EFFECT OF MICROPLASTIC COEXISTENCE CONDITIONS ON THE ENVIRONMENTAL BEHAVIOR OF ATRAZINE ON SOIL

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Abstract. The objective of this study was to explore the environmental impact of microplastics on the coexisting contaminant atrazine in soil. The highest adsorption of atrazine under PE coexistence circumstances was 66.18 mg/kg and 67.85 mg/kg for black and black calcium soils, which were 1.21-fold and 0.83-fold greater respectively than the control soil. The Freundlich isothermal adsorption equation better described the isothermal adsorption characteristics of black and black calcium soils with added microplastics to the co-existing pollutant atrazine, and their adsorption capacities K_f in descending order were: black calcium soil + 2%PE > black soil + 2%PE > black calcium soil > black soil. The black clay + 2%PE adsorption constant K_f was 14.513 *L*/kg, which was 2.11 times higher than the control black clay adsorption constant K_f, and the black calcium clay + 2%PE adsorption constant K_f was 15.926 *L*/kg, which was 1.01 times higher than the control black calcium clay adsorption constant K_f. The adsorption free energy $\Delta G^\theta < 40$ kJ/mol and the thermodynamic fitting parameter $\Delta H^\theta < 40$ kJ/mol show that the adsorption is physical and that it is an exothermic, spontaneous reaction. The thermodynamic parameter value $\Delta S^\theta < 0$ shows that adsorption confusion gradually reduces. The adsorption capacity of atrazine in both soils containing PE decreased as the Ca^{2+} concentration in the solution increased. Under sterilized conditions, the half-life time of black soil and black calcium soil was increased by 23.43% and 10.53%, respectively. As 2%PE polyethylene microplastics were introduced to the two unsterilized soils, the degradation rate dropped by 27.78% and 20%, respectively, as compared to the control soils.
Keywords: *micro plastic, black soil, black calcium soil, adsorbent, degradation*

Introduction

Microplastic is often described as plastic particulate pollution having a particle size of less than 5 mm (Yong et al., 2020). Microplastics come in a variety of forms, with the most prevalent being polypropylene (PP), polyethylene (PE), polyvinyl chloride (PVC), and polystyrene (PS) (Wang and Wang, 2017). Because of their low cost, light weight, durability, and corrosion resistance, microplastics are widely employed in commercial, industrial, and agricultural applications (Andrady, 2011). As a result, the global consumption of microplastics has directly increased from 1.7 million tons in 1950 to 335 million tons in 2016. PE (polyethylene) is a widely used microplastic in agricultural applications to protect crops, reduce weeds, and regulate temperature. Polyethylene microplastics that remain in the soil are brittle and disintegrate into particles over time (Duis and Coors, 2016), becoming enrichment.

Atrazine is a triazine-based selective herbicide that is most commonly employed on maize, although it is also used on sugarcane, sorghum, and landscape vegetation (Yue et al., 2017). Atrazine has a long residual period in the soil, and despite being banned in

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the EU, it may now be found in soil, water, and other habitats in some locations remote from agriculture (Huang, 2021). According to reports, several areas of the EU have tested their groundwater at amounts as high as 0.1 ug·L^{-1} (Vonberg et al., 2014). Vryzas et al. (2009) analyzed 147 chemicals in surface water throughout Greece and discovered that atrazine and its degradation components had the greatest detection rates. Atrazine concentrations in surface and groundwater have surpassed controlled limits in several places of northern China, and the discharge of wastewater with high atrazine concentrations into the soil has resulted in many occurrences of toxic mortality of rice seedlings (Wu, 2020). Yu (2015) discovered atrazine at levels ranging from 0.018 to 0.116 mg·kg^{-1} in the soil of arable layer cultivating maize in Jilin Province. Previous local and international research has concentrated on the environmental behavior of soil in terms of atrazine adsorption and degradation. Yue et al. (2017) found that the maximum equilibrium sorption of atrazine by three soils was in the order of alluvial soil > laterite soil > rice soil. Qu (2014) discovered that boosting microbial activity and light could improve atrazine breakdown by soil.

There are many studies on the migration of antibiotics and pesticides in the marine system by microplastics, but few studies on the migration and transformation of co-pollutants—pesticides—in the soil-microplastics mixed system, particularly on the environmental behavior of atrazine, which is widely used in Jilin Province's typical soil. This study chose polyethylene microplastics, which are commonly used, to investigate the influence of microplastic retention on atrazine absorption in black soil and chernozem (Jilin Provincial Soil Fertilizer Station, 1998). The major goal is to understand the mechanism of atrazine adsorption in soil with microplastics, the effect of environmental parameters such as temperature and ionic strength on the adsorption process, and the effect of microplastics on atrazine degradation in soil. To establish a rigorous theoretical foundation for assessing and managing the environmental risks of combined microplastics and atrazine pesticides in soil.

Materials and methods

Test soil

Hengfa Plastic Chemical Co. supplied the PE polyethylene microplastics utilized in this work. The test soils were black soil and black calcium soil from the experimental fields of Jilin Agricultural University and Nong'an County, respectively, in October 2021. Samples were collected at depths ranging from 0 to 20 cm, naturally dried, and sieved through a 100-mesh sieve for the adsorption isotherm test and a 20-mesh screen for the soil degradation test before being sealed and kept. *Table 1* shows the fundamental physicochemical parameters of the test soil. Sterilized soil was created by sterilizing the soil in an autoclave at 121°C for 30 min and then constantly extinguishing it for 3 days (Shao et al., 2019).

Table 1. *Physical and chemical properties of test soil*

Soil type	Organic matter g·kg^{-1}	Cation exchange capacity cmol·kg^{-1}	pH	Particle composition/%		
				Clay particle	Silt	Sand
Black soil	30.4	23.8	6.77	38.80	21.24	39.96
Black calcium soil	25.5	18.63	7.36	35.18	31.39	33.43

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Experimental design

The adsorption test design was based on Li's (2020) work; the degradation test design was based on Zhao et al. (2021); and the atrazine analysis method was based on Cao (2014).

Adsorption kinetics experiment

Two grams of black soil and black calcium soil containing PE (final concentration of 2%) were weighed separately, and 50 ml of atrazine solution (with 0.01 $mol \cdot L^{-1}$ $CaCl_2$ and containing 0.01 $mol \cdot L^{-1}$ NaN_3 as an inhibitor) at a concentration of 10 $mg \cdot L^{-1}$ was added as a background solution, shaken well, and then shaken at 25°C in a thermostat at 180 $r \cdot min^{-1}$ for 0, 3, 10, 30, 60, 150, 420, 600, and 1440 min, respectively. The contents of atrazine in the supernatant were measured by high-performance liquid chromatography using a 0.22 μm organic filter membrane after centrifugation for 10 min at 4500 $r \cdot min^{-1}$, and the average results were obtained from three parallel trials. As controls, black soil with no microplastic additions and black calcium soil were employed.

Adsorption isotherm

Two grams of black soil and black calcium soil containing PE (final concentration of 2%) were weighed separately, 50 ml of atrazine solution (with 0.01 $mol \cdot L^{-1}$ $CaCl_2$ and containing 0.01 $mol \cdot L^{-1}$ NaN_3 as inhibitor) at concentrations of 5, 10, 15, 20 and 25 $mg \cdot L^{-1}$ was added as background solution, shaken well, and shaken at 25℃ under a gas bath constant temperature oscillator. The absorbance of the supernatant was measured by centrifugation for 10 min at 4500 $r \cdot min^{-1}$ with a high-speed centrifuge (GL-20B, Shanghai Anting Scientific Instruments) for 1440 min, and the average values were taken for three parallel experiments. Black soil without microplastic addition and black calcium soil were used as controls.

Adsorption thermodynamics

Two grams of black soil and black calcium soil containing PE (final concentration of 2%) were weighed into 50 mL of different concentrations of 5, 10, 15, 20 and 25 $mg \cdot L^{-1}$ atrazine solution, and the temperature of the constant temperature oscillator was set at 15℃ (±0.5℃), 25℃ (±0.5℃) and 35℃ (±0.5℃), respectively, and the other experimental designs were referred to Adsorption isotherm test, and the mean values were taken for the three groups of parallel experiments. Black soil without microplastic addition and black calcium soil were used as controls.

Effect of cationic strength on adsorption

The concentrations of $CaCl_2$ in the background electrolyte were set as 0, 0.01, and 0.10 $mol \cdot L^{-1}$ (containing 0.01 $mol \cdot L^{-1}$ NaN_3) $CaCl_2$ solution, and the other experimental designs were referred to Adsorption isotherm test, and the mean values were taken for the three parallel experiments. Black soil without microplastic addition and black calcium soil were used as controls.

Soil degradation test

Weigh 200 g of two kinds of test soils (sterilized and non-sterilized) containing 2%PE and control test soils (sterilized and non-sterilized) with different treatments into

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250 ml conical flasks, evenly drop 20 ml of 100 mol·L^{-1} atrazine solution, add deionized water to adjust the water content of the soil, seal with cotton plugs and put into a constant temperature incubator at 25℃ and regularly supplement with deionized water to adjust the Water content in the soil. The water content of the sterilized soil was adjusted by adding sterilized deionized water to the sterilized soil. The residual atrazine concentration in the soil was measured at 1 d, 3 d, 7 d, 14 d, 21 d and 30 d respectively. Three parallels were set up for each treatment.

Analytical method

Determination of atrazine in soil: weigh 5 g of soil sample, add 0.3 g of dried anhydrous magnesium sulfate, add 10 ml of acetonitrile, vortex and mix for 1 min and then sonicate for 15 min, centrifuge at 5000 r·min^{-1} for 5 min, and measure the concentration of atrazine in the supernatant.

Liquid chromatographic conditions: the mobile phase was 60:40 methanol–water, the mobile phase flow rate was 1 mL·min^{-1}, the column temperature was 30℃, the injection volume was 10 μL, the UV detection wavelength was 210 nm, and the retention time was 5 min.

The average recoveries were 83.06%~93.50% with the relative standard deviations of 1.62%~3.02%. The minimum detection concentration of AT in soil was 0.500 mg·kg^{-1}. The accuracy and sensitivity of the method met the requirements.

Data analysis

Expression of atrazine adsorption capacity

$$C_g = \frac{(C_o - C_e)}{m} V \quad \text{(Eq.1)}$$

In formula: q_e is the adsorption amount in soil (mg/kg); C_o is the initial concentration of solution (mg/L); C_e is the solution concentration at equilibrium (mg/L); V is the volume of solution (mL); m is the weight of soil sample (g).

First-order dynamics model

$$q_t = q_e \left(1 - e^{-kt}\right) \quad \text{(Eq.2)}$$

In formula: k is pseudo first order adsorption rate (min^{-1}).

Second-order dynamics model

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{(Eq.3)}$$

In formula: q_2 is the equilibrium adsorption capacity (mg/kg); k_2 is the pseudo-second-order kinetic adsorption rate (kg/(mg·min)). q_e is the adsorption capacity at time t (mg/kg).

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Langmuir isothermal adsorption model

$$q_e = \frac{Q_m K_L C_e}{(1+K_L C_e)} \quad \text{(Eq.4)}$$

In formula: Q_m is the maximum adsorption capacity of monolayer adsorption. K_L represents the adsorption surface temperature constant (*L*/mg).

Freundlich isothermal adsorption model

$$q_e = K_f C_e^{\frac{1}{n}} \quad \text{(Eq.5)}$$

In formula: n is temperature-dependent constant velocity and is a nonlinear factor of the equation. K_f is the constant rate of soil adsorption.

Adsorption thermodynamic parameters

$$\ln^K = -\frac{\triangle H^\theta}{RT} + \frac{\triangle S^\theta}{R}$$
$$\triangle G^\theta = \triangle H^\theta - T\triangle S \quad \text{(Eq.6)}$$

In formula: K is constant velocity of adsorption equilibrium; ΔG^θ is the Gibbs free energy change (kJ/mol); ΔH^θ is enthalpy change (kJ/mol); ΔS^θ is the adsorption entropy change (J/(k·mol)).

Intragranular diffusion model

$$q_e = K_p^{\frac{1}{2}} + C \quad \text{(Eq.7)}$$

In formula: K_p is the diffusion rate constant in particles (mg/(kg·min$^{1/2}$)). C is the rate constant.

Degradation kinetic model

$$C_t = C_0 \exp^{-kt}$$
$$t_{1/2} = \frac{\ln^2}{k} \quad \text{(Eq.8)}$$

In formula: C_t is the residual concentration of AT in soil at time t (mg/kg). C_o is the initial concentration (mg/kg); k is the constant first-order degradation rate (d^{-1}). T is degradation time (d); $t_{1/2}$ is the degradation half-life (*d*).

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Results

Shape of microplastics

Figure 1 displays a SEM picture of PE, which demonstrates that the surface of the PE microplastic is rougher and has raised and depressed areas, which can give a greater adsorption area for adsorption AT.

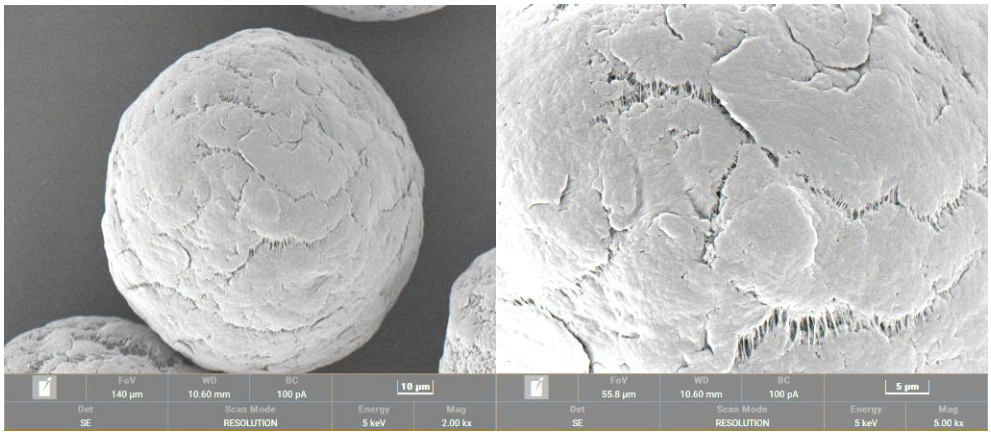

Figure 1. *SEM of PE*

Microplastic FTIR spectroscopy

Figure 2 depicts the FTIR spectra of PE microplastics before and after AT adsorption. The characteristic peaks at 3419 cm^{-1} are caused by O-H bond stretching motion, the characteristic peak at 2921 cm^{-1} is caused by C-H bond stretching motion (Zhang, 2018), the characteristic peak at 1650 cm^{-1} may be caused by carboxyl (C = O) stretching vibration, the characteristic peaks at 1390 cm^{-1} and 1033 cm^{-1} may be caused by the stretching vibration of the C-OH bond and the pulling motion of the C-O bond, respectively (Song et al., 2023), and the characteristic peak at 719 cm^{-1} The oxidation of microplastics in air may produce the appearance of O-H and C-O bonds in the infrared characteristic spectrum (Böhning et al., 2016), as may the oxidation of C-H bonds that break to generate C-O bonds (Luo et al., 2020). The infrared spectrogram shows that no new groups were formed after atrazine adsorption by microplastics, indicating that no covalent bonds were formed during atrazine adsorption by microplastics, proving that the adsorption process of atrazine adsorption by microplastics is primarily influenced by intermolecular van der Waals forces and microporous filling mechanisms (Zhang, 2018).

Adsorption kinetics

Figure 3 depicts the kinetics of adsorption of two soils (black soil and black calcium soil) at a concentration of 10 $mg \cdot L^{-1}$ AT under PE (100 mesh) coexistence conditions. The slope of adsorption progressively slows down as adsorption proceeds, showing that the two soils and the additional microplastics are split into quick adsorption and slow adsorption, with eventually the process of adsorption tending to equilibrium (Yue et al., 2017). The highest equilibrium adsorption was 95.6%, 95.2%, 94.2%, and 93.4% in the first 1 h of adsorption for black soil, black calcium soil, and two soils with 2%PE, respectively. Without PE, the maximum adsorption capacities of the two soils (black soil and black calcium soil) were 30 $mg \cdot kg^{-1}$ and 37.175 $mg \cdot kg^{-1}$,

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respectively, while with 2% PE, the maximum adsorption capacities were 66.175 mg·kg^{-1} and 67.85 mg·kg^{-1}, respectively. Under PE coexistence circumstances, the adsorption capacities of black soil and black calcium soil were enhanced 1.206 times and 0.825 times, respectively (*Table 2*).

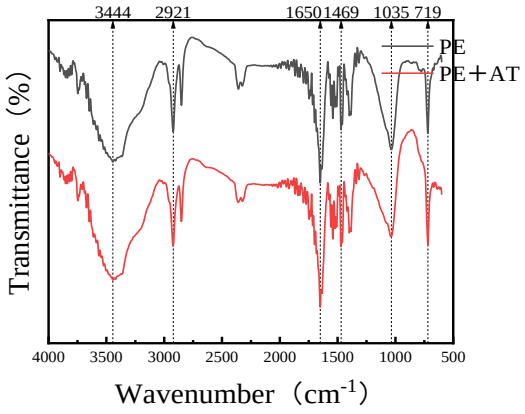

Figure 2. *Fourier spectrum before and after atrazine adsorption by microplastics*

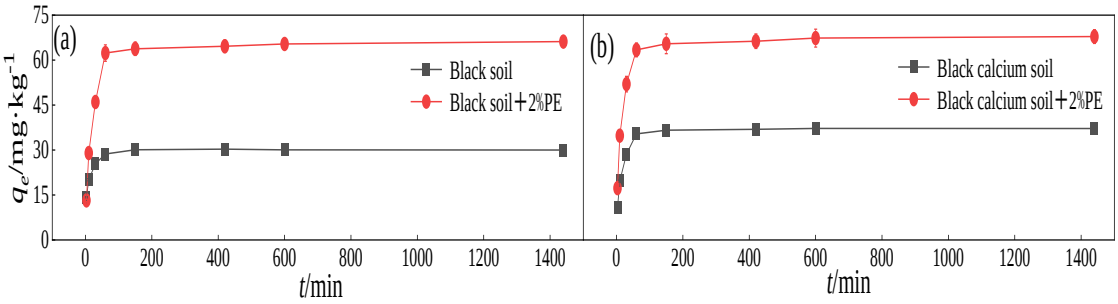

Figure 3. *Adsorption kinetics of AT in soil and micro plastic soil. (a) Plot represents the kinetic model of AT adsorption by black soils and black soils containing 2%PE at AT concentration of 10 mg·L^{-1}, (b) plot represents the kinetic model of AT adsorption by black calcium soils and black calcium soils containing 2%PE at AT concentration of 10 mg·L^{-1}*

Table 2. *Adsorption kinetics fitting parameters*

Adsorbent	Quasi-first-order dynamics model			Quasi-second-order dynamics model		
	K_1	q_1	R^2	K_2	q_2	R^2
Black soil	0.153	29.018	0.835	0.0126	31.037	0.999
Black soil + PE	0.051	64.677	0.979	0.0014	66.622	0.999
Black calcium soil	0.073	36.331	0.952	0.0045	37.383	0.999
Black calcium soil + PE	0.069	65.698	0.968	0.0018	68.213	0.999

The fitted curves of the intraparticle diffusion sorption kinetics model for AT in two soils are shown in *Figure 4*: black soil, black calcium soil, and soil having 2%PE (*Eq. 7*). *Figure 4* shows that the entire adsorption process, which is separated into three stages (liquid film diffusion, intraparticle diffusion, and adsorption equilibrium), is

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linearly fit with $t^{1/2}$ and q_e, with the parameter k_i indicating the magnitude of the adsorption rate at each stage. All of the adsorption steps in the diagram satisfy the order $k_{i1\text{liquid film diffusion}} > k_{i2\text{particle diffusion}} > k_{i3\text{adsorption equilibrium}}$.

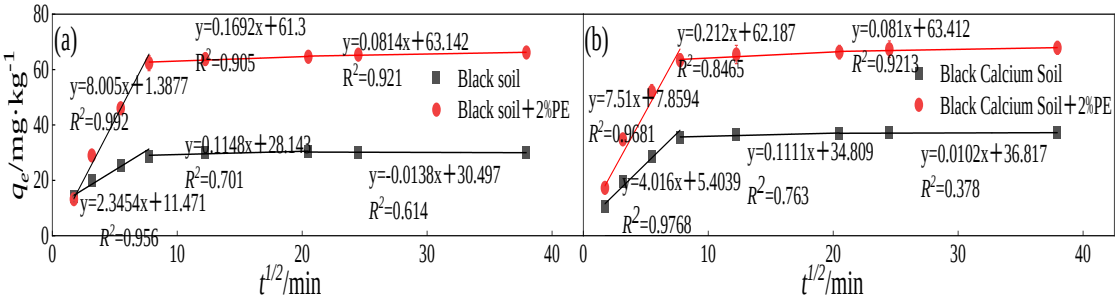

Figure 4. *Fitting curve of intraparticle diffusion adsorption kinetic model. (a) Plot represents the internal diffusion model of black soil and black soil containing 2% PE for AT at AT concentration of 10 mg·L^{-1}, (b) plot represents the internal diffusion model of black calcium soil and black calcium soil containing 2% PE for AT at AT concentration of 10 mg·L^{-1}*

Adsorption isotherm

At 25°C, *Figure 5* depicts AT sorption isotherms for black soil, black calcium soil, and two soils having 2%PE fitted with the Freundlich equation (*Eq. 5*). *Figure 5* shows that the equilibrium sorption of AT by the black soil containing 2%PE and the black calcium soil compared to the two control soils without PE was substantially different ($p < 0.05$) at varied AT concentrations. To better investigate the sorption characteristics of the two soils for AT under the coexistence of PE (100 mesh), the Langmuir and Freundlich isothermal sorption models were fitted, and it was discovered that the Freundlich model better describes the sorption characteristics based on the fitted values of the Freundlich isotherm model in *Table 3* (R^2 = 0.969–0.993). The adsorption curves are "*L*-shaped nonlinear adsorption curves," and 1/n is consistent with 1, suggesting that AT adsorption does not increase as concentration increases. It is probable that the high concentration of AT might clog the pores of SOM (soil organic matter) and prevent its entrance into the pores, resulting in poorer soil sorption of atrazine (Chen et al., 2020). The Freundlich fitted sorption constants K_f black soil and black calcium soil were 4.666 $L \cdot kg^{-1}$ and 7.939 $L \cdot kg^{-1}$, and the addition of 2%PE K_f to the two soils was 14.513 $L \cdot kg^{-1}$ and 15.926 $L \cdot kg^{-1}$.

Table 3. *Adsorption isotherm fitting parameters of soil and soil containing microplastics for AT*

Soil type	Langmuir isothermal adsorption model			Freundlich isothermal adsorption mode		
	Q_m	K_L	R^2	1/n	K_F	R^2
Black soil	651.321	0.00611	0.99	0.908	4.666	0.992
Black soil + PE	551.421	0.0208	0.983	0.91	14.513	0.985
Black calcium soil	284.381	0.0211	0.992	0.79	7.939	0.993
Black calcium soil + PE	670.652	0.0187	0.966	0.819	15.926	0.969

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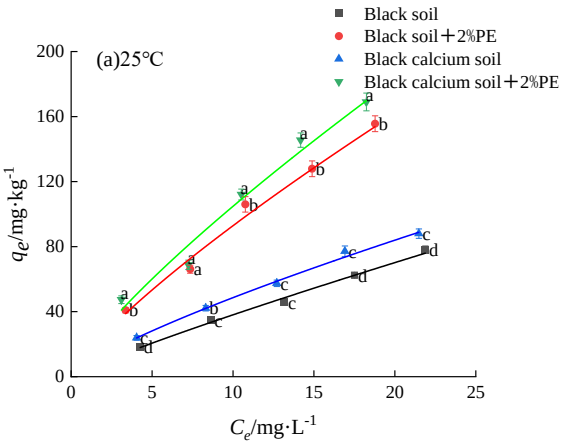

Figure 5. *Adsorption isotherm of AT in soil and soil containing microplastics. Different lowercase letters represent significant differences between different treatments ($p < 0.05$)*

Effect of temperature on the adsorption of atrazine on soil under microplastic coexistence conditions

Figure 6 depicts the AT sorption isotherms for two soils (black soil and black calcareous soil) containing 2%PE and fitted with the Freundlich equation (*Eq. 5*) at various temperatures. The equilibrium sorption of AT by the two soils containing 2%PE at 15°C was substantially different ($p < 0.05$) from the equilibrium sorption of AT by the two soils containing 2%PE at 35°C for varied AT concentrations, as shown in *Figure 6*. The Freundlich model, as shown in *Table 4*, better describes the sorption characteristics of AT in both soils containing 2%PE at different temperatures ($R^2 > 0.961$). As can be seen from *Table 4*, at 15°C, the fitted adsorption constants K_f were 16.173 $L \cdot kg^{-1}$ for black clay + 2%PE and 17.493 $L \cdot kg^{-1}$ for black calcium clay + 2%PE, respectively, while at 35°C, the fitted adsorption constants K_f fell by 23.66% and 17.88%, respectively. This suggests that the adsorption capacity of both soils decreases gradually with rising temperature following the addition of microplastics. As shown in *Table 5*, this is compatible with the thermodynamic fitting parameters (Eq. cf. *Eq. 6*) ΔH^{θ}, which are all 0 and represent exothermic reactions. The free energy of atrazine adsorption in both soils and additional microplastics was 40 $kJ \cdot mol^{-1}$, showing that the adsorption process was mostly regulated by physical adsorption. The thermodynamic fitting parameter $\Delta H^{\theta} < 40$ $kJ \cdot mol^{-1}$ may also be used to demonstrate that the adsorption is mostly physical (Sun et al., 2016). The thermodynamic parameter values ΔS^{θ} are all zero, suggesting that the adsorption confusion is rapidly decreasing.

Effect of ionic strength on soil adsorption of atrazine under microplastic coexistence conditions

Figure 7 depicts the sorption isotherms of AT for two soils containing 2%PE and fitted with the Freundlich equation (Eq. cf. *Eq. 5*) at different ionic strengths. The equilibrium sorption of AT for two soils containing 2%PE at Ca^{2+} concentrations of 0 $mol \cdot L^{-1}$ at different AT concentrations is significantly different from the equilibrium sorption of AT for two soils containing 2%PE at 35°C ($p < 0.05$), as shown in *Figure 7*. At a concentration of 10 $mg \cdot L^{-1}$ of atrazine, the equilibrium adsorption of black soil + 2%PE at a $CaCl_2$ ion concentration of 0 $mol \cdot L^{-1}$ was 68.933 $mg \cdot kg^{-1}$, the equilibrium

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adsorption of black calcium soil + 2%PE was 71.7 mg·kg^{-1}, and the adsorption of black soil + 2%PE at an ion concentration of 0.1 mol·L^{-1} was 55.85 mg·kg-1 and the equilibrium adsorption of black calcium soil + 2%PE was 64.15 mg·kg^{-1}, which decreased by 23.43% and 10.53%, respectively, indicating that the adsorption of atrazine by the two soils containing PE was unfavorable as the Ca^{2+} ion concentration increased.

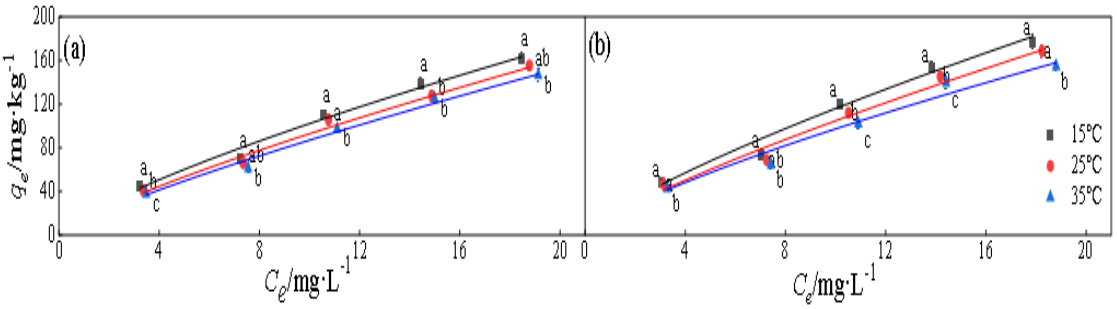

Figure 6. *Thermodynamic curve of adsorption of AT in soil containing microplastics. (a) Figure represents 2%PE black soil, (b) figure represents 2%PE black calcium soil. Different lowercase letters represent significant differences between different treatments ($p < 0.05$)*

Table 4. *Thermodynamic fitting eigenvalues of adsorption AT in soil containing microplastics*

Soil type	T (℃)	Langmuir Isothermal adsorption model			Freundlich Isothermal adsorption model		
		Q_m	K_L	R^2	$1/n$	K_f	R^2
Black soil + PE	35	638.197	0.0158	0.986	0.845	12.346	0.986
	25	551.421	0.0208	0.983	0.91	14.513	0.985
	15	550.585	0.023	0.981	0.797	16.173	0.982
Black calcium soil + PE	35	609.986	0.0187	0.961	0.822	14.365	0.961
	25	670.652	0.0187	0.966	0.819	15.926	0.969
	15	653.402	0.0214	0.972	0.812	17.493	0.973

Table 5. *Thermodynamic parameter values of adsorption AT in soil containing microplastics*

Soil type	T (℃)	ΔG^0 (kJ·mol^{-1})	ΔH^0 (kJ·mol^{-1})	ΔS^0 (kJ·mol^{-1})
Black soil + PE	35	-6.627	-9.931	-10.73
	25	-6.628		-11.08
	15	-6.665		-11.34
Black calcium soil + PE	35	-6.824	-9.178	-8.87
	25	-6.858		-8.56
	15	-6.825		-8.88

Effect of microplastic on the degradation of atrazine in soil

Figure 8 depicts the degradation kinetic curves of AT for two soils having 2%PE (black soil and black calcareous soil) using a degradation kinetic model (equation refers to *Eq. 8*). The degradation of atrazine by black soil (sterilized, non-sterilized), black

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calcium soil (sterilized, non-sterilized), and their control soils was better matched with first order reaction kinetics under PE coexistence circumstances, with $R^2 > 0.885$. The rates of decomposition were as follows: black soil > black calcium soil > black soil (sterilized) > black calcium soil (sterilized) The half-life of black soil was 38.5 days, whereas that of black calcium soil was 46.2 days, a 16.67% increase. This may be owing to the increased organic matter and clay content of black soil compared to black soil containing calcium, which may be more conducive to microbial growth and reproduction, hence increasing the soil's capacity for microbial degradation (Li et al., 2017). Black soil (sterilized) had a half-life of 53.3 days, and black calcium soil (sterilized) had a half-life of 57.8 days, which were 38.44% and 25.11% longer than for sterilization, respectively. *Table 6* demonstrates that the addition of 2% PE microplastics to both dark soils increased the half-life of atrazine degradation. The addition of 2%PE microplastic to unsterilized soil increased the half-lives of black soil and black calcium soil by 14.8 days and 16.8 days, respectively. The addition of 2%PE microplastic to sterilized soil increased the half-lives of black soil and black calcium soil by 23.7 days and 21.2 days, respectively, indicating that the microplastic primarily inhibited the chemical degradation of atrazine by soil.

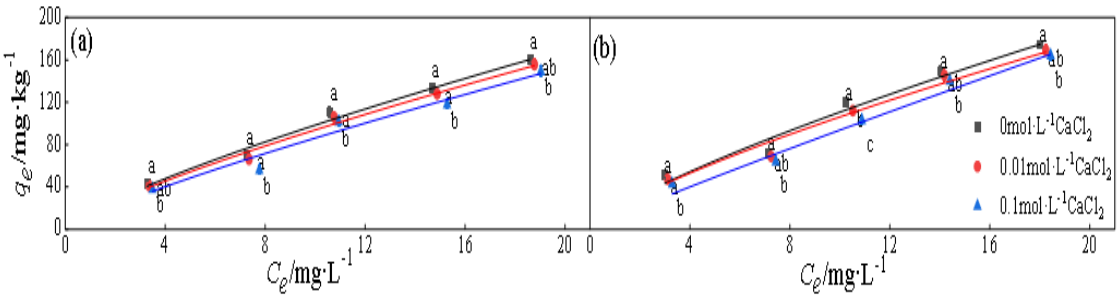

Figure 7. *Effect of ion concentration on the adsorption AT of two soils under microplastic coexistence conditions. (a) Figure represents 2%PE black soil, (b) figure represents 2%PE black calcium soil. Different lowercase letters represent significant differences between different treatments ($p < 0.05$)*

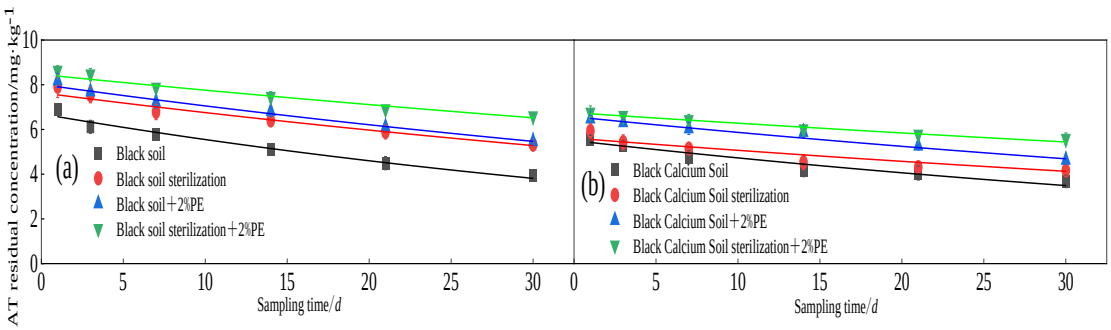

Figure 8. *Kinetic curves of AT degradation by two soils under microplastic coexistence conditions. Table 5 Kinetic parameters of soil degradation. (a) Graph represents the degradation kinetic curves of black soil (sterilized/unsterilized) and black soil containing 2%PE (sterilized/unsterilized) on AT, (b) graph represents the degradation kinetic curves of black calcium soil (sterilized/unsterilized) and black calcium soil containing 2%PE (sterilized/unsterilized) on AT*

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Table 6. *Soil degradation kinetic parameters*

Soil type		Degradation kinetics equation	rate constant/d^{-1}	R^2	$T_{1/2}$/d
Black soil	Non-sterilized	$y = 6.657e^{-0.018x}$	0.018	0.979	38.5
	Sterilized	$y = 7.66e^{-0.013x}$	0.013	0.971	53.3
Black soil + PE	Non-sterilized	$y = 8.107e^{-0.013x}$	0.013	0.988	53.3
	Sterilized	$y = 8.597e^{-0.009x}$	0.009	0.972	77.0
Black calcium soil	Non-sterilized	$y = 5.560e^{-0.015x}$	0.015	0.885	46.2
	Sterilized	$y = 5.669e^{-0.012x}$	0.012	0.900	57.8
Black calcium soil + PE	Non-sterilized	$y = 6.600e^{-0.011x}$	0.011	0.971	63.0
	Sterilized	$y = 6.633e^{-0.007x}$	0.007	0.970	99.0

Analysis

PE has a low crystallinity rubbery region that provides more adsorption area (Zhang et al., 2021). Zhao et al. (2021) studied that the addition of 2%PA and 2%PMMA to soil species increased the adsorption of isomycetes by 120% and 150% compared to no addition. Chen et al. (2020) studied that the equilibrium adsorption of triclosan by polyethylene microplastics was 1.3 times higher than that of control soil. Wang (2021) added 1% polyethylene agricultural film microplastics to agricultural soils than without microplastics farmland sorption of Zn^{2+} became smaller, which may have affected the quality of agricultural soils to some extent. Fitting parameters using quasi primary kinetics and quasi secondary kinetics are shown in *Table 2* and it can be seen that the secondary fit ($R^2 > 0.999$) better describes the adsorption process. It is consistent with the results of Wang (2021) who studied the adsorption of sulfamethoxazole by two microplastics, PE and PS, in soil and the fitting effect quasi-secondary adsorption kinetics was slightly better. Sun et al. (2021) studied the adsorption of atrazine in sterilized and unsterilized soil added with 5% cotton straw biochar in three stages, the first stage was a marginal diffusion effect to control the adsorption rate faster, the second stage to the internal diffusion of biochar adsorption rate becomes slower, and the third stage until the adsorption equilibrium experimental results are consistent. In the liquid film diffusion stage, the adsorption rate is maximum in this stage because of the concentration difference between the solid and liquid surfaces, and the partitioning effect and van der Waals forces that make atrazine occupy both soil and PE surfaces rapidly (Song, 2022). PE has short internal pore channels (Zhang et al., 2017), and the addition of a certain percentage of microplastic to the soil may make atrazine enter the internal adsorption active site faster, making the adsorption rate faster in the second stage. The fitted value C of the internal diffusion model represents the thickness of the particle boundary layer, and the fitted adsorption curve does not pass through the origin ($C \neq 0$), indicating that adsorption is a complex process containing a combination of surface adsorption and intra-particle diffusion control.

Sun et al. (2019) found that the Freundlich isothermal sorption model ($R^2 > 0.944$) could better fit the isothermal sorption-desorption model of atrazine for three soils. The addition of microplastics to black and black calcium soils increased the K_f by 2.11 and 1.01 times, respectively. The addition of 2%PE to both soils improved the ability of the soil to adsorb atrazine due to the properties of microplastics such as large specific surface area, complex structure, and more adsorption active sites (Hu et al., 2020) and

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the fact that PE have larger rubber-like structural domains than other microplastics, making them more capable of adsorbing hydrophobic organic matter (Sun et al., 2021), it is also possible that microplastics can improve the soil's own ability to adsorb atrazine van der Waals forces capacity of the soil itself to adsorb atrazine, making the soil with the addition of microplastics more capable of adsorbing atrazine. In a study by Zhao et al. (2021), the addition of 2%PA and 2%PMMA to soil increased the K_f by 20.19% and 186%, respectively, compared to the original soil, demonstrating that microplastics could improve the adsorption capacity of soil for isomycetes. times, 4.7 stimes and 4.4 times, respectively. Shi (2020) found that the adsorption capacity of two microplastics (PP, PE) in seawater for ciprofloxacin was less than that in pure water, and ciprofloxacin was prone to polymerization in seawater with higher ionic concentration, which made it difficult to enter the adsorption sites inside the microplastics, resulting in a weakened adsorption capacity for ciprofloxacin. Chen (2021) studied the effect of marine microplastics on the adsorption behavior of levofloxacin, and as the ionic strength increases, Na^+ may adsorb to the surface of for microplastics due to electrostatic adsorption, resulting in fewer adsorption active sites and thus a weaker adsorption capacity for levofloxacin. Wang (2021) studied that the equilibrium adsorption of sulfamethoxazole in solution was reduced due to the presence of Ca^{2+} in solution forming competitive adsorption with sulfamethoxazole on the surface of the solid phase medium.

Qu (2014) discovered that the rate of atrazine breakdown in the unsterilized group was faster than in the sterilized group, showing that microorganisms had a role in atrazine degradation. Zhao et al. (2021) discovered that adding PA and PMMA to soil may extend the half-life duration of isoxaflutole, and that the greater the adsorption capacity of microplastics on isoxaflutole, the greater the retarding impact on isoxaflutole degradation in soil. Li (2020) discovered that the half-life of pesticide degradation in soils with added microplastics was longer than in control soils, which could be attributed to microplastics' ability to adsorb and desorb pesticides, influence soil physicochemical properties, and affect the number of microorganisms in the soil to delay the degradation of isomycarb and putrescine.

Conclusion

(1) The adsorption of atrazine with PE microplastics and their control soils onto two typical black soils (black soil and black calcium soil) from northeast China followed quasi-secondary kinetics, and the fitted R^2 values were all greater than 0.999. The adsorption process was separated into quick and slow adsorption, with the adsorption essentially reaching equilibrium after 24 h. Surface adsorption and internal particle diffusion both affected the adsorption.

(2) The Freundlich isothermal adsorption model accurately describes the isothermal adsorption of atrazine in two soils and two soils having 2%PE, and its fitted value R^2 is in the range of 0.969-0.993, and its 1/n is consistent with 1, which belongs to the "*L*-shaped nonlinear adsorption curve," indicating that as the concentration of AT increases, AT's adsorption capability rapidly reduced as its concentration increased. The fitted adsorption constants K_f had the following magnitudes: black calcium soil + 2%PE > black soil + 2%PE > black calcium soil > black soil. The adsorption free energies ΔG^{θ} were all < 40 kJ·mol^{-1}, showing that the physical adsorption mechanism was primarily controlling the adsorption process. The thermodynamic fitting parameters

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ΔH^{θ} were all zero, indicating an exothermic reaction, and ΔS^{θ} were all zero, suggesting that the adsorption confusion steadily diminished. The capacity of both soils plus 2%PE to absorb atrazine rapidly decreased as Ca^{2+} content increased.

(3) By comparing the degradation rates of sterilized soil and unsterilized soil, we discovered that the soil destroyed atrazine not only microbially but also chemically and that the addition of 2%PE to black soil and black calcium soil may slow the rate of soil degradation of atrazine.

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