values presented in Table 3 show that the sorption capacity of WTRs for chlorpyrifos was greater than that of paddy soil. This result is likely mainly due to the different organic matter contents and surface area of the WTRs (107 mg·g⁻¹ and 78.5 m²·g⁻¹, respectively) and paddy soil (19 mg·g⁻¹ and 18.3 m²·g⁻¹, respectively). Like other hydrophobic organic contaminants, the sorption behavior of chlorpyrifos is largely determined by the type and content of organic matter in

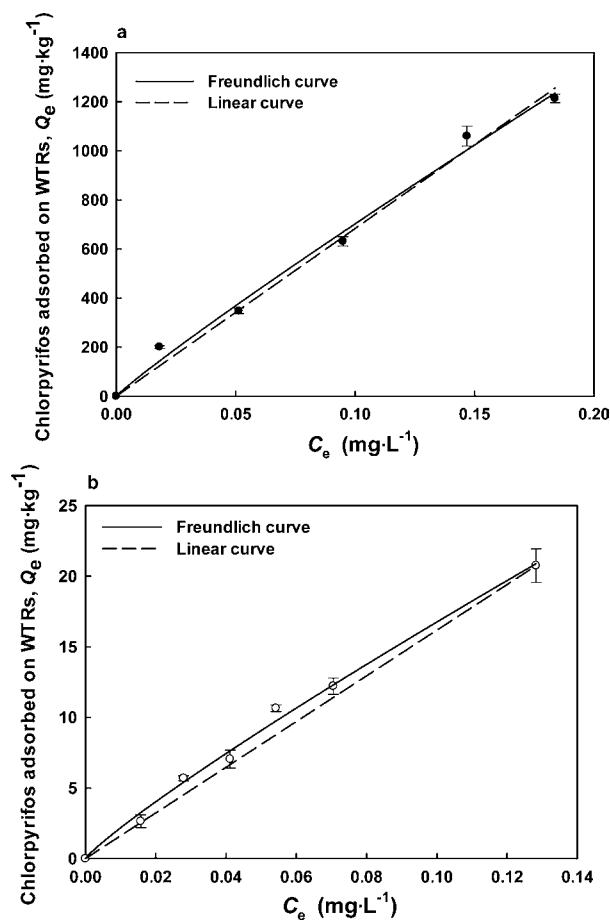


Figure 2. Adsorption isotherms of chlorpyrifos to WTRs and paddy soil at near-neutral pH conditions. The error bars represent the standard error from triplicate samples. Initial chlorpyrifos concentrations ranged from 0.10 to 0.80 mg·L⁻¹.

the adsorbents.^{39,40} The organic matter content in WTRs is 5 times greater than that of paddy soil. Additionally, the values of log K_{oc} (Table 3) suggested that the sorption capacity of organic matter per unit mass in the WTRs surpassed that of paddy soil by approximately 1 order of magnitude across a range of different chlorpyrifos concentrations. These data indicated that the type of organic matter in WTRs (84.1% humin) is more suitable for chlorpyrifos sorption than that in paddy soil (57.9% humin).

Other materials including biomass (such as sawdust, peat moss, peanut shell, coconut husk, and rice husk), inorganic minerals, and modified minerals have also been tested for chlorpyrifos sorption ($C_0 < 1$ mg·L⁻¹). The log K_{oc} and K_D values obtained for these sorption materials were within the ranges of 4.2–4.4 and 640–4341 L·kg⁻¹, respectively.³⁰ A comparison between these sorption materials and the WTRs examined herein shows that WTRs exhibit a greater chlorpyrifos sorption capacity.

Effects of pH on Chlorpyrifos Sorption by WTRs.

Figure 3 shows the effects of solution pH on the chlorpyrifos sorption capacity of WTRs. The adsorbed quantity of chlorpyrifos on WTRs was higher at lower pH values (Figure 3). The amount of chlorpyrifos sorbed declined by nearly 10% as the pH increased from 4.1 to 7.2. Statistical analysis indicated that the difference in the quantity of chlorpyrifos sorbed at pH 4.1 and 7.2 was not significant ($p < 0.05$).

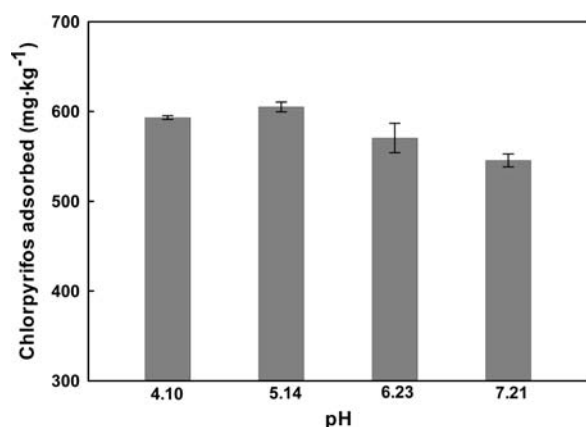


Figure 3. Effect of pH on the adsorption of chlorpyrifos to WTRs. The error bars represent the standard errors from triplicate samples. The initial chlorpyrifos concentration was 0.35 mg·L⁻¹.

Chlorpyrifos is a nonionic pesticide, and its physicochemical properties will not change with the solution pH. However, a pH increase would contribute to the dissolution of organic matter in solution and the deprotonation and hydrolysis of functional groups on the surface of the adsorbents.⁴¹ These factors may weaken the affinity and hydrogen bond interactions between WTRs and chlorpyrifos. This is the most likely explanation for the slight inhibition of chlorpyrifos sorption to WTRs with increasing solution pH. A similar phenomenon has been observed for diuron sorption by wheat char.⁴² Overall, the initial solution pH only slightly affected the sorption of chlorpyrifos by WTRs. This finding could likely be explained by the fact that humin, the major organic matter of WTRs, is stable under acidic and neutral conditions.

Effects of Ionic Strength on Chlorpyrifos Sorption by WTRs. The ionic strength effect is related to adsorbate surface concentration.⁴³ Hence, two initial chlorpyrifos concentrations were investigated in this study. Figure 4 reveals the influence of the solution ionic strength on chlorpyrifos sorption to WTRs. Under initial chlorpyrifos concentrations of 0.28 and 0.50 mg·L⁻¹, the sorption amounts decreased by 14.7 and 9.6%, respectively, with increasing Ca²⁺ concentration from 0.005 to 0.05 M. In contrast, the quantity of chlorpyrifos sorbed was

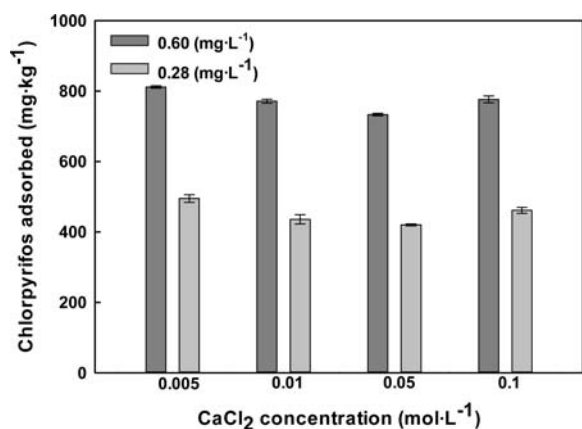


Figure 4. Effect of background CaCl₂ solution ionic strength on the adsorption of chlorpyrifos to WTRs at two initial chlorpyrifos concentrations. The error bars represent the standard errors from triplicate samples.

significantly enhanced when the Ca²⁺ concentration reached 0.1 M.

Lee et al.⁴³ proposed three stages to describe the complicated effects of ionic strength on phenanthrene and pyrene binding to humic substances. These three stages are inhibition, promotion, and plateaus in sorption as the ionic strength increases, and consistent results were achieved in this study. In the low range of Ca²⁺ concentrations, the quantity of chlorpyrifos adsorbed to WTRs decreased with increasing Ca²⁺ concentration. This inhibition effect may be explained by a decrease in sorption sites caused by the aggregation of WTRs as electrostatic repulsion between adsorbent particles in solution has been shown to weaken in the presence of electrolyte ions,^{44–46} perhaps by compressing the electric double layer. When the Ca²⁺ concentration reached 0.1 M, a salting-out effect likely occurred, resulting in a decrease in chlorpyrifos solubility in solution and thereby enhancing chlorpyrifos sorption to WTRs. Considering the actual concentration of Ca²⁺ in natural waters and soil pore waters, the highest Ca²⁺ concentration investigated in this study was 0.1 M.

Effects of LMWOAs on Chlorpyrifos Sorption by WTRs. Figure 5 illustrates the effect of LMWOAs (MA and

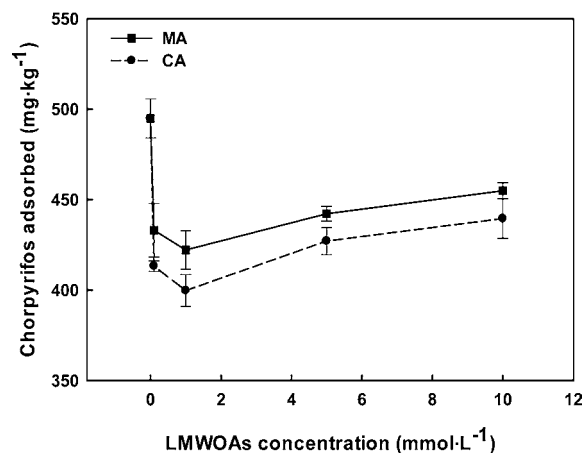


Figure 5. Adsorption of chlorpyrifos to WTRs in the presence of malic acid (MA) and citric acid (CA) across a range of initial organic acid concentrations. The error bars represent the standard errors from triplicate samples. The initial chlorpyrifos concentration was 0.27 mg·L⁻¹.

CA) on chlorpyrifos sorption to WTRs. In comparison to the control group, the addition of increasing concentrations of MA and CA resulted in 8–16 and 11.2–19.2% reductions in chlorpyrifos sorption, respectively. Both MA and CA significantly inhibited chlorpyrifos sorption to WTRs ($P < 0.05$). As the MA and CA concentrations increased from 0.1 to 1 mM, the quantity of chlorpyrifos sorbed further decreased; however, the inhibition effects of the LMWOAs significantly abated with increasing MA and CA concentrations ranging from 1 to 10 mM ($P < 0.05$).

Organic matter can be combined with Fe/Al compounds through carboxyl and hydroxyl functional groups. However, it has been reported that Fe/Al minerals and LMWOAs could form organic acid–metal complexes in solution.^{47,48} Thus, the linkage between organic matter and the substrates would be disrupted and organic matter weakly bound to Fe/Al minerals could be released into solution, thereby enhancing chlorpyrifos solubility in solution. The probability of organic matter release

in the presence of LMWOAs has been further confirmed via analysis of the dissolved organic matter in WTRs extracted by LMWOAs using three-dimensional excitation–emission matrix (EEM) fluorescence spectroscopy (Supporting Information, Figure S2 and Table S2). The LMWOAs could also compete with organic pollutants for surface sorption sites.⁴⁹ All of these mechanisms likely contributed to a decrease in chlorpyrifos sorption to WTRs in the presence of the LMWOAs.

Compared to the MA, the CA exhibited a greater inhibitory effect, likely due to structural differences between these two LMWOAs. The CA has more carboxyl functional groups, which facilitates stronger complexation between CA and Fe/Al minerals in the WTRs. When the MA and CA concentrations reached 1 mM, the surface of the WTRs likely became more hydrophobic due to surface coating of the WTRs by LMWOAs, which increased the sorption of chlorpyrifos. Thus, the inhibitory effects of MA and CA abated as their respective concentrations increased. Previous work has shown that humic acid coating of gibbsite and kaolinite enhanced chlorpyrifos sorption to these minerals.⁵⁰

Conclusions. The adsorption behavior of chlorpyrifos to WTRs can be separated into the following two distinct stages: initial rapid adsorption followed by a slower adsorption over a long period. The $\log K_{oc}$ and K_F values for chlorpyrifos sorption to WTRs reached 4.90 and 5967 $\text{mg}^{1-n} \cdot \text{L} \cdot \text{kg}^{-1}$, respectively. The type and content of organic matter and the surface area influenced the greater extent of chlorpyrifos adsorption by WTRs compared to paddy soil in the present study. Low pH was conducive to chlorpyrifos adsorption by WTRs. The effect of solution ionic strength on chlorpyrifos adsorption varied with the Ca^{2+} concentration. The addition of LMWOAs (MA and CA) significantly inhibited chlorpyrifos adsorption, but the extent of inhibition was dependent upon the concentration of the LMWOAs. In summary, the WTRs exhibited a high adsorption capacity for chlorpyrifos at environmentally relevant pH (4–7) and ionic strength. The results of this study indicated that WTRs containing substantial organic matter may be useful for chlorpyrifos sorption from agricultural wastewaters or as amendments for soils to reduce nonionic pesticides leaching into groundwater.

■ ASSOCIATED CONTENT

Supporting Information

Additional tables and figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ ABBREVIATIONS AND NOMENCLATURE

WTRs, drinking water treatment residuals; LMWOAs, low molecular weight organic acids; MA, malic acid; CA, citric acid;

Fe/Al, iron and aluminum; ICP-AES, inductively coupled plasma–atomic emission spectrometer; HPLC, high-performance liquid chromatography; PTFE, polytetrafluoroethylene

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