Effects of different factors on the adsorption–desorption behavior of Glyamifop and its migration characteristics in agricultural soils across China

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ABSTRACT

Rice weeds strongly inhibit the production of rice because they compete with rice. Glyamifop is a novel herbicide for controlling rice weeds and being tested in paddy fields. Based on our previous studies, Glyamifop offers excellent control for rice weeds and has no negative effects on rice plant growth as well as rice yields. However, the adsorption–desorption and migration behaviors of Glyamifop in paddy soils are still not well resolved. In this study, we investigated the adsorption–desorption and migration characteristics of Glyamifop in paddy soils collected from four provinces in China, using batch equilibrium, soil column leaching, and thin-layer chromatography tests combined with liquid chromatography–tandem mass spectrometry (LC-MS) analysis. The results showed that all the soils had a relatively high adsorption capacity for Glyamifop, and both Freundlich adsorption and desorption constants were positively correlated with soil cation exchange capacity, organic carbon content, and organic matter content ($P < 0.05$). Moreover, despite the initial solution pH, temperature, humic acids, and surfactants also had strong effects on the adsorption of Glyamifop in soil, while the leachability and mobility of Glyamifop were very low in most soils. Therefore, due to the relatively low leachability and mobility of Glyamifop as well as its high adsorption capacity in soil, Glyamifop can serve as an excellent herbicide for rice weeds and cause little pollution to the environment.

1. Introduction

Rice weeds strongly inhibit the production of rice, a staple food for more than half of the world population. The use of herbicides has become indispensable in controlling weeds to ensure rice yields [1,2]. However, despite part of herbicides was up-taken by the target weeds, considerable portions of herbicides entered the soil, becoming an organic pollutant [3]. Moreover, anthropogenic organic pollutants such as herbicides may further migrate from contaminated soil into surface water and groundwater [4,5]. Adsorption is a key process controlling herbicide migration in soils [6]. It is well accepted that the environmental fate of an herbicide is determined by its adsorption–desorption and migration behaviors in soil. Therefore, it is highly essential to gain a full understanding of the adsorption–desorption and migration

behaviors of an herbicide in soil before commercializing it.

Glyamifop is a novel herbicide that was recently developed by Zhongqi Technology Co., Ltd. in Jiangsu Province, China. Its chemical name is (R)-(2-(4-(6-chlorobenzoxazol-2-yloxy))phenoxy)propionyl) glycine ethyl ester, and its molecular formula is $C_{23}H_{18}ClFN_2O_4$. Its water solubility is 0.652 mg/L, octanol–water partition coefficient is 5.67 and Henry's constant is 0.0621 pa $\times$ m^3/mol, as determined by our preliminary measurement according to OECD guidelines for the testing of chemicals [7]. The structure of Glyamifop is shown in Fig. 1. Since 2020, Zhongqi Company has planned to produce 1,500 tons of the herbicide annually and commercialize it across China. At present, Glyamifop is still in the field-testing stage. Based on a one-year field trial, we found that Glyamifop offered excellent control for rice weeds such as *barnyardgrass* and *Stephanotis* in direct-seeded rice production.
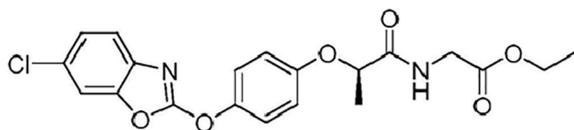
Fig. 1. Chemical structure formula of Glyamifop.

Glyamifop has no negative effects on the growth of rice plants as well as subsequent crops. Moreover, a residual analysis method for Glyamifop in rice and the environment has been developed by our group [8]. The final residues of Glyamifop in rice are below the instrument detection line, indicate there is almost no Glyamifop residue in rice. However, the adsorption–desorption and migration behaviors of Glyamifop in paddy soils remain unclear.

The process of Glyamifop adsorption in soil may depend not only on Glyamifop properties (such as water solubility and octanol–water partition) but also on soil physicochemical properties (such as cation exchange capacity (CEC), organic matter content (OM)) and environmental conditions (such as temperature, pH) [9,10]. The adsorption–desorption behavior of herbicides varies among different paddy soils, due to the complexity of soil properties and various climatic conditions across different regions [11,12]. Many studies have shown that soil OM can markedly affect the adsorption of herbicides. In some rural areas, animal compost, straw and coal ash are frequently used to fertilize the soil, and such measures would like to enhance the adsorption of organic pollutants in the soil [13–15]. At the same time, domestic sewage contains surfactants, and their influent into the farmland would also affect the adsorption of organic pollutants in the soil [16]. Besides, herbicides also contain large amounts of surfactants. Temperature and pH are key factors for determining the water solubility of organic pollutants [17], however their influence on Glyamifop in soil has not been investigated. We therefore hypothesized that soil physicochemical properties and environmental factors actively participate in modifying the adsorption–desorption behavior of Glyamifop in paddy soils.

Water flow is the major driver of herbicide migration from soil to surface water and groundwater [11]. With increasing herbicide application, considerable herbicide residues can migrate from top soil to deep soil or even groundwater driven by irrigation or rainfall leaching [18]. Particularly in the case of heavy rainfall, the leaching of herbicides becomes highly active, leading to groundwater pollution by the herbicides [19,20]. Furthermore, herbicide residues may also enter other water bodies through groundwater runoff or other soils through surface runoff, threatening human safety and environmental health. It is reasonable to speculate that water flow would enhance migration of Glyamifop in paddy soils.

The objectives of this study were to: (1) verify the Glyamifop residue analysis methods in different types of soil; (2) analyze the adsorption kinetics and isothermal adsorption–desorption characteristics of Glyamifop under different paddy soil conditions (soil type, OM, and pH value); (3) evaluate the adsorption capacity of Glyamifop in different paddy soil types under different environmental conditions (temperature, initial solution pH, and exogenous addition of humic acids and surfactants); and (4) explore the migration characteristics of Glyamifop by leaching in different paddy soil types. In this study, we investigated the adsorption, desorption, and migration characteristics of Glyamifop in soils collected from four paddy regions in China. The effects of different factors (soil properties, environmental conditions, and exogenous additives) on the environmental behavior of Glyamifop were systematically evaluated using batch equilibrium, soil column leaching, and thin-layer chromatography tests combined with liquid chromatography–tandem mass spectrometry (LC-MS) analysis. The results would provide the method to detect the Glyamifop residue in different types of soil which will help us to detect the adsorption herbicides capacity of different soils. And contribute to our understanding of the environmental behavior of Glyamifop and its potential environmental risk

before applying it in paddy fields [21].

2. Materials and methods

2.1. Experimental soils

In 2020, paddy soils without Glyamifop application were collected from four provinces in China: Jiangxi (S1), Hubei (S2), Zhejiang (S3), and Heilongjiang (S4). The soils were classified as Ferrasols (S1), Lixisols (S2), Anthrosols (S3), and Phaeozems (S4) according to the World Soil Resources Standard Library [22]. At each sampling site, 0–20 cm surface soil samples were collected using a soil auger, and directly transported to the laboratory. The soil samples were air-dried, and plant roots and other impurities were manually removed. Then, the soils were ground and passed through a 2-mm sieve. The basic physicochemical properties of the soils (Table 1) were tested as follows. The gravity method was employed to determine the soil texture [23]. The soil pH was measured in soil suspensions (soil:water = 1:2.5, w/v) using a pH meter [24]. The dichromate digestion method was utilized to measure the soil organic carbon (OC) and OM [25,26]. The soil CEC was determined using the ammonium ion exchange method [27].

2.2. Preparation of standard solutions

A Glyamifop standard (0.1 g, > 99%; Zhongqi Technology Co., Ltd., China.) was accurately weighed (accurate to 0.0001 g) into a 100-mL volumetric flask using an analytical balance (ATX2240; Shimazu Enterprise Management Co., Ltd., China). Then, approximately 80 mL of chromatographically pure acetonitrile (McLin Co., Ltd., Nanchang, China) was added to the flask. The standard solution was placed in an ultrasonic water bath (KQ2200E ultrasonic cleaner, Kunshan Ultrasonic Instrument Co., Ltd., China), which was operated until the solution was clear and transparent without any precipitation. After cooling to room temperature (25 °C), the stock standard solution was adjusted to a volume of 100 mL with pure acetonitrile to give a final Glyamifop concentration of 1000 mg/L. The solution was stored at 4 °C fridges before further use. A series of working standards of Glyamifop (0.05, 0.1, 0.5, 1, and 2 mg/L) were then prepared by diluting the stock standard solution with pure acetonitrile. The blank matrix is prepared according to the 2.4 Sample Pretreatment procedure, but no herbicide is added in the process, then the blank matrix solution was obtained by centrifugation of soil samples and the subsequent filtration of the supernatant by 0.22 um organic membrane filter. Similarly, a series of matrix standards of Glyamifop (0.05, 0.1, 0.5, 1, and 2 mg/L) were obtained by diluting the stock standard solution with the blank matrix solution.

2.3. Glyamifop measurement by LC-MS

The Glyamifop extracted from soil samples was qualitatively analyzed by LC (1260 series; Agilent Technologies, Santa Clara, USA) equipped with an Agilent Eclipse XDB-C18 column (2.1 mm × 100 mm, 1.8 μm; Agilent Technologies). The mobile phase consisted of 0.1% formic acid in water and pure acetonitrile (35:65, v/v). The column was operated at 30 °C with a flow rate of 1 mL/min, with a standard 10 μL sample loop. The Glyamifop was further quantified by a single-stage quadrupole mass spectrometer (6120 series, Agilent Technologies) equipped with an electrospray ionization source. The ionization source was operated in positive ion mode with selected ion monitoring, and the source parameters were as follows: $m/z = 441.2$, source temperature = 350 °C; ion spray voltage = 3000 V; nebulizer gas pressure = 35.0 kPa; and collision-induced dissociation voltage = 130 V. The retention time of Glyamifop was approximately 5.1 min [8].

Table 1
Basic physicochemical properties of the experimental soils used in this study.

Soil	Soil type	Sampling site	Texture				pH	CEC (cmol/kg)	OC (%)	OM (%)
			Sand	Silt	Clay	Texture				
			(%)	(%)	(%)					
S1	Ferrosols	Jiangxi (N28°46′, E115°36′)	40.37	43.96	15.67	Sandy loam	5.27	11.99	0.55	0.95
S2	Lixisols	Hubei (N35°06′, E118°21′)	58.10	32.50	9.40	Sandy	6.38	10.19	0.45	0.78
S3	Anthrosols	Zhejiang (N29°14′, E121°48′)	32.99	23.18	43.83	Loam	7.34	12.90	1.32	2.28
S4	Phaeozems	Heilongjiang(N41°36′, E127°53′)	38.10	36.43	25.47	Sandy loam	6.11	30.36	7.13	12.29

CEC is the cation exchange capacity; OC is the organic carbon content; and OM is the organic matter content.

2.4. Sample Pretreatment

Seven steps were adopted to extract Glyamifop from the soils: 1) a 2-g spiked sample was transferred into a 50-mL polypropylene centrifuge tube followed by the addition of 5 mL ultrapure water and 10 mL pure acetonitrile; 2) the tube was vortexed for 2 min using an XH-C vortex mixer (Yuexin Instrument Manufacturing Co., Ltd., Changzhou, China); 3) 1 g of NaCl (McLin Co., Ltd.) and 2 g of MgSO$_4$ (McLin Co., Ltd.) were added to the tube followed by vortexing for another 2 min; 4) the tube was centrifuged at 8801 × g for 5 min using a TG16WS high-speed freezing centrifuge (Changsha Xiangzhi Centrifuge Instrument Co., Ltd., Changsha, China); 5) 1.5 mL of the supernatant was transferred into a 2.5-mL tube containing 150 mg of MgSO$_4$ and 100 mg of N-propylethylenediamine (McLin Co., Ltd.) for purification; 6) the tube was vortexed for 1 min and then centrifuged for 5 min at 3435 × g; 7) the supernatant was removed using a 1.0-mL sterile syringe and filtered through a 0.22-μm organic membrane filter. The filtrate was collected for the downstream analysis by LC-MS. For other aqueous samples, a 5-mL sample was extracted with 5 mL pure acetonitrile followed by the addition of 1 g of NaCl and 2 g of MgSO$_4$. After vortexing and centrifugation, 1.5 mL of the supernatant was purified with 150 mg of MgSO$_4$ and 50 mg of octadecylsilane (McLin Co., Ltd.) following a similar procedure as above noted step 5.

2.5. Adsorption-desorption experiment design

Adsorption-Desorption Kinetics Test. The equilibrium oscillation method recommended by the U.S. Environmental Protection Agency [28] was employed to investigate the adsorption–desorption of Glyamifop in soil. The stock solution was diluted with 0.01 mol L^{-1} CaCl$_2$ (to maintain the ionic strength) and 200 mg/L NaN$_3$ (as a bioinhibitor) to make a standard working solution of Glyamifop (2 mg/L) [29]. A 2.0-g soil sample was added to a 50-mL centrifuge tube containing 10 mL standard working solution of Glyamifop (2 mg/L). Repeat 9 such tubes the 9 tubes were shaken at 298 K and 180 rpm for 0.5, 1, 2, 4, 6, 8, 12,

16, and 24 h in order. Five milliliters of the supernatant were removed from each centrifuge tube after the adsorption reached an equilibrium. CaCl$_2$ (0.01 mol L^{-1}) containing Glyamifop without soil and 0.01 mol L^{-1} CaCl$_2$ containing soil without Glyamifop served as controls to evaluate the loss caused by the adsorption of Glyamifop on the centrifuge tube as well as the natural degradation of Glyamifop. Each treatment has three replicates. The collected samples were analyzed by LC-MS analysis.

Isothermal Adsorption-Desorption Test. The adsorption–desorption equilibrium time of Glyamifop in the four soils was 24 h (Fig. 2). For the isothermal adsorption test, the initial Glyamifop concentration was set at 0.05, 0.1, 0.5, 1, and 2 mg/L. After shaking for 24 h, the sample solution was centrifuged, and Glyamifop amount in the supernatant was determined by LC-MS. The Glyamifop loss in the aqueous represented the adsorption capacity of Glyamifop in soil. The isothermal desorption test was performed immediately after the isothermal adsorption test. A 5-mL portion of the supernatant was removed from the centrifuge tube, and an equal volume of 0.01 mol L^{-1} CaCl$_2$ without Glyamifop was added to the tube. The mixture was shaken for 24 h. After centrifugation, Glyamifop amount in the supernatant was determined. The Glyamifop mass increase in the aqueous indicated the desorption capacity of Glyamifop in soil.

Mass Conservation Test. At the end of the desorption test, the concentration of Glyamifop desorbed in the soil was determined by LC-MS. The concentrations of Glyamifop in the solution phase and soil phase were pooled, and the overall recovery rate (RR) was obtained to verify whether the mass of Glyamifop was conserved or not during the adsorption–desorption test.

2.6. Evaluation of factors affecting Glyamifop adsorption

The effects of temperature on the adsorption behavior of Glyamifop in soil were determined by isothermal adsorption tests with five temperature levels (278, 288, 298, 308, and 318 K). Three pH levels (4.0, 7.0, and 9.0) were used to evaluate the effects of initial solution pH on Glyamifop adsorption in soil. The pH was adjusted by 0.01 mol L^{-1} HCl
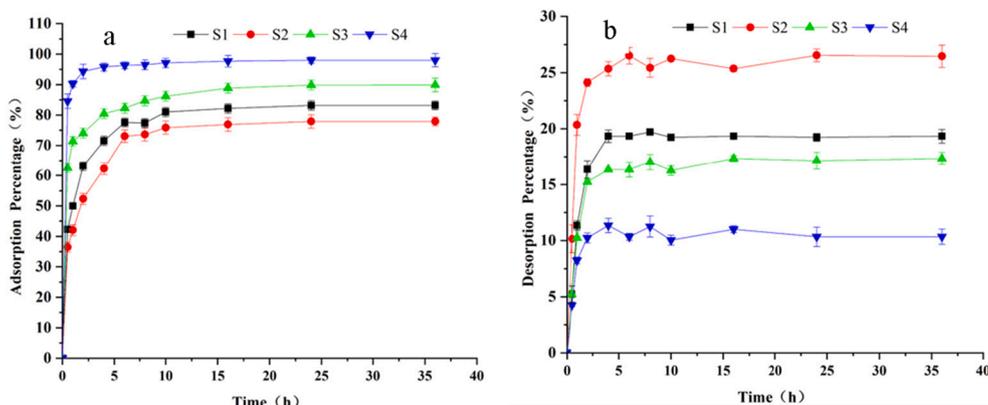

Fig. 2. Adsorption (a) and desorption (b) kinetic curves of Glyamifop in four different types of paddy soils (S$_1$ to S$_4$ are defined in Table 1). Values are the means ± standard error (n = 3).

or NaOH. To determine the effects of humic acids on the adsorption behavior of Glyamifop in soil, the soil samples were pretreated with H_2O_2 to remove OM [30]. Briefly, a 50-g soil sample was weighed into a 2-L glass and the soil surface was wetted with distilled water. Subsequently, 30% H_2O_2 (Shanghai Macleans Biochemical Co., Ltd., China) was continuously added to the beaker, and the soil sample was stirred in a fume hood until no more bubbles were produced. After repeatedly washing with distilled water, the excess H_2O_2 was removed, and the resultant soil sample was naturally air-dried, ground, and sieved. Two humic acids, coal humic acid (CHA) and biochemical fulvic acid (BFA; 90%, Pingxiang Red Land Humic Acid Co. Ltd., China), were independently added to the H_2O_2-pretreated soil samples at five weight concentrations (0%, 0.5%, 1%, 2%, 5%, and 10%) for isothermal adsorption tests. The effects of surfactants on Glyamifop adsorption in soil were also analyzed by adding three kinds of surfactants in five concentrations (0, 0.5, 1.5, 2, and 5 times the critical micelle concentration (CMC)). The surfactants included: Tween80 (CMC = 40 mg/L); hexadecyl trimethyl ammonium bromide (CTAB; CMC = 348 mg/L); and sodium dodecyl benzene sulfonate (SDBS; CMC = 550 mg/L; Beijing Chemical Plant, China). All tests were conducted in triplicate.

2.7. Determination of Glyamifop migration in soil

Soil Column Leaching. Soil columns were constructed using polyvinyl chloride (PVC) pipe with a length of 40 cm and an inner diameter of 4.0 cm. A 180-µm nylon screen was placed at the bottom of the PVC pipe followed by the addition of a 1-cm-thick layer of quartz sands. Then, a soil sample (0.6–0.7 kg, ≤ 0.25 mm) was weighed into the PVC pipe to obtain a soil column with a soil depth of 30 cm. A funnel with a diameter of 6 cm was connected to the bottom of each soil column, and a 250-mL conical flask was placed under each funnel. The soil column was oriented vertically and saturated with 0.01 mol L^{-1} $CaCl_2$ solution from the bottom to obtain an equilibrium state and remove air from the soil. After the saturation, the water in the column was leached driven by the gravity. The leaching test was carried out under 25 °C and dark conditions. Glyamifop was added quantitatively from the top of the soil column according to Eq. (12). From the beginning of the test, artificial rainfall (pH = 6.47) was simulated at an intensity of 200 mm/48 h (equivalent to 251 mL per column). The leachate was collected every 12 h for the analysis of leached Glyamifop. After leaching, the soil column was divided into three sections in 10-cm intervals. The contents of Glyamifop (mass fraction of total Glyamifop added) in each soil section and the leachate were determined.

Soil Thin-layer Chromatography. A 10-g soil sample (accurate to 0.01 g, ≤ 0.25 mm) was weighed into a beaker followed by the addition of 7.5 mL distilled water. The mixture was stirred to a uniform slurry, which was then evenly spread on an 8 × 20-mm glass plate using a glass rod. The soil thickness was maintained between 0.5 and 1.0 mm to minimize the negative influence of soil thickness variation on thin-layer chromatography analysis. The thin-layer plate coated with the soil was air-dried at a temperature of 298 K under dark conditions. Subsequently, 20 µL of the stock solution of Glyamifop (1000 mg/L in 0.01 mol L^{-1} $CaCl_2$ solution) was added at a distance of 2 cm from the baseline of the thin-layer plate. Two parallel tests were carried out for each treatment. After the solvent evaporated, the plate was placed in a chromatography tank at an inclined angle of 30°. The tank was filled with ultrapure water (water depth = 0.5 cm) as a spreading solvent. The experiment was completed when the solvent spread from the baseline of the thin-layer plate to 18 cm from the baseline. After drying, the soil on the thin-layer plate was divided into six segments at an equal distance. The contents (mass) of Glyamifop in each soil segment and its distribution on the thin-layer plate were determined.

2.8. Data analysis

The linear and Freundlich models were applied to describe the

relationship between the soil-adsorbed concentration and solution equilibrium concentration of Glyamifop [31,32]:

$$Linear\ model : C_s = KC_e + C_0, \tag{1}$$

and

$$Freundlich\ model : C_s = K_{F-ads}C_e^{1/nF-ads} \tag{2}$$

where C_s (mg/kg) is the concentration of Glyamifop adsorbed by the soil under the adsorption equilibrium; C_e (mg/L) is the concentration of Glyamifop in the aqueous; C_0 (mg/kg) is the concentration of Glyamifop adsorbed by the soil when the Glyamifop concentration in aqueous solution is 0 under the adsorption equilibrium; K_{F-ads} [(mg/kg)/(mg/L) $^{1/n}$)] is the Freundlich adsorption coefficient; and $1/n_{F-ads}$ is the Freundlich exponent, an empirical constant for adsorption. C_s was obtained using Eq. (3):

$$C_s = [(C_0 - -C_e) \times V] / M, \tag{3}$$

where V is the volume of the solution (10 mL), and M is the mass of the soil (2.0 g). The concentration of Glyamifop adsorbed by the soil under the ith desorption equilibrium (C_{si}, in mg/kg) was obtained using Eq. (4):

$$C_{si} = \frac{C_0 \times V}{M} - \frac{C_{ei} \times V}{2M} - \frac{V}{M} \sum_{n=1}^{i} C_e i - 1, \tag{4}$$

where C_{ei} (mg/L) is the concentration of Glyamifop in the aqueous under the ith desorption equilibrium.

The hysteresis coefficient (H) for the adsorption and desorption of Glyamifop was obtained using Eq. (5):

$$H = (1/n_{F-des}) / (1/n_{F-ads}) \tag{5}$$

where $1/n_{F-des}$ is the empirical constant for the desorption. When $0.7 < H \leq 1.0$, the desorption rate is similar to the adsorption rate, and the adsorption and desorption isotherms coincide without hysteresis; $H < 0.7$ means the desorption rate is significantly lower than the adsorption rate, indicating a positive hysteresis; and $H > 1.0$ indicates a negative hysteresis [33].

The distribution coefficient (K_d) of Glyamifop was calculated based on the distribution ratio of Glyamifop in the water-soil system using Eq. (6):

$$K_d = C_s/C_e \tag{6}$$

The adsorption constants of OM (K_{OM}) and OC (K_{OC}) for Glyamifop were calculated using Eqs. (7) and (8) respectively:

$$K_{OM} = K_{F-ads}/OM \times 100\%, \tag{7}$$

and

$$K_{OC} = K_d/OC \times 100\% \tag{8}$$

The Gibbs free energy (ΔG, kJ/mol) and partial molar free energy ($-F$, J/mol) for Glyamifop adsorption were estimated using Eqs. (9) and (10) respectively:

$$\Delta G = -RTlnK_{OM}, \tag{9}$$

and

$$- -F = RTln(C_e/ C_0), \tag{10}$$

where R is the gas constant (8.314 J/K•mol), and T is the absolute temperature in degrees Kelvin.

The mass of Glyamifop added to each soil column (M, µg) was calculated according to Eq. (11) [34]:

$$M[\mu g] = \frac{A[kg/ha]·10^9[\mu g/kg]·d^2[cm^2]·\pi}{10^8[cm^2/ha]·4} \tag{11}$$

where A is the rate of Glyamifop application (kg/ha), and d is the diameter of the soil column (cm).

According to the content of Glyamifop in each section of soil and the leachate, the leaching rate of Glyamifop in each soil column was obtained according to Eq. (12):

$$Ri(\%) = \frac{mi}{mo} \times 100, \qquad (12)$$

where R_i (%) is the leaching rate of Glyamifop in each soil section (0–10, 10–20, and 20–30 cm) and the leachate ($i = 1, 2, 3,$ and 4); m_i (mg) is the mass of Glyamifop in each soil section and the leachate; m_o (mg) is the total mass of the added Glyamifop. The mobility of Glyamifop in soil was classified into four classes: easily leachable, $R_4 > 50\%$; leachable, $R_3 + R_4 > 50\%$; slightly leachable, $R_2 + R_3 + R_4 > 50\%$; and very-slowly leachable, $R_1 > 50\%$ [35].

The retention factor (R_f) of Glyamifop in each thin soil layer was calculated according to Eq. (13) [36]:

$$R_f = \frac{\sum Zi * Mi}{Zw \sum Mi} \qquad (13)$$

where Z_i is the average distance of Glyamifop in the ith soil segment from the baseline, M_i is the mass of Glyamifop in the ith soil segment (μg), and Z_w is the distance between the solvent front and the baseline. The mobility of Glyamifop was classified as follows: very-slowly mobile, $R_f = 0$–0.09; slightly mobile, $R_f = 0.10$–0.34; moderately mobile, $R_f = 0.35$–0.64; mobile, $R_f = 0.65$–0.89; and highly mobile, $R_f = 0.9$–1.00 [32].

Data processing and statistical analysis were performed in SPSS Statistics 22.0 (IBM SPSS, Armonk, NY, USA). The adsorption curves of Glyamifop were plotted using OriginPro 8.0 (OriginLab Corp., Northampton, MA, USA).

3. Results and discussion

3.1. Adsorption-desorption characteristics of Glyamifop in soil

3.1.1. Adsorption-desorption kinetics

The adsorption–desorption kinetic curves of Glyamifop in the four different soils are shown in Fig. 2. All soils showed high adsorption capacities for Glyamifop. Adsorption of Glyamifop by soil increased sharply within the first 2 h, indicating a stage of rapid adsorption. While the adsorption of Glyamifop slowed down from 2 to 8 h. After 8 h, Glyamifop concentration in the solution remained unchanged, indicating an adsorption equilibrium. The percentage of adsorption of Glyamifop in different soils decreased in the following order: S4 (97.99) > S3 (89.89) > S1 (83.17) > S2 (77.91) (Fig. 2a).

The desorption process of Glyamifop in soil was also divided into two

stages. Firstly, desorption of Glyamifop increased rapidly from 0 to 2 h and then increased slowly from 2 to 6 h. Secondly, desorption of Glyamifop fluctuated slightly from 6 to 18 h, and equilibrium was reached within 24 h. The percentage of desorption of Glyamifop in different soils was S2 (26.46) > S1 (19.24) > S3 (17.15) > S4 (10.34) (Fig. 2b). Based on these results, the adsorption–desorption time for Glyamifop to reach an equilibrium in soil was determined as 24 h. Comparison of the adsorption–desorption kinetic curves revealed that the soils with a higher Glyamifop adsorption capacity have a lower desorption capacity. The is consistent with the adsorption and desorption experiments results of other herbicides [37].

3.1.2. Adsorption-desorption isotherms

The adsorption–desorption isotherms of Glyamifop in the four different soils are shown in Fig. 3. The isothermal adsorption curves are S-shaped, indicating that adsorption of Glyamifop by soil increased along with the increase of solution Glyamifop. Among different soils, the largest slope of the adsorption and desorption curve was obtained in S4, indicating that Glyamifop can be easily adsorbed by S4 but difficult to desorb from the soil. Such a phenomenon may be explained by the extremely high OM in S4 (Table 1). Similarly, OM and the high octanol–water partition coefficient has been reported to play a crucial role in pesticide (or herbicide) adsorption by soils [38,39].

3.1.3. Mass conservation

The overall RRs of Glyamifop from the solution phase and soil phase after the adsorption–desorption test are shown in Table S3. Up to 85% of RRs was achieved under all conditions, which meets the requirements of mass conservation of Glyamifop for the adsorption–desorption test [40]. This result indicates that Glyamifop is not strongly affected by hydrolysis, photolysis, and microbial decomposition during its adsorption and desorption in soil. Therefore, the decrease of Glyamifop in the solution can be primarily attributed to its adsorption by soil [40].

3.2. Isothermal Adsorption-desorption characteristics

3.2.1. Isothermal adsorption characteristics

The linear and Freundlich model parameters for the adsorption of Glyamifop in the four soils are listed in Table 2. The R^2 values for the linear model were generally close to the corresponding Freundlich model; however, the C_0 values of the linear model were < 0, which is not reasonable. In contrast, the Freundlich model is more reasonable for describing the adsorption of Glyamifop in soil. The Freundlich constant $K_{F\text{-}ads}$ is related to the adsorption capacity and strength of the soil, while the empirical Freundlich constant $1/n_{F\text{-}ads}$ describes the shape of the adsorption curve [41]. The $K_{F\text{-}ads}$ values of Glyamifop in the four soils ranged from 12.4560 to 187.8700 (mg/kg)/(mg/L)$^{1/n}$, indicating the used soils have a relatively high adsorption capacity. The $1/n_{F\text{-}ads}$ values
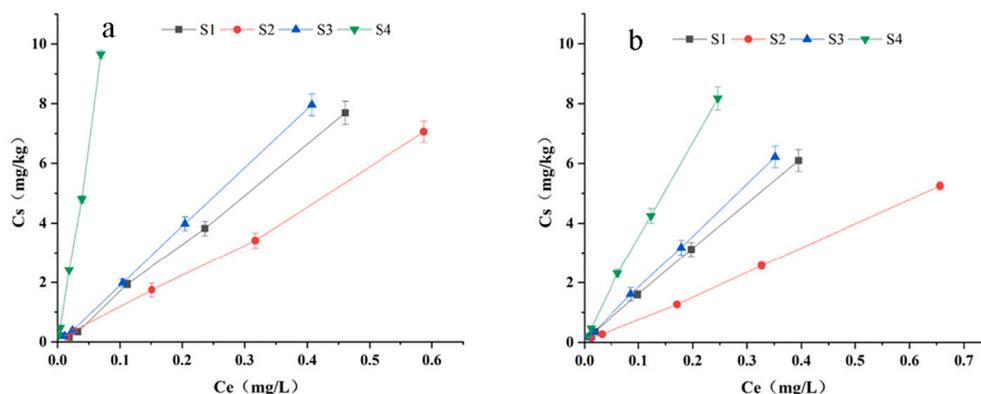

Fig. 3. Isothermal adsorption (a) and desorption (b) curves of Glyamifop in different paddy soils (S$_1$ to S$_4$ are defined in Table 1). Values are the means ± standard error ($n = 3$).

Table 2

Comparison of the linear and Freundlich models for Glyamifop adsorption in different soils.

	Linear model			Freundlich model		
	$K \pm SE$ (mL/g)	C_0 (mg/kg)	R^2	$K_{F-ads} \pm SE$ (mg^{1-n}·L^n/kg)	$1/n_{F-ads}$	R^2
S1	16.996 ± 0.336	−0.043 ± 0.131	0.998	17.170 ± 0.788	1.035 ± 0.044	0.998
S2	11.841 ± 0.427	−0.043 ± 0.131	0.996	12.456 ± 0.538	1.081 ± 0.055	0.998
S3	19.707 ± 0.065	−0.061 ± 0.014	0.999	19.964 ± 0.238	1.179 ± 0.051	0.999
S4	138.898 ± 5.267	−0.163 ± 0.192	0.994	187.870 ± 28.870	1.113 ± 0.053	0.998

S_1 to S_4 are defined in Table 1.Values are the means ± standard error (n = 3); C0 (mg/kg) is the amount of soil adsorption when the Glyamifop concentration is 0 at the adsorption equilibrium.

were > 1 for all soils (1.0350–1.1790), indicative of S-type adsorption isotherms [42]. In the aqueous with a low concentration of Glyamifop, the affinity of Glyamifop to soil was low; as the Glyamifop concentration increased, the affinity of Glyamifop to soil also increased.

3.2.2. Isothermal desorption characteristics

For the Freundlich desorption parameters, the $1/n_{F-des}$ values (0.929–1.033; Table S4) were smaller than that of $1/n_{F-ads}$, indicating that the adsorption of Glyamifop in these soils was irreversible [43]. The hysteresis coefficient H is an indicator for quantitatively describing the degree of the irreversible adsorption. The H values of Glyamifop in the four soils ranged from 0.8238 to 0.9552 (Table S4), indicating that the desorption and adsorption rates of Glyamifop were similar, with no obvious hysteresis. Among the soils, S3 and S4 have a lower Glyamifop desorption rate due to their higher contents of clay and OM compared to S1 and S2 (Table 1).

3.3. Relationships between Freundlich Adsorption–desorption characteristics and soil physicochemical properties

The adsorption–desorption capacity of a soil for an herbicide is related to the properties of both the herbicide and the soil [29,44,45]. A correlation analysis was conducted between the adsorption–desorption constants (K_{F-ads} and K_{F-des}) of Glyamifop and the physicochemical properties of soil to reveal the key factors controlling Glyamifop adsorption in soil. Both K_{F-ads} and K_{F-des} had a positive relationship with soil clay content, CEC, OC, and OM (slope > 0) and a negative relationship with soil pH (slope < 0; Table 3). Significant correlations were observed between K_{F-ads} with CEC, OC, and OM (r^2 = 0.9930, 0.9870, and 0.9870, respectively; $P < 0.01$) and between K_{F-des} with CEC, OC, and OM (r^2 = 0.9060, 0.9090, and 0.9090; $P < 0.05$). S4 had the highest contents of OM and CEC, hence its adsorption capacity for Glyamifop was also the strongest. Since glyamifop presents high octanol–water partition coefficient, hence, it is a compound of low polarity, and thus is expected its interaction based on a hydrophobic process. Meanwhile, the soil with a higher CEC content can also provide more adsorption sites

[46], contributing to the adsorption capacity promotion. In contrast, soil clay content and pH had a weak influence on the adsorption–desorption kinetics of Glyamifop in soil.

3.4. Gibbs free energy of Glyamifop adsorption in soil

The adsorption constant of OC (K_{OC}) indicates the mobility of an herbicide in soil [47]. In the present study, the K_{OC} values of Glyamifop in all the soils exceeded 1500 (1608.3330–2512.0480; Table 4), suggesting low mobility of Glyamifop in the soils. The change in Gibbs free energy (ΔG) can be used to quantitatively evaluate the adsorption reaction and the driving force of the adsorption [48]. For Glyamifop, the absolute values of ΔG in the four soils were < 40 kJ/mol (−18.5855 to −16.7901 kJ/mol at 298 K; Table 4), indicating that Glyamifop adsorption mainly occurred via physical adsorption in the soils. The ΔG values were all < 0, suggesting that Glyamifop adsorption in the four soils was spontaneous. The partial molar free energy (–F) can be used to evaluate the adsorption capacity of soil; a higher –F value means a stronger soil adsorption capacity [49]. Among the soils tested, the highest –F value of Glyamifop was obtained in S2 (–3035.6825 J/mol) while the lowest in S4 (–8338.9733 J/mol; Table 4). A negative relationship was observed between the –F and K_{F-ads} values of Glyamifop in the four soils (r = 0.9858). Thus, the smaller the –F value of Glyamifop, the easier that Glyamifop is adsorbed by the soil.

3.5. Effects of different factors on Glyamifop adsorption in soil

3.5.1. Effects of temperature

Table 5 lists the thermodynamic parameters of Glyamifop adsorption in the four soils at different temperatures. ΔG values in S1-4 ranged from −15.3465 to –4.0345 at 278 K, −18.6416 to −16.2935 at 288 K, −18.5808 to −16.7854 at 298 K, −18.2523 to −14.8003 at 308 K, and −16.0543 to −16.6868 at 318 K. Along with increasing temperature from 278 to 318 K, the ΔG values of S1-S4 increased firstly and then decreased. Similarly, the K_{F-ads} values of S1&S2 and S3&S4 increased firstly from 278 to 298 K and from 278 to 288 K, then decreased from 298 to 318 K and from 288 to 318 K, respectively. The adsorption of herbicides in soil is an exothermic process; thus, the increasing temperature tends to decrease herbicide adsorption in soil [50]. The above results indicate that both the low and high temperatures reduced the soil adsorption capacity for Glyamifop. On the one hand, the low temperature can reduce the activity of adsorption sites on soil particles, thereby reducing their adsorption capacity for Glyamifop; on the other hand, high temperatures increase the water solubility of Glyamifop and may also affect the structure of soil OM. These effects could increase the solubility of hydrophilic functional groups in soil OM and reduce the soil OM abundance, therefore reducing the adsorption capacity for Glyamifop [51].

3.5.2. Effects of initial solution pH on Glyamifop adsorption in soil

Under the experimental conditions, the Glyamifop adsorption capacities of the different soils decreased when the initial pH of the aqueous solution was upregulated, although the effects were not significant (Fig. 4a). Increasing soil pH results in the ionization of carboxyl groups in soil OM, which is conducive to the combination of water

Table 3

Linear correlations between the Freundlich adsorption–desorption constants for Glyamifop and soil physicochemical properties.

Parameter	Adsorption					Desorption				
	Clay (%)	pH	CEC (cmol/kg)	OC (%)	OM (%)	Clay (%)	pH	CEC (cmol/kg)	OC (%)	OM (%)
Slope	0.656	−11.768	9.087	31.464	18.251	0.251	−0.377	0.928	3.148	1.826
Intercept	43.901	133.210	−89.290	−7.106	−7.106	11.626	19.910	2.365	11.062	11.062
Significance level	0.885	0.883	**0.004**	**0.009**	**0.009**	0.589	0.965	**0.048**	**0.0490**	**0.049**
Correlation coefficient (*r*)	0.013	0.014	**0.993**	**0.987**	**0.987**	0.169	0.001	**0.906**	**0.909**	**0.909**

S_1 to S_4 are defined in Table 1. The significance level < 0.05 or correlation coefficient (r) > 0.9(bolding data) indicates a significant correlation between physicochemical properties and adsorption–desorption capcity.

Table 4
Adsorption constant of organic carbon (K_{OC}), Gibbs free energy (ΔG), and mean partial molar free energy change ($-F$) for Glyamifop in different soils at 298 K.

Soil	K_d	C_e/C_0	$K_{F\text{-}ads}$ (mg^{1-n}·L^n·kg^{-1})	K_{OC}	K_{OM}	ΔG (kJ/mol)	$-F$ (J/mol)
S$_1$	13.820	0.230	17.170	2512.048	1810.768	−18.586	−3636.822
S$_2$	10.120	0.294	12.456	2248.889	1605.607	−18.288	−3035.683
S$_3$	21.238	0.204	19.964	1608.333	877.281	−16.790	−3942.332
S$_4$	143.458	0.035	187.870	2340.131	1777.705	−18.540	−8338.973

S$_1$ to S$_4$ are defined in Table 1. Kd is the soil adsorption coefficient; Ce and C0 are the initial concentration and adsorption equilibrium concentration of Glyamifop in CaCl2 solution, respectively.

Table 5
Thermodynamic parameters of Glyamifop adsorption in the four different soils.

Soil	$K_{F\text{-}ads}$(mg/kg)/(mg/L) 1/n					ΔG (KJ/mol)				
	278 K	288 K	298 K	308 K	318 K	278 K	288 K	298 K	308 K	318 K
S1	5.130 ± 0.239	8.570 ± 0.088	17.170 ± 0.788	10.210 ± 0.643	4.120 ± 0.346	−14.280	−16.294	−18.581	−17.873	−16.054
S2	3.780 ± 0.103	7.701 ± 0.100	12.456 ± 0.538	9.720 ± 0.347	3.435 ± 0.246	−14.035	−16.509	−18.274	−18.252	−16.095
S3	12.330 ± 0.375	41.340 ± 0.750	19.964 ± 0.238	7.380 ± 0.300	5.213 ± 0.345	−14.283	−17.965	−16.785	−14.800	−14.362
S4	91.310 ± 8.346	254.230 ± 13.917	187.870 ± 28.870	80.340 ± 5.231	58.23 ± 4.453	−15.347	−18.642	−18.539	−16.986	−16.687

S$_1$ to S$_4$ are defined in Table 1. $K_{F\text{-}ads}$ is the empirical constant for adsorption and ΔG is the Gibbs free energy of absorption. Values are the means ± standard error (n = 3).

molecules [52]. Therefore, the aqueous solution with a higher pH competed with herbicide molecules for the adsorption sites, leading to a reduction of the soil adsorption capacity for Glyamifop. Conversely, reducing the pH could enhance the adsorption of humus from solution to soil particles, thereby increasing the soil adsorption sites for herbicides [51].

The adsorption capacities of S1, S2, and S3 for Glyamifop were not strongly affected by the solution pH. In contrast, the adsorption capacity of S4 decreased considerably with increasing the pH. This is most likely attributed to the high OM in S4. Increasing the initial solution pH promoted the dissolution of soil OM [51], which then competed with Glyamifop for the adsorption sites, hence reduced the soil adsorption capacity for Glyamifop.

3.5.3. Effects of humic acids on Glyamifop adsorption in soil

Humic acids are a class of natural polymeric organic materials that can adsorb OM and metal ions. Two typical humic acids (e.g., CHA and BFA) were tested in this study. The effects of various CHA and BFA concentrations on Glyamifop adsorption in the four soils are shown in Fig. 4b. In absence of humic acids, the adsorption differences of the four soils were much lower than those without OM removal, indicating that OM content has a great impact on the ability of the soil to absorb herbicides. When inputs of CHA increased, changes of the mean adsorption capacity of Glyamifop in the soil can be divided into three stages: (1) rapid increase (CHA = 0%–2%); (2) moderate increase (CHA = 2%–5%); and (3) slow increase (CHA = 5%–10%). When inputs of BFA increased, changes of the mean adsorption capacity of Glyamifop in the soil can be divided into four stages: (1) rapid increase (BFA = 0%–1%), which was smaller than that of CHA; (2) slight decrease (BFA = 1%–2%); (3) rapid decrease (BFA = 1%–5%); and (4) slow decrease (BFA = 5%–10%).

Both CHA and BFA are rich in carboxyl and hydroxyl groups, which can form complexes with herbicide molecules [53]. Since CHA is water-insoluble, it tends to precipitate into the soil and adsorbs solution Glyamifop, thereby increasing the Glyamifop adsorption capacity of the soil. Such a process can be further enhanced by increasing CHA input into soils. However, continuous CHA addition could lead to the gradual decrease of the effective adsorption sites, which could even reach saturation at high concentrations of CHA. Conversely, BFA is water-soluble, despite a portion of the added BFA was adsorbed on the soil. The adsorbed BFA can adsorb solution Glyamifop. Other portions of the added BFA were dissolved in solution and formed complexes with Glyamifop in solution [54]. Therefore, an increase of BFA addition is most likely to increase the dissolved BFA, which would compete strongly

with the soil for Glyamifop, thus could reduce the Glyamifop adsorption capacity of the soil.

3.5.4. Effects of surfactants on Glyamifop adsorption in soil

The effects of different types and concentrations of surfactants on Glyamifop adsorption in the four soils are shown in Fig. 4c. Continuous increase of Tween80 addition induced the first increase and then decrease of the soil adsorption capacity for Glyamifop, which can be divided into three stages: (1) 0–1 CMC Tween80, rapid increase; (2) 1–2 CMC Tween80, slow increase; (3) 5 CMC Tween80, decrease. Tween80 is a nonionic surfactant that reduces surface tension in soil, thus improving soil dispersion and herbicide adsorption [55]. When the concentration of Tween80 in the solution (e.g. 5 CMC) is greater than the critical micelle concentration, the formed micelle will compete with the soil for Glyamifop, resulting in the reduction of Glyamifop adsorption in soil.

When SDBS addition reached 0.5 CMC, the Glyamifop adsorption capacities of the soils decreased compared to control. At low concentrations, the anionic surfactant SDBS may exist primarily as monomers in solution, which would compete Glyamifop with soil. When the addition of SDBS was slightly higher than its CMC, the anionic surfactant SDBS formed semi-micelles on soil particles, thus increasing the soil adsorption capacity for Glyamifop. When the addition of SDBS greatly exceeded its CMC, a large number of micelles were formed in solution. These micelles may enhance the dissolution of OM within the soil, leading to a decrease of the soil adsorption capacity for Glyamifop [56]. Due to the high OM in S4, its adsorption capacity for Glyamifop decreased when the concentration of SDBS increased from 1.5 to 2 CMC.

Among the three surfactants tested, CTAB had the greatest effect on the adsorption of Glyamifop in the soils. Due to the negative charges on soil particles, cationic surfactants such as CTAB can be adsorbed on soil particles by electrostatic attraction, which reduces the hydrophilicity of the particle surfaces and improves the soil adsorption capacity for herbicides [55,57]. However, when the added CTAB reached 5 CMC, the micelles in solution competed with the soil for Glyamifop, resulting in a decrease of soil adsorption capacity for Glyamifop.

3.6. Migration characteristics of Glyamifop

3.6.1. Leachability of Glyamifop in soil columns

The leaching behavior of herbicides in soil (movement performance) refers to their vertically downward movement along with the soil profile with infiltration water. Leachability is an important factor for
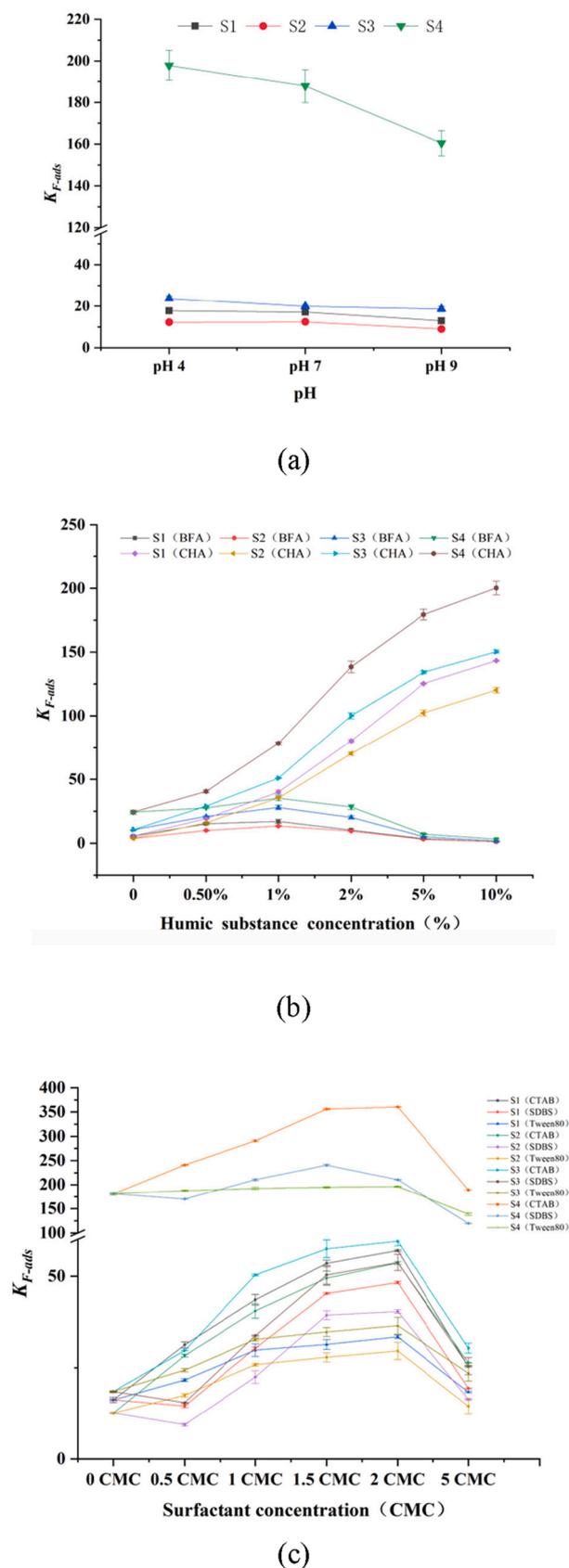
(a)

(b)

(c)

Fig. 4. Influence of initial solution pH (a), humic acids (b), and surfactants on the adsorption of Glyamifop in paddy soils (S_1 to S_4 are defined in Table 1). Values are the means ± standard error ($n = 3$).

determining whether herbicides will enter the groundwater and cause pollution or not [58]. The results of Glyamifop leaching in the different soils are summarized in Table S5. After leaching of 251 mL 0.01 mol L^{-1} CaCl$_2$, the contents of Glyamifop residues in the 0–10 cm section of the soil column decreased in the following order: S4 > S3 > S1 > S2. Accordingly, the leaching rate of Glyamifop was S2 > S1 > S3 > S4. According to the R_i value, the leachability of Glyamifop was classified as leachable in S2, slightly leachable in S1 and S3, and very slowly leachable in S4. Leachate of Glyamifop was not detected in S4, possibly due to its high OM and Glyamifop adsorption capacity. Together with the above adsorption experiments, our results indicate that a higher adsorption capacity corresponds to a lower leachable rate of Glyamifop in soil.

3.6.2. Mobility of Glyamifop in thin soil layers

The contents and distributions of Glyamifop on thin-layer plates coated with different soils are summarized in Table S6. The mobility of Glyamifop in the four different soils decreased in the following order: S2 > S1 > S3 > S4. Based on the R_f value, the mobility of Glyamifop was classified as slightly mobile in S1, S2, and S3 and immobile in S4. The R_f value of Glyamifop was negatively correlated with the overall K_{F-ads} value in the soils ($r^2 = 0.8332$). This indicates that a higher adsorption capacity corresponds to a lower mobility of Glyamifop in the soil.

4. Conclusions

In this study, we systematically investigated the adsorption, desorption, and migration behaviors of Glyamifop in four different soils. We found that all the experimental soils had a high adsorption capacity for Glyamifop. The highest adsorption capacity was obtained in the Phaeozem soil, while the lowest adsorption capacity in the Lixisols. The adsorption parameters were well fitted by the Freundlich model. Based on the linear regression analysis, the Freundlich adsorption and desorption constants (K_{F-ads} and K_{F-des}, respectively) of Glyamifop showed significantly positive relationships with soil OC, OM, and CEC. Glyamifop adsorption occurred spontaneously as an irreversible and physical process in the soils. Relatively low or high temperatures reduced the soil adsorption capacity for Glyamifop. The initial solution pH had little effect on Glyamifop adsorption in the soils. Overall, the soil adsorption capacity for Glyamifop increased when CHA was added, but firstly increased then decreased with continuous BFA addition. Different surfactants also had prominent effects on Glyamifop adsorption in the soils. With continuous Tween 80, SDBS, or CTAB addition, the soil adsorption capacity for Glyamifop firstly increased then decreased. The leachability and mobility of Glyamifop in soil columns and on thin-layer plates were negatively correlated with the soil adsorption capacity for Glyamifop. The stronger the adsorption capacity of the soil, the lower the leaching rate of Glyamifop. Our results demonstrate that Glyamifop can only slightly or very slowly migrate in all the tested soils except the Lixisols. Thus, the risk of Glyamifop migration into surface water and groundwater is low, supporting Glyamifop can serve as an excellent herbicide with low environmental risk.

CRediT authorship contribution statement

Lang Liu: Conceptualization, Methodology, Software, Investigation, Writing - original draft. **Lei Rao:** Validation, Formal analysis, Visualization. **Junhao Hu:** Resources, Writing - review & editing, Supervision, Data curation. **Wenwen Zhou:** Writing - review & editing. **Baotong Li:** Resources, Writing - review & editing, Supervision, Data curation. **Limei Tang:** Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2021.106646.

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