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Influence of Nonionic Surfactants on the Adsorption and Elution of Atrazine in Agriculturally Modified Soils

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Abstract: The Hetao Irrigation District, situated in the Northwest of China, serves as a significant commercial grain base. Widespread use of atrazine, an herbicide in the region, has resulted in significant environmental issues, impacting the ecosystem equilibrium and sustainable agricultural development. The co-adsorption of the globally employed atrazine herbicide along with two nonionic surfactants, Tween-80 and Brij30, onto soils treated with HCl and H₂O₂ was investigated. The study revealed that the adsorption isothermal curves of surfactants on soil adhered to a two-stage adsorption model. Various types of adsorption isothermal curves, such as S-type or L-type, influenced the adsorption capacity of atrazine on the soil. Observations indicated that S-type or L-type isothermal curves of surfactants interconverted with alterations in soil polarity. Moreover, it has been uncovered that the adsorption properties of Tween 80 in the soil are intricately connected to its ability to elute atrazine within the same soil. This discovery provides theoretical support for a prudent reduction in herbicide usage in the Hetao Irrigation District in the upcoming years.

Keywords: Hetao Irrigation District; nonionic surfactant; atrazine; chemical treatment; adsorption model



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1. Introduction

The Hetao Irrigation District serves a pivotal role as a key agricultural production hub in western China, significantly contributing to national food security [1]. Various pesticides, including insecticides, fungicides, and herbicides, are predominantly employed in irrigation areas. In Bayannur City, situated in the Hetao Irrigation District of Inner Mongolia, China, the projected pesticide consumption for 2023, as per the city's yearbook statistics, is estimated at 2026.95 tons, with herbicides comprising 1310.76 tons, representing over 64% of the total pesticide consumption. Some of these agents undergo solidification within the soil, persisting for extended durations. However, rainwater or irrigation runoff can result in the leaching of pesticides into rivers, posing a potential threat to aquatic ecosystems. Statistical data indicate that approximately 45% of pesticides in irrigation areas undergo solidification in the soil, contributing to an overall loss rate of around 75% [2]. Residual pesticides can adversely affect soil microorganisms and non-target plants, fostering the development of resistant pests, compromising water quality, and indeed posing a substantial threat to aquatic ecosystems and drinking water resources [3,4]. Atrazine, a widely used herbicide, is frequently identified as a contaminant with a long half-life, high mobility, and stability in soils, surface water, and groundwater in numerous countries [5]. Several countries in the European Union have prohibited its usage. However, its affordability and efficient control of broad leaf weeds have ensured its status as one of the most widely utilized herbicides globally, until recently [6]. Jilin Province, situated in Northeast China, is the primary region for corn cultivation, where approximately

16,000 tons of atrazine were applied in 2013 [7]. Approximately 402 tons of atrazine were used in Bayannur City, Inner Mongolia, China, in 2023 [8]. As the application of atrazine increases, soil saturation of atrazine adsorption occurs, leading to the pollution of surface water and groundwater through surface runoff and leaching by non-adsorbed atrazine [9]. A study revealed that atrazine concentrations in agricultural fields could surpass 300 µg/L following rainfall in the Midwestern United States [10]. Hence, the widespread application of atrazine represents a significant threat to both human health and aquatic ecosystems.

Surfactants, being amphiphilic substances, offer a distinct advantage in reducing water–soil interfacial tension, enhancing the hydrophilicity of hydrophobic compounds, and contributing to soil diversification. Upon entering soils or water bodies polluted by organic pesticides, surfactants can influence or alter the original transport and fate behavior of organic pesticides through interactions such as adsorption, desorption, leaching, biodegradation, photodegradation, and other processes [5,11]. This interplay between surfactants and organic pesticides underscores the need to understand their dynamic interactions for effective management and remediation of contaminated environments. Therefore, surfactants have been of major concern in the environmental research regarding organic pesticides fate and transformation. In particular, for surfactant enhanced remediation (SER) to remove organic pesticides from contaminated soil, which was widely studied over the past decade, it is very important to focus on surfactant adsorption behavior in soils and the effect on the adsorption or elution of organic pesticides in soils. In addition, when using SER, sorption of surfactant on soil is inevitable, which may significantly influence the retention of organic pesticides in soil [11,12]. For SER, most of the previous studies mainly focused on the remediation of diverse soils and different organic pesticides, the use of different surfactant and their concentration, different mixed surfactants and their appropriate combination ratio, the influencing factors, and their optimal values for surfactant-based washing [4,12].

It is generally believed that adsorption behavior of surfactants in soils is associated with key factors, including organic matter content, clay mineral composition, and amorphous metal oxides (SiO_2 , Al_2O_3 , and Fe_2O_3). Previous studies have reported that SiO_2 , montmorillonite, and vermiculite components in soils could contribute to nonionic surfactants adsorption, and the adsorption was not necessarily related to the content of organic matter of soils. However, several studies have examined the adsorption contribution of the organic matter in soils and sediments. For instance, Cano and Dorn [13] found a positive correlation between the adsorption ability of alcohol polyoxyethylene ether (AE) and alkylphenol polyoxyethylene ether (APE) to soils and the organic matter content. Brownawell et al. [14] reported analogous results in their investigation of Triton X-100 adsorption on soil materials. However, the affinities of nonionic surfactants for various sediment materials defy interpretation solely based on organic carbon content or the fraction of montmorillonite + vermiculite. Presently, the effects of soil composition on the adsorption of nonionic surfactants remain inadequately elucidated due to the lack of quantitative consideration for variations in their adsorption capabilities.

Over an extended period, extensive researches have been dedicated to elucidating surfactant adsorption phenomena at solid/liquid interfaces. Various types of adsorption isotherms, such as Langmuir-type (L), S-type (S), and two plateaux-type (LS), have been documented [13,15]. Among the various adsorption modes for surfactant adsorption, the isotherm equation developed by Zhou et al. [16], employing a two-step mechanism and mass-action treatment, emerges as the most typical and representative, which is capable of interpreting the diverse types of surfactant adsorption isotherms published in the literature. Regrettably, there is a scarcity of literature examining the general isotherm equation or utilizing the two-step adsorption model to interpret the effects of surfactants on the adsorption of organic compounds in solids (such as soils, sediments, etc.). Additionally, nonionic surfactant is cheaper and less toxic because it is more biodegradable, and it can also enhance the sorption of organic compounds onto soils and then reduce their concentrations and mobility in soil solution [16]. Lee et al. [17] suggested that the number of organic compounds released to the surfactant solution depends on the organic compound water

solubility (S_w) and the surfactant polarity. The research results indicated that besides the S_w of the organic compounds, the distribution coefficient of organic compounds between the solid and the solution was regarded as a function of the soil organic matter (SOM) constituents and the chemical structure of the organic compounds [18]. Meanwhile, Zhou and Zhu [16] proposed a distribution of organic compounds between the aqueous phase and the solid phase with the addition of nonionic surfactant to the balance of these two effects: (i) the partition of organic compound into aqueous phase surfactant micelles and (ii) the sorption of organic compound by the soil-sorbed surfactant. In fact, variation of surfactant adsorption isotherm types on soil was caused by aggregation ways of surfactant hydrophobic groups or surfactant hydrophilic groups on the soil surface [19], which undoubtedly influences the adsorption of organic compounds onto the soil, making it intriguing to explore these relationships.

The research reported here focused on the followings issues: (a) soil treatment by different chemical methods in order to change surface property or composition of soil; (b) investigation of adsorption behavior of nonionic surfactants (Tween-80 and Brij30); (c) elucidation of the influence of nonionic surfactants on the distribution of organic pesticide (atrazine) in these soils; (d) examining the process of nonionic surfactants in removing atrazine from soil, focusing on the correlation between surfactants adsorption behavior and atrazine elution effectiveness. We hypothesized that (1) chemical treatment alters soil polarity, thereby affecting the aggregation pattern of surfactant hydrophobic or hydrophilic groups on the soil surface, leading to changes in adsorption isotherm types; (2) the influence of surfactants on pesticide adsorption extends beyond their application in soil particles and aqueous solutions; (3) when using surfactants to leach pesticides from contaminated soil, the effectiveness is not solely determined by the quantity of surfactants applied but requires a comprehensive evaluation of soil properties, surfactant characteristics, and concentration levels. The findings will offer further insights into the study of the migration behavior of nonionic surfactants or organic pesticides in soil, furnishing valuable information for the advancement of SER.

2. Material and Methods

2.1. Soil Sample Treatment

The soil sample was collected from Yuanzi Drainage Experiment Station, Bayannur Academy of Agriculture & Animal Husbandry Sciences, China. Subsequently, it was transported to the laboratory in coolers, air-dried, crushed, and sieved through a 2 mm mesh. The following treatments were then applied:

- A. HCl-treat: The soil sample was initially mixed with HCl solution (0.1 mol/L) and then treated as outlined by Zhao et al. [20]. For this treatment, the great mass of sediment carbonate (mainly CaCO_3 and MgCO_3) was eliminated, and the percentage of organic carbon content of soil on dry-weight basis increased accordingly.
- B. H_2O_2 -treat: following the procedure outlined by Zhao et al. [20]. After this treatment, the great mass of the soil organic carbon (approximately 90%) was removed due to the oxidation of H_2O_2 .

The soil characteristics are presented in Table 1. Soil organic carbon contents and CEC were determined following established protocols (Italian Forests and Agriculture Ministry, 1992. D.M. 79 Official Methods of Analytical Chemistry of Soil, Rome, Italy). X-ray fluorescence spectroscopy (S4 PIONEER, Bruker, Germany) analyzed the Al_2O_3 , SiO_2 , and Fe_2O_3 content of the soil samples. A laser particle size analyzer (25HT161226, Sympatec, Clausthal-Zellerfeld, Germany) assessed the particle size distribution of the soil samples. The pH values were measured in slurries made at a soil/water ratio of 1:1. As demonstrated in Table 1, the soil exhibited slight acidity, with a pH ranging from 5.02 to 5.88 after various treatments. The organic carbon content exhibited the following decreasing order: HCl-treat > untreated > H_2O_2 -treat. After treatment with HCl, the fraction of cosmic particles increased, accompanied by a decrease in sand particles. In contrast, H_2O_2 treatment revealed that the soil's organic matter was mainly present

in the clay component, and the levels of active mineral components (Fe_2O_3 , Al_2O_3 , SiO_2) substantially rose in the soil samples.

Table 1. Physical and chemical properties of soils used.

Sediment Properties	Untreat	HCl-Treat	H_2O_2 -Treat
f_{oc} ^a (%)	2.26	2.76	1.02
CEC ^b (mmol/kg)	92.0	100.7	82.7
pH	5.68	5.02	5.88
Cosmid (φ ^c < 0.002 mm) (%)	31.2	34.1	28.2
Powder (0.002 mm < φ < 0.02 mm) (%)	32.6	32.4	33.5
Sand (φ > 0.02 mm) (%)	36.1	33.5	38.2
Fe_2O_3 (%)	5.6	5.4	6.1
Al_2O_3 (%)	14.1	13.8	15.2
SiO_2 (%)	60.5	60.3	61.3

^a represents soil organic carbon content. ^b represents soil cation exchange capacity. ^c represents soil particle size.

2.2. Chemicals

Atrazine was procured from Bayannur Academy of Agriculture & Animal Husbandry Sciences, Bayannur City, China with a purity > 99%. Tween-80, Brij30, and other compounds such as HCl and H_2O_2 were AR grade reagents purchased from Shanghai Chemical Reagent Co., Shanghai, China. The physico-chemical properties formula of Tween-80 (Polyoxyethylene (20) sorbitan monooleate), Brij30 (polyoxyethylene lauryl ether), and atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) are provided in Table 2.

Table 2. The selected properties of nonionic surfactants used in this study.

Surfactant	CH ^a	EO ^b	MW ^c (g/mol)	CMC ^d (mmol/L)	HLB ^e
Brij30	12	4	362	0.0331	9.7
Tween-80	18	20	1308	0.0130	15.0
Organic pesticide	MW ^c (g/mol)		mole solubility (mg/L)		LogP ^f
Atrazine	215.68		30		1.53

^a CH represents carbon number of hydrophobic group; ^b EO represents number of ethylene oxide group (hydrophilic group); ^c MW represents molecular weight; ^d CMC represents critical micelle concentration; ^e HLB represents hydrophilic lipophilic balance number; ^f LogP represents octanol-water partition factors; CMC and HLB calculated by Ahn et al. [21]; mole solubility and LogP calculated by Cao et al. [22].

2.3. Adsorption Surfactants onto Soil

Adsorption isotherm experiments were conducted to elucidate the equilibrium partitioning behavior of two surfactants, Tween-80 and Brij30, utilizing a conventional batch equilibration method [23,24]. Various amounts of surfactants, along with 0.5 g of soil, were combined in Erlenmeyer flasks with stoppers. The solutions contained 0.005 mol/L CaCl_2 and 200 mg/L NaN_3 as a biocide. Subsequently, the flasks were then gently shaken for 24 h at 25 ± 1 °C in the dark. Preliminary rate studies dictated this time to be adequate for equilibration. Following agitation, the suspensions were transferred to Corex centrifuge tubes with a Teflon lined-cap, the tubes were centrifuged at 8000 rpm for 20 min to separate the water and solid phases. The aliquots of supernatant were taken for analysis to determine the surfactant concentration using a spectrophotometer (UV-8000A spectrophotometry, Shanghai Chemical Instrument Inc., Shanghai, China), and the sorbed concentration of surfactants in the soil phase was calculated by a model as shown below, where Q is the amount of surfactant adsorbed on soil at equilibrium, $\mu\text{mol/g}$; C_0 is the surfactant adding concentration, mmol/L; C_e is the surfactant concentration at equilibrium, mmol/L; V is solution volume, mL; M is the soil adding weight, mg.

$$Q = \frac{(C_0 - C_e)V}{M} \quad (1)$$

In addition, a control with no surfactant in solution was set up in all tests. The adsorption isotherms of surfactants on soils were analyzed by OriginPro 8.5, and possible adsorption model diagrams of surfactant on soil was plotted by 3Dmax (2022) software.

2.4. Adsorption of Atrazine in Soil–Surfactant–Water Mixtures

Atrazine adsorption isotherms in soil–water mixtures were determined through batch equilibrium experiments in the presence of surfactants. Varied amounts of atrazine (1.6, 3.2, 6.4, 12.8, and 25.6 mg/L) were added to 50 mL Erlenmeyer flasks with stopper, which contained 0.5 g of soil sample and 20 mL of a given concentration of Brij30 or Tween-80 concentrations solution with 0.005 mol/L CaCl₂ and 200 mg/L NaN₃ as a biocide. The flasks were then agitated for 24 h at 25 ± 1 °C on a reciprocating shaker at 150 rpm, a duration previously validated for equilibrium. Subsequently, the suspensions were centrifuged at 8000 rpm for 30 min to separate the solution and solid phases. An amount of 2 mL of supernatant was then transferred into glass vials containing 10 mL of hexane. The vials were sealed with caps and shaken for 2 h on a reciprocating shaker. After atrazine was separated from Soil–Surfactant–Water mixtures using hexane as extractant. The hexane extracts were then analyzed for atrazine content using gas chromatography (GC, SP-7890Plus, Tengzhou, China). The sorbed amounts of pesticide were computed simply by Formula (1), where Q is the amount of atrazine adsorbed on soil at equilibrium, mg/kg; C_0 is the atrazine adding concentration, mg/L; C_e is the atrazine concentration at equilibrium, mg/L; V is solution volume, mL; M is the soil adding weight, mg. In addition, to eliminate the effect of surfactants on the analysis of atrazine, the blanks with the same surfactant concentrations but without atrazine were also analyzed. Atrazine adsorption isotherms were fitted by using linear adsorption equations as shown below:

$$Q = K_d C_e \quad (2)$$

where Q is the amount of atrazine adsorbed on soil at equilibrium, mg/kg; C_e is the atrazine concentration at equilibrium, mg/L; K_d is Henry's isotherm model equilibrium constant, mg L/kg.

2.5. Elution Experiments of Atrazine from Soils

According to reference [23], dynamic lysimetric experiments were conducted to investigate the transportation of atrazine facilitated by surfactants. A glass chromatography column (30 cm in length and 40 mm in diameter) was packed with 80 g of soil. The column was plugged with glass wool at both ends and contained a large pore-diameter fritted disc sealed at the outlet. After packing, the columns were gradually saturated from the bottom with electrolyte solution (0.01 mol/L CaCl₂) [24]. For the contaminant-elution experiments, a solution containing 5 mL of atrazine (200 mg/L) was pumped into the soil-packed column. To ensure uniform and complete contamination of the soil columns, the solution was continuously introduced until the effluent concentrations of atrazine matched the influent concentrations. After contamination, the columns underwent elution with 300 mL of surfactant solutions at varying concentrations (0, 0.008, 0.028 mmol/L) by a peristaltic pump. Distilled water was used to elute atrazine as a blank control group.

2.6. Analytical Methods

The concentration of Brij30 or Tween-80 in aqueous solution was determined using a spectrophotometer with a KI-I₂ mixed solution as the developer. This method relies on the reaction between ethylene oxide group of polyoxy-ethylene nonionic surfactants and KI-I₂ mixed solution, causing the changes in VIS adsorption spectrum of nonionic surfactant solutions [23], and the concentration of Brij30 or Tween-80 was proportional to the absorption value at 500 nm. The potential interferences arising from components of soil tested were evaluated by mixing the soil extraction containing Fe, Al, and Ca ions and dissolved organic matter with Brij30 or Tween-80 standards (Thermo Fisher SCIENTIFIC, Shanghai, China). There were no significant differences between

standards prepared in double deionizer water or the mixture [25]. The GC analysis was conducted using a Model 6890A Hewlett Packard gas chromatograph (JINGKERUIDA, Beijing, China), equipped with a Supelco SPB-1 (ALAB INSTRUMENT, Hangzhou, China) fused silica capillary column (30 m × 0.2 mm ID, 0.2 μm film) for atrazine separation. Blank experiments without soil were conducted for the tested compound, with recoveries ranging from 87% to 94%. Measured equilibrium concentrations were not adjusted for the recoveries. All analytical determinations utilized standard external calibration curves within their linear response regions and were performed well above the instrumental and method detection limits.

3. Results

3.1. Adsorption of Nonionic Surfactants on Soils with Different Chemical Treatments

Zhou et al. [16] proposed a hypothetical model of surfactant adsorption on solid surfaces and believed that the adsorption occurs in two stages. In the first stage, individual nonionic surface-active molecules are adsorbed by direct interaction with the solid surface through van der Waals forces, and the adsorption in this stage belongs to monolayer adsorption. In the second stage, the adsorption of surface-active molecules increases dramatically through the hydrophobic interaction between carbon and hydrogen chains, forming surface micelles. The adsorption monomers in the first stage act as active centers that lead to the formation of surface micelles, and the adsorption in this stage belongs to multilayer adsorption. Additionally, Zhou et al. [16] derived a general formula for adsorption isotherms as follows:

$$Q = \frac{Q_0 K_1 C_e \left(\frac{1}{n} + K_2 C_e^{n-1} \right)}{1 + K_1 C_e \left(1 + K_2 C_e^{n-1} \right)} \quad (3)$$

where Q is the amount of surfactant adsorbed at equilibrium, C_e is the surfactant concentration at equilibrium, Q_0 is the limiting adsorption at high concentrations, K_1 and K_2 are the equilibrium constants involved in the first and second step, respectively, and n is the aggregation number of surface hydrophobic aggregates or hemimicelles. The equation could interpret surfactant L- and S-types adsorption isotherms due to its several important limiting cases. If $K_2 \rightarrow 0$ and $n \rightarrow 1$, it reduces to an L-type equation which can be used to describe the adsorption behavior of surfactants on the solid interface only occurring in the first step:

$$Q = \frac{Q_0 K_1 C_e}{1 + K_1 C_e} \quad (4)$$

If $n > 1$, $K_2 C_e^{n-1} \gg 1$ or $K_1 C_e \ll 1$, Equation (3) is reduced to an S-type equation which can be applicable for describing the adsorption behavior of surfactants on the solid interface, occurring in both the first and second steps.

$$Q = \frac{Q_0 K_1 K_2 C_e^n}{1 + K_1 K_2 C_e^n} \quad (5)$$

The adsorption isotherms of nonionic surfactants Brij30 and Tween-80 on two different treated soils (HCl-treat and H₂O₂-treat) and untreated soil are illustrated in Figure 1. The experimental data were fitted to the general isotherm Equation (3) and are summarized in Table 3. For Tween-80 adsorbed to untreated soil or HCl-treat soil and Brij30 adsorbed to HCl-treat soil, Table 3 indicates that their K_2 covered the range of $1.000 \times 10^{-41} \sim 3.927 \times 10^{-16}$ and n covered the range of 0.8568~1.067. Clearly, their K_2 tended towards zero and n tended towards 1, so their isotherms agreed well with the L-type Equation (4) (Figure 1 and Table 3). On the contrary, Table 3 reveals that the n values for Tween-80 adsorbed to H₂O₂-treat soil and Brij30 adsorbed to untreated soil or H₂O₂-treat soil were more than 1, with variation ranges of their $K_2 C_e^{n-1}$ (C_e of 0.20 mmol/L) $45.27 \sim 1.081 \times 10^5$, indicating that the $K_2 C_e^{n-1}$ was significantly

greater than 1. Therefore, their isotherms could be considered as fitting the S-type Equation (5) (Figure 1 and Table 3).

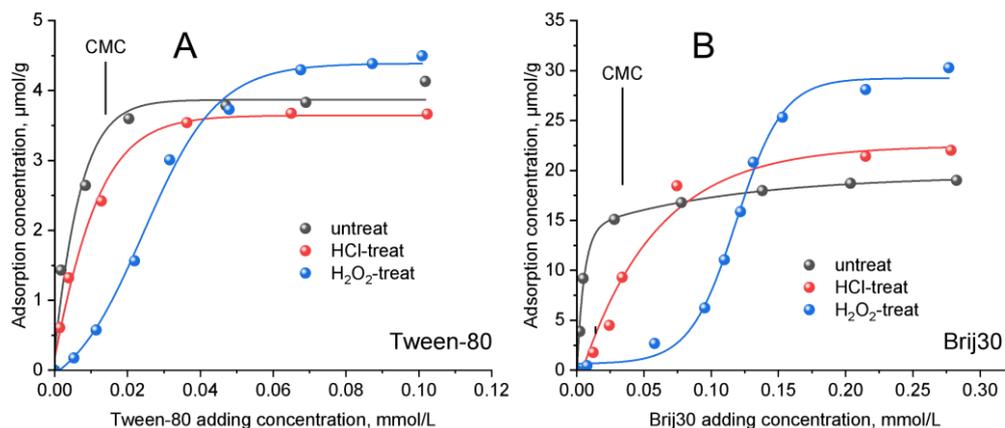


Figure 1. Adsorption isotherms of Tween-80 (A) and Brij30 (B) on different treatment soil.

Table 3. Fitted parameters of two nonionic surfactants adsorbed by soils using the general isotherm equation.

Nonionic Surfactants	Soil Samples	K_1	K_2	n	Q_0 (µmol/g)	R^2	$^a K_2 C_e^{n-1}$	$^b C_0$ (mmol/L)	Following Equation
Tween-80	untreat	129.7	3.927×10^{-16}	0.8568	3.483	0.9944	1.259×10^{-16}	0.0211	L-types
	HCl-treat	288.2	1.000×10^{-41}	1.067	4.367	0.9844	8.968×10^{-42}	0.0446	L-types
	H ₂ O ₂ -treat	28.86	7.054×10^3	3.2837	4.602	0.9987	1.179×10^3	0.0605	S-types
Brij30	untreat	2.780×10^{-3}	1.140×10^6	2.463	21.81	0.9966	1.081×10^5	0.0189	S-types
	HCl-treat	139.3	5.000×10^{-21}	0.9201	17.59	0.9916	5.686×10^{-21}	0.0788	L-types
	H ₂ O ₂ -treat	47.21	6.955×10^6	8.420	29.47	0.9966	45.27	0.1481	S-types

^a values of $K_2 C_e^{n-1}$ when C_e is 0.20 mmol/L; ^b C_0 represents surfactant equilibrium concentration in solution when surfactant reaches saturation adsorption in soil.

Based on a two-step adsorption mechanism, the precondition of surfactant adsorption is that the adsorption capability of adsorption ability of surfactant hydrophilic groups on adsorbent was higher than surfactant hydrophobic groups in the first step [19]. According to Holmberg et al. [26] and Yang et al. [27], the polyoxyethylene nonionic surfactants adsorbed to solid interface in aqueous solution involved both mechanisms: their hydrophobic groups (alkyl group) partition into nonpolar solid interfaces, such as the organic matter in soil, or their hydrophilic groups (ethylene oxide group) aggregated on polar solid interfaces, such as the mineral substance in soil by van der Waals forces, dispersion forces, and hydrogen bonding, and so on.

In the first step, owing to a higher HLB value compared to Brij30 (Table 2), the Tween-80 hydrophilic group extended into water, but the hydrophobic group oriented towards the soil and was partitioned into organic matter upon the approach of surfactant molecules to the soil particle surface, so the adsorption isotherms exhibited an L-type trend with the further increasing of Tween-80 concentration in aqueous solution signifying the adsorption of Tween-80 to untreated soil or HCl-treated soil. However, Brij30 was adsorbed to soil mainly through its hydrophilic groups aggregated on the mineral substances in the soil and its hydrophobic group extending into water. Due to the formation of admicelles on the soil surface, facilitated by hydrophobic interactions among the hydrocarbon chains of the hydrophobic group, Brij30 adsorption on soil increased intensively. Meanwhile, adsorption isotherms of Brij30 on soil exhibited an S-type pattern (e.g., Brij30 adsorbed to untreat soil or H₂O₂-treat soil).

It is noteworthy that that the S- and L-type isotherms exhibit a propensity to interchange from one to the other with the alterations in soil polarity, indicative of changes in soil composition. For example, the adsorption isotherms of Brij30 demonstrate a shift from

S-type to L-type when the organic carbon content of the soil increases due to HCl-treat (Figure 1 and Table 3); conversely, the adsorption isotherms of Tween-80 tend to transition from L-type to S-type when substantial amount of soil organic carbon is removed through H₂O₂-treat (Figure 1 and Table 3).

3.2. Influence of Nonionic Surfactants on Atrazine Distribution between Water and Soil

The adsorption isotherms equation of atrazine on different chemical-treated soils is presented in Table 4, where the adsorption isotherm curves exhibit linearity ($R^2 > 0.9937$), and the adsorption coefficients are proportional to the organic carbon content of soils (the adsorption coefficients values increase in the following order: HCl-treat > untreat > H₂O₂-treat). Hence, atrazine adsorbs to soil through the partitioning of atrazine molecules into soil organic matter [20,28]. The fitting results of linear adsorption equations for atrazine adsorbed to various chemically treated soils in the presence of a given Tween-80 or Brij30 concentration are shown in Table 4. Table 4 shows the adsorption of atrazine on all soils increased when surfactant equilibrium concentration is below 0.008 mmol/L, which is lower than the CMC of the surfactant (CMC is 0.0331 mmol/L for Brij30 and 0.0130 mmol/L for Tween-80), consistent with previous studies [16,29]. When surfactant equilibrium concentration in solution exceeds the CMC, for surfactant with L-type adsorption isotherms (e.g., Tween-80 adsorbed to untreat soil or HCl-treat soil and Brij30 adsorbed to HCl-treat soil), the addition of surfactant reduces the adsorption onto soil for atrazine. However, for surfactant with S-type adsorption isotherms (e.g., Brij30 adsorbed to untreat soil or H₂O₂-treat soil and Tween-80 adsorbed to H₂O₂-treat soil), the atrazine adsorption onto soil significantly increases with the addition of surfactant until reaching saturation adsorption. Beyond this point, further addition of surfactant results in a rapid reduction in atrazine adsorption in solution.

Table 4. The linear adsorption equations of atrazine with different concentrations of nonionic surfactants in soils.

Soils	^a C _e (mmol/L)	Brij 30			Tween-80		
		Linear Equations	R ²	K _d	Linear Equations	R ²	K _d
untreat	0	^b Q = 33.96 C _e	0.9945	33.96	Q = 33.96 C _e	0.9945	33.96
	0.008 (C _e < CMC)	Q = 34.75 C _e	0.9991	34.75	Q = 34.41 C _e	0.9951	34.41
	0.01 (CMC < C _e < C ₀)	Q = 34.26 C _e	0.9932	34.26	Q = 32.23 C _e	0.9922	32.23
	0.18 (C ₀ < C _e)	Q = 31.18 C _e	0.9971	31.18	Q = 29.53 C _e	0.9941	29.53
	0.25 (C ₀ < C _e)	Q = 30.92 C _e	0.9942	30.92	Q = 28.08 C _e	0.9942	28.08
HCl-treat	0	Q = 35.68 C _e	0.9991	35.68	Q = 35.68 C _e	0.9991	35.68
	0.008 (C _e < CMC)	Q = 36.79 C _e	0.9943	36.79	Q = 37.19 C _e	0.9938	37.19
	0.01 (CMC < C _e < C ₀)	Q = 30.82 C _e	0.9941	30.82	Q = 31.55 C _e	0.9904	31.55
	0.18 (C ₀ < C _e)	Q = 34.16 C _e	0.9985	34.16	Q = 33.17 C _e	0.9971	33.17
	0.25 (C ₀ < C _e)	Q = 33.83 C _e	0.9991	33.83	Q = 31.37 C _e	0.9924	31.37
H ₂ O ₂ -treat	0	Q = 23.89 C _e	0.9937	23.89	Q = 23.89 C _e	0.9937	23.89
	0.008 (C _e < CMC)	Q = 31.55 C _e	0.9991	31.55	Q = 32.27 C _e	0.9992	32.27
	0.01 (CMC < C _e < C ₀)	Q = 32.21 C _e	0.9955	35.21	Q = 33.07 C _e	0.9933	33.07
	0.18 (C ₀ < C _e)	Q = 21.09 C _e	0.9975	21.09	Q = 20.61 C _e	0.9934	20.61
	0.25 (C ₀ < C _e)	Q = 20.61 C _e	0.9944	20.61	Q = 19.19 C _e	0.9935	19.19

^a C₀ represents surfactant equilibrium concentration in solution; ^b linear adsorption equations of atrazine in the presence of surfactant.

3.3. Transport of Atrazine

Ren et al. [30] and Zhang et al. [9] assert that Tween80, a nonionic surfactant, exhibits lower elution efficiency for soil pollutants compared to an aqueous solution due to its robust adsorption capacity in soil. In this research, Tween80 at concentrations of 0.008 mmol/L and 0.028 mmol/L were used as eluents, and the elution of atrazine in HCl-treated and H₂O₂-treated soils were studied by the soil column leaching method,

and the elution results are shown in Figure 2. Figure 2 illustrates that at a low Tween80 concentration (0.008 mmol/L), the atrazine elution efficiency in each soil is inferior to that of distillation, yielding rates of 42% and 52% compared to 74% for distilled water. Conversely, at higher concentrations (0.028 mmol/L), Tween80 demonstrated a robust removal efficiency of 79% for atrazine in HCl-treated soils, yet the removal in H₂O₂-treated soils was considerably lower at 23%.

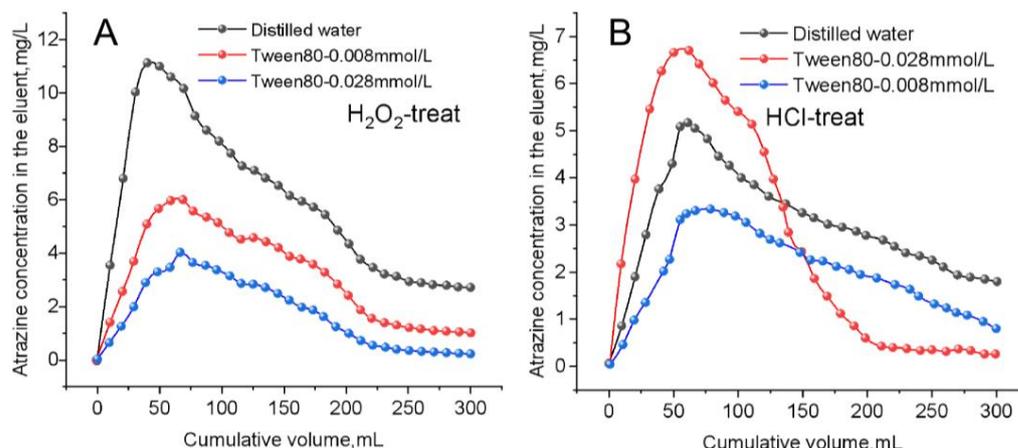


Figure 2. Elution curves of atrazine from H₂O₂ soil (A) and HCl-treated soil (B) with distilled water, 0.008 mmol/L and 0.028 mmol/L of Tween80 solutions.

4. Discussion

Indeed, the above experimental phenomena find support in research findings reported by Holmberg et al. [26], Zhu et al. [31], and Xiao et al. [32]. They proposed that the adsorption process of nonionic surfactant on soils, aligning with the S-type and L-type model, can be delineated through stages I to V (Figure 3). In stage I, characterized by a very low concentration of nonionic surfactant, the primary interaction between the surfactant and soil particles is governed by van der Waals forces and results in the irregular flat adsorption of surfactant molecules on the soil surface. As the concentration of nonionic surfactant increases, soil surface is gradually covered with the irregular flat surfactant molecule, marking the transition to stage II. At this point, the adsorption isotherms exhibit a distinctive turning point.

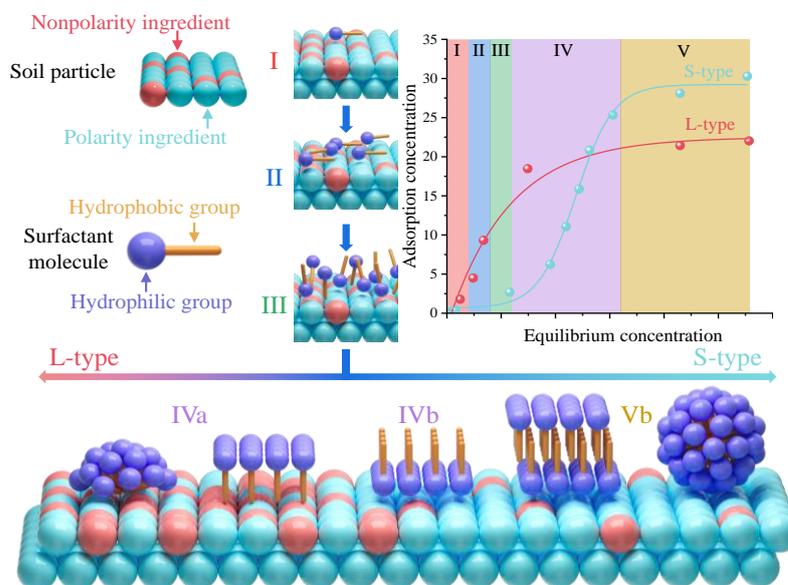


Figure 3. Possible adsorption model of Brij30 and Tween-80 on soil with different chemical treatments.

At stages I and II, the adsorption behavior appeared independent of the character of nonionic surfactant and soil. However, at stage III, as the concentration of nonionic surfactant increased, the irregular flat configuration of the surfactant on the soil surface underwent a transformation, manifesting in two distinct states: on the nonpolar surface of the soil organic matter, the hydrophilic group of the surfactant molecule exhibited an upward curve, while the hydrophobic group maintained a flat orientation on the soil surface due to superior adsorption capacity of the hydrophobic group on the nonpolar components of the soil compared to the hydrophilic group; but on the polar surface of the soil's mineral content, the adsorption behavior was reversed (Figure 3 III).

When the nonionic surfactant forms larger micelle structures in the solution, the adsorption process progresses to stage IV and two situations may happen: If the HLB value of the surfactant increases (e.g., using Tween-80 rather than Brij30) or the soil polarity decreases (e.g., soil treated with HCl), a substantial quantity of surfactant molecules can orient themselves on the soil surface by distributing their hydrophobic groups into the organic matter of the soil. Consequently, the adsorption capacity of the surfactant undergoes a significant increase, ultimately reaching equilibrium (Figure 3 IV_a), and the adsorption isotherms exhibit L-type behavior. Conversely, if the HLB value of the surfactant decreases (e.g., using Brij30 instead of Tween-80) or the soil polarity increases (e.g., soil is H₂O₂-treat soil), surfactant can form double-oriented linear surface hemimicelles or micelles (Figure 3 IV_b and V_b), and the adsorption isotherms exhibit S-type behavior.

It can be seen from Figure 1 and Table 3 that the maximum adsorption capacity at high concentrations Q_0 of S-type adsorption isotherms is 1.15~1.67 times higher than that of L-type adsorption isotherms. This discrepancy is likely attributed to formation of the surface micelles associated with S-type adsorption isotherms significantly enhancing the surfactant adsorption capacity on soil. Consequently, previous studies suggesting a correlation between surfactant adsorption capacity and soil active ingredients (SiO₂, Al₂O₃, and Fe₂O₃) may be rooted in the increased polarity of soil induced by these active ingredients, leading to the formation of extensive surface micelles at the soil interface [27]. Moreover, the maximal coverage of Brij30 and Tween-80 is achieved at equilibrium concentrations well above the CMC, approximately 2 to 3 times higher than the CMC. This conclusion aligns closely with findings reported by Zhu et al. [27].

Combining the two-step adsorption model of surfactants, the influence mechanism of Brij30 and Tween-80 on the distribution of atrazine in soils is illustrated in Figure 3. When the surfactant equilibrium concentration C_e in solution is below the CMC (e.g., Table 4, where equilibrium concentration of Brij30 and Tween-80 in solution is 0.008 mmol/L), atrazine adsorption on soil is increased due to hydrophobicity of soil minerals, which is enhanced by surfactants spreading irregularly on the soil mineral surface. When the surfactant equilibrium concentration C_e in solution exceeds the CMC but remains below the surfactant equilibrium concentration C_0 at saturation adsorption in soil (Table 4), for surfactants exhibiting L-type adsorption isotherms, the adsorption force of atrazine on soil is decreased by the repulsion of neatly arranged surfactant molecules on the soil surface, whose hydrophilic groups extend into the water (Figure 4). However, for a surfactant with S-types adsorption isotherms, before the surfactant reaches saturation adsorption, atrazine adsorption on soil is increased due to atrazine molecules entering the core of micelles or hemimicelles aggregated on the soil surface by the solubilization effect of these surface micelles (Figure 4). Certainly, after the surfactant reaches saturation adsorption, as the surfactant concentration in the solution increases (whether the surfactant is Brij30 or Tween-80), the solubilization effect of micelles in solution for atrazine is more than micelles or hemimicelles aggregated on the soil (Figure 4), thereby reducing atrazine adsorption on the soil (Table 4).

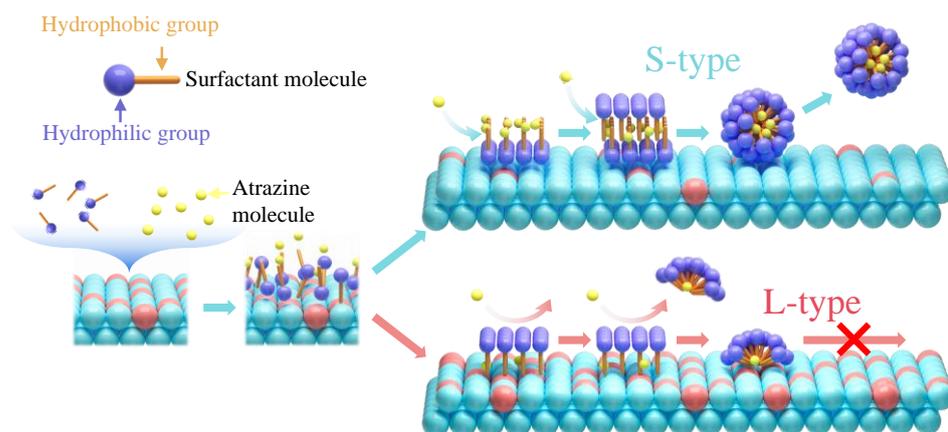


Figure 4. The possible influence mechanism of surfactant on the adsorption of atrazine on soil.

The foregoing conclusion in this paper can be used to explain previous findings by Zhou and Zhu [16], who believed that the applied surfactant could produce two effects on adsorption behaviors of organic contaminant on soil: the portion of the surfactant adsorbed on soil increases contaminant sorption, whereas the portion of surfactant in water promotes contaminant dissolution, which was further confirmed by the transport experiment of atrazine in this paper. With an elevation in organic matter content in HCl-treated soil, Tween80 adheres to soil organic matter via its hydrophobic end. As the concentration increases, more Tween80 adsorbs, causing a higher prevalence of hydrophilic ends facing the water body. This, in turn, intensifies the repulsion effect on atrazine. Additionally, the solubilization effect of Tween80 micelles on atrazine in the solution is enhanced with higher concentrations of Tween80, resulting in an improved elution effect. Conversely, H_2O_2 treatment elevated the relative content of mineral components, promoting the formation of numerous surface micelles. These micelles exhibited a favorable solubilizing and fixing effect on atrazine in the soil, leading to a diminished elution effect.

Hence, in employing the surfactant elution method for treating soil contaminated with organic matter, two primary mechanisms operate within the complex mixed system of water–soil–organic matter–surfactant: Firstly, the solubilization and elution of organic matter occur through surfactant monomers or micelles in the conventional solution. Secondly, the partitioning and adsorption of organic matter happen via surfactant monomers or micelles adsorbed onto the soil surface. The interplay between these two effects dictates the overall elution outcome. Conversely, in scenarios where single-layer adsorption occurs but with the hydrophobic end facing outward (e.g., adsorption on soil with high mineral active ingredient content), organic matter adsorption is enhanced, thus reducing elution effectiveness. However, when surfactant adsorption on the soil occurs in multi-layer fashion, the distribution and adsorption effect of surface micelles formed on organic matter significantly diminish the elution effect. Additionally, L-shaped or S-type isothermal curves offer a rough assessment of surfactant adsorption behavior on soil. When utilizing surfactants for leaching pesticides from contaminated soil, effectiveness is not solely contingent upon the quantity of surfactants applied; rather, it necessitates a comprehensive evaluation of soil properties, surfactant characteristics, and concentration levels.

5. Conclusions

The adsorption behaviors of nonionic surfactant Tween-80 and Brij30 on soils treated by two chemical treatments can be well simulated by the two-step adsorption model. The adsorption isotherms of Tween-80 adsorbed to untreated soil or HCl-treated soil and Brij30 on HCl-treated soil conform to the L-type with a singular plateau, while the Tween-80 on H_2O_2 -treated soil and Brij30 on untreated soil or H_2O_2 -treated soil Brij30 were fit to an S-type isotherm with two plateaus. The S-type and L-type isotherms could switch from one to the other with the change in soil polarity or surfactant HLB value, for which the adsorption process of surfactant on soils was accomplished through stages I to V. The fluctuation in

atrazine adsorption to soil in the presence of surfactant in solution was associated with surfactant type of surfactant adsorption isotherms. When the surfactant concentration exceeds the CMC, the effects of surfactant on atrazine adsorption to soil can be predicted by the changes in the type of surfactant adsorption isotherms. At low concentrations of Tween 80 used for soil flushing, there was minimal impact on atrazine removal. It is noteworthy that higher concentrations of Tween 80 enhance the flushing capacity for atrazine removal in soil with high organic carbon content but yield opposite results in soil with low organic carbon content. Therefore, when employing the surfactant elution method to treat pesticide-polluted soil, attention must be directed to soil properties, particularly organic carbon content, rather than solely focusing on surfactant type, concentration, pesticide properties, and so forth.

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