Adsorption of Tetracycline by Shrimp Shell Waste from Aqueous Solutions: Adsorption Isotherm, Kinetics Modeling, and Mechanism

Jing Chang,† Zhen Shen,† Xiude Hu, Emily Schulman, Chunyue Cui, Qingjie Guo, and Hongjing Tian* 

1. INTRODUCTION

Tetracycline (TC) is a common, low-cost antibiotic with broad-spectrum antimicrobial activity and is therefore widely used for treating infections in both human and veterinary medicine. It has been reported that TC cannot be completely metabolized in the bodies of humans or animals with around 90% of the consumed TC being released into the environment's water and soil through urine. The discharge of TC into the natural environment not only increases the probability of triggering antimicrobial resistance but also expands the risk of transmitting antimicrobial-resistant bacteria through the food chain. In 2009, TC was detected in urban rivers of Shanghai, China with maximum concentrations of 113.89 ng/L, which is slightly higher than that of the urban rivers of eastern Australia. Thus, it is necessary to develop a cost-effective TC removal method for the treatment of wastewater.

Several TC removal methods have been extensively studied, including advanced oxidation, adsorption, and biological treatment. Among these methods, the adsorption method is the most attractive due to features such as high efficiency, low cost, environmental nontoxicity, and simple operation requirements for the treatment process. Several adsorbents have been employed to remove TC from wastewater, such as activated carbons, silicon materials, and polymers. However, the large-scale applications of the adsorbents listed above are restricted due to complex preparation requirements and high cost.

Currently, shell waste produced by the seafood industry is a growing problem with significant environmental and health hazards. Unlike fish, less than 40 wt % of crustaceans are edible, resulting in a large amount of crab, shrimp, and lobster shells being discarded and dumped in landfills. Shrimp is a typical class of the marine crustacean, and 5.16 million tonnes were produced in 2016 in China, with the amount continuing to increase over recent years. Considering SSW accounts for 40–66% of the shrimp body by weight, the annual production of SSW is over 2.6 million tonnes. The main components of SSW are chitin protein and calcium carbonate, and the uses of SSW as an adsorbent for dyes, such as Congo red and acid blue, and toxic elements, such as arsenic, uranium, and fluorine had been reported. As an adsorbent, SSW has shown several advantages, such as low cost, simple preparation, and favorable adsorption capacity, amongst others. As far as we know, there are no published works investigating the potential for adsorption of tetracycline using SSW. This study focused on the application of SSW as an adsorbent for removing TC from aqueous solutions. The surface areas, porosities, and chemical surface groups of the SSW adsorbent were analyzed. Its adsorption performance was extensively tested by varying different experimental conditions, including the pH value, the initial TC concentration, and the contact time. The adsorption
isotherms, kinetics, and mechanism of the adsorption process were investigated in detail.

2. RESULTS AND DISCUSSION

2.1. Characterization of Adsorbent. 2.1.1. Chemical Composition and Surface Morphology. The morphologies of SSW before TC adsorption were characterized by SEM images. Furthermore, the compositions and distributions of various major elements in SSW were identified with EDX mapping. As seen in Figure 1, the surface of SSW was rough and some elliptic cylinder channels were dispersed on the surfaces. As seen in Figure 2 and Table S1, the EDX analysis indicated that SSW consisted mainly of the elements C, N, O, Ca, and P. The mass ratio of Ca to P in SSW was 1.69, which is similar to 1.67, the mass ratio of Ca to P in the hydroxyapatite (Ca₉₀(PO₄)₆(OH)₂), suggesting that SSW contains the hydroxyapatite. After the TC adsorption, the mass ratio of Ca to P was determined to be 1.70, nearly identical to that of the SSW before adsorption, demonstrating that negligible hydroxyapatite leaching occurred during the adsorption at a pH value of 7 for the TC solution. The EDX results also showed that the N content after the adsorption was considerably higher than that before the adsorption. Considering that the element of N was only present in TC, it can be inferred that a large amount of TC was adsorbed by SSW.

The pore textual properties of SSW adsorbents are displayed in Figure 3. The N₂ adsorption—desorption profile curve of SSW was assigned as a type IV isotherm with a type H4 hysteresis loop, indicating the existence of mesopores in the SSW. These characteristics proved that SSW was a mesoporous material with an S BET of 8.90 m²/g and an average pore diameter of 4.47 nm. Since the maximum diameter of TC is 12.7 Å, the TC molecules were able to pass through the pores of the SSW structure. The FT-IR spectra of the SSW before and after the adsorption of TC are shown in Figure 4. The wide peak at 3437 cm⁻¹ was ascribed to the mixed stretching vibrations of many O–H groups in the chitin of SSW. The peaks at 1653, 1556, 1241, and 1030 cm⁻¹ were ascribed to the stretching vibration of C=O groups in amide I, the bending vibration of N–H groups in amide II, the stretching vibration of C–N in amide III, and the P–O antisymmetric stretching vibration in the phosphates of SSW, respectively. There were two characteristic C–O vibration peaks for the carbonate, and the peaks were around 1417 and 872 cm⁻¹, respectively. The presence of amide I, amide II, and...
amid III illustrated that the SSW contained collagen, while the presence of phosphate and carbonate indicated that hydroxylapatite or carbonate apatite was contained in SSW. However, a few peaks underwent notable changes after TC adsorption. The characteristic peak of amid I shifted from 1653 to 1626 cm$^{-1}$, while the characteristic peak of amid II moved from 1558 to 1503 cm$^{-1}$, and both peak strengths increased significantly. It was determined that the secondary structure of the collagen changed after the adsorption, suggesting that a portion of the collagen in SSW interacted with the TC. In addition, the peak at 3437 cm$^{-1}$ changed to 3424 cm$^{-1}$, showing that the hydroxyl group was involved in the adsorption reaction, which resulted in the formation of hydrogen bonds between SSW and TC. The intensity of the peaks at 1417 and 872 cm$^{-1}$ decreased after the TC adsorption, demonstrating that interactions between carbonate and TC molecules occurred during the adsorption as well. Moreover, the peaks at 1450 and 697 cm$^{-1}$ were attributed to the stretching vibration of the C==C bond in the aromatic skeletal and the out-of-plane bending vibration of C–H groups in the aromatic ring of TC, respectively. These characteristic peaks also appeared on the curves of the SSW after TC adsorption, showing that TC was successfully physically adsorbed onto SSW.

2.1.3. TGA Analysis. As shown in Figure 5, TGA was conducted to investigate the composition of SSW. An initial weight loss of 10% occurred in the temperature range of 90–260 °C, which was caused by the evaporation of water. A more substantial weight loss of around 36% was observed in the temperature range of 260–480 °C, which resulted from the decomposition of collagen. The third weight loss of 13% occurred between 480 and 710 °C, which is likely related to the formation of conjugated molecules by the elimination of water and other components of the chitin molecule. The final weight loss between 710 and 830 °C was approximately 14% and was assigned to the release of volatile compounds from SSW.

2.1.4. Fluorescence Spectroscopy. The reaction between the carbonates and TC was verified by fluorescence measurements. The fluorescence emission spectra of TC, the SSW adsorbents after treatment using NaOH solution, and the adsorption products of TC by the NaOH-treated SSW are shown in Figure 6. The aim of the treatment with NaOH solution was to remove the protein in SSW, and thus the major components contained in the residual SSW was the calcium carbonate (CaCO$_3$). As shown in Figure 6, the characteristic peak of TC and the residual SSW was around 560 and 480 nm, respectively. However, the characteristic peak for the adsorption products of the residual SSW moved to 535 nm and its fluorescence intensity became higher significantly. This was because the calcium carbonate in the SSW formed a complex with TC, indicating that TC interacted with the SSW adsorbent during the adsorption process.

2.1.5. $\zeta$-Potential of SSW at Different pH Values. Figure 7 presents the $\zeta$ potential of SSW in aqueous solutions with different pH values. The pH value at which the SSW surface has a net neutral charge is referred to as the pH value at the point of zero charges ($\text{pH}_{\text{pzc}}$). The $\text{pH}_{\text{pzc}}$ value of SSW was determined to be 7.35. It was noted that when the SSW surface was positively charged when the pH value was lower than 7.35 and the surface of SSW was negatively charged when the pH value was higher than 7.35.

2.2. TC Adsorption Performance. 2.2.1. Pretreatment of SSW. It was reported in some previous researches that pretreatment using acid or alkali was able to improve the adsorption capacity of some solid wastes, such as sawdust, cassava, and crab shell. The effect of the pretreatment time using either HCl solution or NaOH solution on the adsorption capacity of SSW was investigated. As illustrated in Figure S1, the TC adsorption capacity of SSW lowered gradually with the increase of the pretreatment time. This was due to the HCl and NaOH solutions’ continuous consumption of certain components of SSW, resulting in the collapse of some pores in the SSW particles. It is shown in Figures 4 and 6 that both proteins and carbonates, both components of SSW, were capable of reacting with TC. However, if an excessive amount of the carbonates and proteins were consumed by HCl or NaOH...
solutions during a lengthy pretreatment, the adsorption capacity of SSW would be severely reduced. Consequently, SSW that did not undergo any pretreatment with HCl or NaOH solutions was utilized as the adsorbent for TC. Table S2 gives a comparison of the prepared adsorbent with some other adsorbents using some wastes as the raw materials, such as spent coffee wastes,34 cow manure,6 and human hair.23 It was displayed that the performance of the SSW adsorbent was favorable in this comparison.

2.2.2. Effect of the Initial pH Value. Figure S2 demonstrates the effects of the initial pH value of the TC aqueous solutions on the adsorption capacity of SSW. As the initial pH value increased from 2 to 12, the adsorption capacity of the adsorbents first increased and then decreased, which agreed well with results from previous studies.12,34 At various pH values, TC could exist in the form of different species in solution because of its classification as an amphoteric molecule with many ionizable functional groups.35 As shown in Figure S3, the TC molecule was hydrophilic and existed as TC⁺ when the pH value was lower than 3.3, TC₀, when the pH value was within the range of 3.3–7.7, TC⁻, when the pH value was between 7.7 and 9.7, and TC²⁻, when the pH value was higher than 9.7.36,37 As shown in Figure S7, the surfaces of the SSW particles were positively charged at pH values below 7.35. Therefore, a strong electrostatic repulsion between TC⁺ and SSW inhibited the adsorption of TC when the pH value was lower than 3.3. In this case, both the hydrogen bonds and the π bonds formed between TC and SSW were the two major forces during adsorption at low pH values.12,38 When the pH value rose above 3.3, the adsorption capacity was boosted, with the highest value of 161.68 mg/g observed at a pH value of 7.0. During the growth of the pH value from 3.3 to 7.0, the dominant ions of TC in the solution changed from TC⁺ to TC₀, while there were scarcely any positively charged or negatively charged ions on the SSW surface. Thus, the electrostatic repulsion was the lowest in this range and it was favorable for TC to adsorb onto SSW, resulting in the highest adsorption capacity when the pH value was 7.0. When the pH value continued to increase beyond 7.0, the dominant ions converted into TC⁻ and TC²⁻ and the SSW surface became negatively charged. Consequently, a strong electrostatic repulsion reappeared, and the adsorption of TC by SSW was prevented. Therefore, the following adsorption experiments were performed at pH = 7.0.

2.3. Adsorption Kinetics. The adsorption kinetics describe the effects of contact time and adsorption temperature on the TC adsorption rate. Kinetic studies were carried out by adding 0.01 g of adsorbent into 25 mL of TC solution with a concentration of 100 mg/L at different temperatures from 25 to 55 °C. In addition, three frequently used kinetic models, including pseudo-first-order, pseudo-second-order, and the Elovich model, were utilized to fit the adsorption data. The kinetic models are listed in Table S3, the related nonlinear
curves are displayed in Figure 8, and the kinetic parameters are calculated and shown in Table 1. For both the pseudo-first-order and the Elovich models, the values $R^2$ were notably lower than 1, while the values $\Delta q_e$ were higher than zero. It was concluded that both models were unable to fit the experimental data well. Nevertheless, the pseudo-second-order kinetic model displayed a high value of $R^2$ (0.9985–0.9987) and a low value of $\Delta q_e$ (1.05–3.96%). The value $q_{e,cal}$ was calculated according to the pseudo-second-order model and was very close to $q_{e,exp}$, implying that the pseudo-second-order kinetic model fit well with the adsorption data. In fact, the pseudo-second-order model is typically used to describe chemisorption processes rather than physisorption. Therefore, the exchange of electrons or valency between the TC and SSW adsorbent during the adsorption process was not negligible.19,40

The adsorption of TC onto SSW was also analyzed by the two-compartment first-order model, which regarded the adsorption as a two-domain process. As listed in Table 1, the values $R^2$ were high (0.9991–0.9995) and the values $\Delta q_e$ were low (0.95–1.56%), indicating that the two-compartment model agreed well with the experimental data. The values of $f_{fast}$ and $k_{fast}$ were larger than $f_{slow}$ and $k_{slow}$, respectively. The ratio of $f_{fast}$ to $f_{slow}$ was higher than 1, suggesting that the fast adsorption stage played a predominant role in the overall adsorption process. It is commonly accepted that the hydrogen bond between the hydroxyl groups in TC molecules and the oxygen-containing groups on the SSW surface, as well as the $\pi-\pi$ electron-donor–acceptor interactions, were responsible for the fast sorption of TC.12

### 2.4. Adsorption Isotherm

Adsorption isotherms were used to reveal the relationship between the adsorption capacity of SSW and the TC concentration in the residual solutions at adsorption equilibrium. Three adsorption isotherms, including the Langmuir, Freundlich, and Temkin isotherm models, were used to fit the experimental data when the adsorption equilibrium was reached. The isotherm models are listed in Table S3. To identify the model that best describes the adsorption isotherms and the adsorption curves, both the determination coefficient, $R^2$, and the normalized standard deviation, $\Delta q_{iso}$ of every model were calculated and used as bases for comparison.

$$R^2 = 1 - \frac{\sum_{i=1}^{n} (q_{e,exp} - q_{e,cal})^2}{\sum_{i=1}^{n} (q_{e,exp})^2 - \left(\frac{\sum_{i=1}^{n} q_{e,exp}^2}{n}\right)^2}$$

(eq 1 and 2)
where \( q_{\text{exp}} \) and \( q_{\text{cal}} \) are the experimental adsorption capacity (mg/g) and the calculated adsorption capacity (mg/g), respectively, and \( N \) is the number of experimental data points.

In the fitting process, the initial TC concentration ranged from 0 to 800 mg/g while the adsorption temperature was varied between 25 and 55 °C. Plots of the nonlinear fittings corresponding to the above three isotherms were drawn in Figure 9, and the related parameter values are listed in Table 2.

### Table 2. Adsorption Isotherm Coefficients for Different Isotherm Models

| model   | parameter | 25 °C      | 35 °C      | 45 °C      | 55 °C      |
|---------|-----------|------------|------------|------------|------------|
| Langmuir| \( q_m \) (mg/g) | 381.75     | 383.10     | 396.22     | 408.80     |
|         | \( K_L \) (L/mg) | 0.0209     | 0.0276     | 0.0447     | 0.1726     |
|         | \( \Delta q_e \) (%) | 1.30       | 4.74       | 5.47       | 6.96       |
|         | \( R^2 \) | 0.9996     | 0.9914     | 0.9958     | 0.9938     |
| Freundlich| \( K_F \) ((mg/g)-(L/mg)^1/n) | 68.3688    | 81.9960    | 108.2919   | 178.2722   |
|         | \( n \) | 3.7665     | 4.1389     | 4.8542     | 7.1189     |
|         | 1/n | 0.2655     | 0.2416     | 0.2060     | 0.1405     |
|         | \( \Delta q_e \) (%) | 18.34      | 5.07       | 16.35      | 37.52      |
|         | \( R^2 \) | 0.9561     | 0.9636     | 0.9580     | 0.9309     |
| Temkin | \( A_T \) (L/mg) | 0.3105     | 0.5230     | 1.2218     | 16.7206    |
|         | \( B_T \) (J/mol) | 35.1690    | 38.9020    | 43.7023    | 57.7383    |
|         | \( \Delta q_e \) (%) | 6.5534     | 15.4995    | 6.7960     | 11.8600    |
|         | \( R^2 \) | 0.9874     | 0.9914     | 0.9871     | 0.9643     |

\[
\Delta q_e = \sqrt{\frac{\sum((q_{\text{exp}} - q_{\text{cal}})/q_{\text{exp}})^2}{N - 1}} \times 100\% \quad (2)
\]

Figure 9. Adsorption isotherms of SSW at (a) 25 °C, (b) 35 °C, (c) 45 °C, and (d) 55 °C (adsorbent dosage = 0.4 g/L, pH = 7, time = 36 h).

The Temkin model illustrates that the heat of adsorption is inversely proportional to the surface area covered by the adsorbate molecules, which is due to adsorbent–adsorbate interactions. \( B_T \) is Temkin constant related to the heat of adsorption, where a positive value of \( B_T \) indicates an endothermic adsorption process. The values \( B_T \) were between 35.1690 and 57.7383 J/mol for TC adsorption from the aqueous solution, which indicated that the adsorption of TC by SSW was endothermic. The equilibrium binding constant \( A_T \) is a parameter that corresponds to the maximum binding capacity of 1.30–6.96%. This indicated that the Langmuir isotherm was capable of describing the adsorption behavior. In the Langmuir isotherm, \( K_L \) is an important evaluation parameter related to the affinity of the binding sites. If the range \( K_L \) is between 0–1 and increases with increasing temperature, adsorption of TC onto the SSW adsorbent is deemed favorable, especially at high temperatures. As observed in Table 2, \( K_L \) increased from 0.0209 to 0.1726 with an increase in temperature. The results showed that SSW had a high capacity for TC adsorption, especially at high temperatures.
energy. The values of $A_T$ increase with increasing temperature, indicating the adsorption process is endothermic. With the increase of the adsorption temperature from 25 to 55 °C, the values of $A_T$ increased from 0.3105 to 16.7206 L/mg, indicating that the adsorption of TC by SSW was endothermic.

In the adsorption process, the standard Gibbs free-energy change $\Delta G^0$, the standard molar adsorption enthalpy $\Delta H^0$, and the standard entropy change $\Delta S^0$ were calculated according to the Van’t Hoff equation shown by eqs 3 and 4. Their results are available in Table 3.

$$\Delta G^0 = -RT \ln(K) = -RT \ln(1000M_{CO_2}K_L)$$  \hspace{1cm} (3)

$$\ln(K) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$  \hspace{1cm} (4)

### Table 3. Calculated Changes of the Enthalpy, Entropy, and Gibbs Free Energy

| Temperature (°C) | $\Delta G^0$ (kJ/mol) | $\Delta H^0$ (kJ/mol) | $\Delta S^0$ (J/(mol·K)) |
|------------------|-----------------------|-----------------------|--------------------------|
| 25 °C            | -22.8318              | 54.80                 | 258.47                   |
| 35 °C            | -24.3101              | 54.80                 | 258.47                   |
| 45 °C            | -26.3741              | 54.80                 | 258.47                   |
| 55 °C            | -30.8876              | 54.80                 | 258.47                   |

where $R$ is the gas constant equaling 8.314 J/(mol·K), $T$ is the adsorption temperature (K), $K$ is the equilibrium constant of adsorption (L/mol),$^{44-47}$ $K_L$ is the equilibrium constant in the Langmuir equation (L/mg), and $M_{CO_2}$ is the molecular weight of CO$_2$ (g/mol).

The absolute values of $\Delta G^0$ increased as the adsorption temperature rose, showing that the adsorption was favorable at high temperatures. $^{48}$ Furthermore, $\Delta H^0$ was 54.80 kJ/mol, and the positive value indicated an endothermic characteristic of the adsorption process. $\Delta S^0$ was calculated to be 258.47 J/(mol·K), where the resulting positive value revealed an increase in the degree of randomness at the solid–liquid interface during the adsorption. $^{49}$ Similar results have also been reported in the adsorption of amoxicillin by guava seeds. $^{50}$

#### 2.5. Adsorption Mechanisms

Both the intraparticle diffusion model and the liquid film diffusion model were employed to determine the mechanism and rate-limiting steps of the TC adsorption. During this process, the transfer of TC molecules was affected by either the liquid film diffusion, or the intraparticle diffusion, or a combination of both. Figure 10 depicts the nonlinear plots $q_t$ versus $t^{1/2}$ at adsorption temperatures of 25, 35, 45, and 55 °C. Table 1 lists the values of the parameters required for the intraparticle diffusion model, including $k_{sp}$, $C_p$ and $R^2$. The intraparticle diffusion constant, $k_{sp}$, corresponds to the slope of the straight line, and $C_p$ is related to the boundary layer thickness. $^{52}$ As shown in Figure 10, each adsorption process carried out at the various temperatures is divided into three periods based on the three sequential straight lines resulting from the successful fitting of adsorption models to the data. The first stage describes the region where the adsorption is liquid film diffusion-controlled as the TC molecules transfer from the solution to the surface of the SSW. The adsorption in this stage proceeded more quickly than in the other two stages. The fittings plotted in the first stage for adsorption temperatures of 25, 35, 45, and 55 °C, did not pass through the coordinate origin, indicating that intraparticle diffusion was not the only rate-limiting step in the adsorption process. $^{52}$ During the second slower stage, TC molecules were transported into the pores of the SSW particles, resulting in an intraparticle diffusion rate-limiting step. The third and final step was the slowest due to the low TC concentration in the remaining solution, and it was assumed to exist in approximate adsorption equilibrium. Both values $k_{sp}$ for the second and the third stages were lower than that of the first stage, which was due to the slowing of intraparticle diffusion as the concentration of TC in the solution decreased. $^{51,52}$ Additionally, the liquid film diffusion model was also employed for determining the rate-limiting step in the adsorption process. The model is presented in Table S3, and the corresponding plot of $\ln(1 - q_t/q_e)$ versus $t$ is shown in Figure 6. It is proposed that the liquid film diffusion is the rate-limiting step of the adsorption when the plot of $\ln(1 - q_t/q_e)$ versus $t$ shows a straight line passing through the coordinate origin. In other situations, such as when the plot is nonlinear or linear without passing through the coordinate origin, the adsorption process is controlled by liquid film diffusion or a combination of liquid film diffusion and intraparticle diffusion. As observed in Figure 6, all plots of the data fitting were approximately linear and none of them pass through the coordinate origin. So, the liquid film diffusion was not just one of the rate-limiting steps in the adsorption of TC by SSW. Thus, the rate-limiting steps of the adsorption involved both intraparticle diffusion and liquid film diffusion. Similar results were also obtained for the adsorption of TC by macadamia nutshells. $^{53}$

### 3. CONCLUSIONS

The raw SSW without any pretreatment was proven to be a cost-effective adsorbent for TC adsorption in aqueous solutions. The TC adsorption performance of SSW was the best when the pH value of the solution was in the range of

![Figure 10](https://dx.doi.org/10.1021/acsomega.9b03781)  
Figure 10. (a) Intraparticle diffusion and (b) liquid film diffusion plots for TC adsorption onto SSW at 25, 35, 45, and 55 °C (adsorbent dosage = 0.4 g/L, initial TC concentration = 100 mg/L, pH = 7).
6.0—8.0. The maximum TC adsorption capacity of 400 mg/L of the SSW in aqueous solutions was 229.98 mg/g for 36 h at 55 °C. For the adsorption, the Langmuir model fits best with the adsorption isotherms data, while the pseudo-second-order model best described the adsorption kinetics data. The values of the Gibbs free-energy changes ranged from −1.50 to −6.66 kJ/mol, and the enthalpy change was determined to be 47.61 kJ/mol, indicating that the adsorption of TC by SSW was spontaneous and endothermic. Both the intraparticle diffusion and the liquid film diffusion were identified as the rate-limiting steps in the TC adsorption.

4. EXPERIMENTAL SECTION

4.1. Preparation of TC Solutions. TC (C_{22}H_{25}ClN_{2}O_{5}, purity, 90%) was purchased from Aladdin Biochemical Co., Ltd, China. Hydrochloric acid (HCl, purity, 36%) and sodium hydroxide (NaOH, purity, 99%) were purchased from Sinopharm Chemical Reagent Co., Ltd, China. All reagents used in this work were of analytical grade, and all were used as purchased without further purification. One gram of TC was dissolved in 1 L of deionized water to prepare the standard TC stock solution with a TC mass concentration of 1000 mg/L and was then diluted to prepare additional solutions with the required TC concentrations. The pH of the TC solutions was adjusted to the required values using either 0.1 mol/L of NaOH or 0.1 mol/L of HCl.

4.2. Preparation of Adsorbent. SSW were collected from a local seafood processing plant in Qingdao, China. First, they were repeatedly washed with deionized water to remove dirt from the surface, then, the cleaned samples were dried in a drying oven at 80 °C for 48 h. Some of the SSW samples were not treated any further, while others underwent additional treatment steps using an HCl solution, NaOH or 0.1 mol/L of HCl.

During treatment, the dried SSW were first added into the HCl solution (3 wt %) under stirring at 25 °C for 2, 3, 6, and 12 h to remove calcium carbonate. After being washed with deionized water repeatedly until the pH stabilized at 7, the samples were added to the NaOH solution (8 wt %) at 25 °C for 2, 3, and 4 h to remove protein. Next, the samples were washed and dried. The dried samples were mechanically ground in a grinder for 20 min and sieved to collect each of the different samples with particle sizes between 150 and 250 μm. All of the samples were then stored in a desiccator until required for the subsequent experiments. To determine the optimal adsorbent for TC, differently treated adsorbents were employed.

4.3. Adsorption Experiments. The adsorption experiments were carried out in a conical flask containing 25 mL of TC solution. First, 0.01 g of SSW adsorbent was poured into the TC solution and the conical flask was placed in a gas bath thermostatic oscillator with an agitation speed of 120 rpm at 25 °C. The agitation duration would last until the adsorption reached the equilibrium. Then, the suspensions were filtered using a microporous membrane with an average pore size of 0.45 μm to collect the supernatants. The TC concentration of the supernatant was measured by a UV—vis spectrophotometer (Shimadzu, UV-1800, Japan) with a maximum wavelength of 357 nm. To determine the optimum adsorption conditions of SSW, TC adsorption experiments were carried out by adjusting the initial pH value from 2 to 12, the initial TC concentration from 25 to 800 mg/L, and the contact time from 0 to 48 h. The adsorption capacity at a certain time, $t$, was referred to as $q_t$ (mg/g) and was calculated using eq 5.

$$q_t = \frac{(C_0 - C_f) V}{W}$$  \hspace{1cm} (5)

where $C_0$ and $C_f$ were the TC concentration in the solution before adsorption and the TC concentration of the suspensions when the adsorption proceeded at a certain time $t$ (mg/L), respectively. $q_t$ is the adsorption capacity at $t$ time (mg/g). $V$ is the TC solution volume (L), and $W$ is the mass of SSW (g). When the reaction time is enough and the adsorption reaches the equilibrium, $C_e$ and $q_e$ equal to $C_f$ and $q_t$, respectively. The TC removal efficiency was calculated using eq 6.

$$\text{TC removal} = \frac{C_0 - C_t}{C_0} \times 100\%$$  \hspace{1cm} (6)

where $C_0$ and $C_t$ have the same definition as those in eq 5.

4.4. Characterization of the Adsorbent. The structure and morphology of the SSW adsorbents were determined using scanning electron microscopy (SEM, JEOL7500F, Japan). Energy-dispersive X-ray (EDX) spectroscopy performed alongside SEM was used to estimate the surface elemental composition of SSW adsorbents. The N2 adsorption—desorption isotherms were tested at a temperature of 77 K to obtain the surface characteristics of SSW using an automated specific surface area and porosity analyzer (Micromeritics ASAP 2020). The surface areas and the pore size distributions were determined using the Brunauer—Emmett—Teller (BET) method and Barrett—Joyner—Halenda (BJH) method, respectively. Fourier transform infrared spectroscopy (FT-IR, Bruker TENSOR-27, Germany) was employed to evaluate the surface functional groups of SSW. The samples were scanned within the wavenumber region of 4000—600 cm$^{-1}$. Thermogravimetric-derivative thermogravimetry analysis (TG-DTG, NETZSCH STA 409PC/PG, Germany) was used to investigate the thermal stability of the SSW adsorbents under a nitrogen atmosphere with a flow rate of 100 mL/min and a heating rate of 10 K/min from room temperature to 1173 K. The fluorescence properties of the samples were analyzed by fluorescence spectroscopy (Hitachi F-7000, Japan), and ζ potential was measured using an electroacoustic spectrometer (MALVERN NanoZS90, U.K.) with pH values recorded between 2.0 and 12.0.
Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.9b03781

Author Contributions

J.C. and Z.S. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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LIST OF ABBREVIATIONS

- $q_e$: the equilibrium adsorption capacity (mg/g)
- $q_m$: the maximum adsorption capacity (mg/g)
- $q_t$: the adsorption capacity at $t$ time (mg/g)
- $q_{exp}$: the experimental adsorption capacity (mg/g)
- $q_{cal}$: the calculated adsorption capacity (mg/g)
- $R$: the gas constant (8.314 J/(mol·K))
- $R^2$: the determination coefficient
- $T$: the adsorption temperature (K)
- $t$: time (h)
- $V$: the TC solution volume (L)
- $W$: the mass of SSW (g)
- $\Delta G^0$: the standard Gibbs free-energy change (kJ/mol)
- $\Delta H^0$: the standard molar adsorption enthalpy (kJ/mol)
- $\Delta S^0$: the standard entropy change (J/(mol·K))
- $\delta$: the normalized standard deviation (%)
- $\alpha$: the initial adsorption rate (mg/(g·h))
- $\beta$: the Elovich constant (mg/g)

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