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The adsorption–degradation effect of peanut shells loaded with sulphonamide-degrading bacteria

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ABSTRACT

Sulfonamide antibiotics are potentially harmful to the ecological environment and human health, and control of pollution with these compounds has received much attention. In this study, removal of the four sulfonamides sulfamethoxazole, sulfamethazine, sulfamethazine, and sulfamethoxamine from the water was investigated using a composite material prepared from peanut shells and sulfonamide-degrading bacteria. Adsorption–degradation of the sulfonamides with the composite material was investigated using orthogonal static experiments and dynamic experiments. Scanning electron microscopy, X-ray photoelectron spectroscopy, Fourier transform infrared spectrometry, and other microscopic detections and analytical techniques were used to explore the mechanism of action. When the sulfonamide concentration was 0.5 mg/L, the removal rates (%) of sulfamethoxazole, sulfamethazine, sulfamethazine, and sulfamethoxamine by the peanut shell composite were 89.69%, 78.39%, 71.38%, and 88.55%, respectively. The optimum conditions for preparation of the composite material were 50 mL of basic medium, a peanut shell:bacteria ratio of 1.5 g/2.5 mL, and a fixation time of 36 h. The dynamic experiments showed that the composite material performed well for removal of sulfonamides present at the low (0.05 mg/L) and high (5.0 mg/L) concentrations, with average removal rates of 79.89% and 61.53%, respectively. The removal of sulfonamides in water by the composite material occurred mainly by physical and chemical adsorption and biodegradation. Physical and chemical adsorption occurred through the porous structure and active functional groups (C–O, –OH, N=C–O, CH, C=O, $–CH_3$, and $–CH_2–$) of the peanut shell composite. Biodegradation mainly involved metabolism by sulfonamide-degrading bacteria immobilized on the peanut shells.

Keywords: Sulfonamide; Peanut shell; Degrading bacteria; Adsorption; Degradation

1. Introduction

Sulfonamide antibiotics are widely used in the livestock and poultry breeding industries, where more than 45%–90% of the quantity administered to an animal is eliminated as the original drug or metabolites in animal excrement and then enters water bodies in the environment [1,2]. It is relatively common for residues of sulfonamides to be detected

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in the water. Many studies have reported the presence of such residues in surface water [3,4], groundwater [5,6], and sewage treatment plant effluent [7]. Because sulfonamides are difficult to degrade, their inputs are continuous, and they easily migrate [8], they can cause serious damage to the environment and human health. Therefore, development of highly efficient techniques for removal for sulfonamides from water is a focus of environmental research.

The main methods for removing antibiotics from water are oxidation, membrane filtration, adsorption, and microbial degradation. The oxidation method is rapid and provides complete degradation of antibiotics but it has relatively high operating costs and is not suitable for large-scale wastewater treatment. Membrane filtration changes the antibiotics from one state to another rather than destroying them, and the antibiotics may return to the environment again. Compared with other methods, adsorption and microbial degradation methods have received more attention. The adsorption method is very efficient, simple, and inexpensive. Over the past 10 y, adsorption methods have been extensively studied for the removal of antibiotics from water. Various high-performance adsorbents have been developed, including carbonaceous adsorbents (e.g., activated carbon [9–12], carbon nanotubes [13,14], graphite [15,16], bio-carbonaceous materials [17]), clay minerals (e.g., montmorillonite [18–21], zeolite [22,23], kaolinite [24,25], illite [26], and palygorskite [27]), polymer resins [28–32], mesoporous materials [33–39], and solid waste (e.g., sawdust, straw, medicine residues, and livestock and poultry manure) [40–43]. To date, many studies have reported on the use of highly efficient adsorbents to remove sulfonamides from water. Adams et al. [44] studied the adsorption of sulfonamides from simulated wastewater using powdered activated carbon. They found that when the dosage of activated carbon was 10 mg/L, the removal rate of sulfonamides from river water reached 49%–73%, and when the dosage was increased to 20 mg/L, the removal rate increased to 65%–100%. Bao et al. [45] found that a new type of magnetic nanocomposite, CoFeM48, showed good adsorption performance for five kinds of sulfonamides, with a sulfamethoxamine (SMX) removal rate of 82%. Zheng et al. [43] used reed bamboo to prepare biochar to adsorb SMX from water at different temperatures (300°C–600°C). They found that biochar prepared at a high temperature (600°C) had the best adsorption effect for SMX. However, the adsorption method suffers from limited adsorption capacity of the adsorbent. In application, it is often necessary to regenerate or replace the adsorbent.

The microbial degradation method is efficient, inexpensive, environmentally friendly, and sustainable. Zhang et al. [46] screened bacteria from soil with antibiotics used to grow spinach and found that Achromobacter could remove 96.08% of tylosin. Shao et al. [47] explored the biodegradation of oxytetracycline with *Ochrobactrum* sp. KSS10 under different conditions and found that the KSS10 strain degraded 63.33% of oxytetracycline in 96 h. Because sulfonamides migrate easily [8], they cannot provide a stable carbon source during microbial degradation, resulting in low degradation rates. Jiang et al. [48] isolated the cold-resistant bacteria *Pseudomonas psychrophila* HA-4 in a low-temperature (10°C) environment and achieved a degradation rate of 20%–34% using SMX as the sole carbon source and energy source at temperatures of 5°C–30°C. Gauthier et al. [49] showed that *Rhodococcus rhodochrous* degraded SMX species under pure culture conditions. The degradation mechanism was co-metabolism with glucose, and the degradation rate was only 20%. Larcher and Yargeau [50] showed that *Pseudomonas aeruginosa* could also degrade SMX by co-metabolism with glucose. They also found that *Rhodococcus equi* degraded 15% of SMX in the absence of glucose and 29% of SMX in co-metabolism with glucose [49]. These results show that microbial degradation is not stable or efficient when sulfonamides are used as the sole carbon source or in co-metabolism with glucose [51–53]. In response to this, carrier-immobilized microorganism technology has attracted much attention. Kao et al. [54] established a biological permeable reactive barrier in the laboratory using a soil column to treat groundwater contaminated with tetrachloroethylene. Vesela et al. [55] constructed biological permeable reactive barrier using lignite as a carrier to remediate groundwater contaminated with organic wastewater discharged from chemical plants. The removal rate of BTEX was as high as 99.9%. In this study, sulfonamides were removed from water using sulfonamide-degrading bacteria attached to an adsorbent. A composite material will not suffer from loss of function for the adsorbent material or instability of the carbon source during adsorption–degradation [56].

In this paper, taking into consideration the characteristics of sulfonamides, we selected materials for study that were inexpensive, easy to access, plentiful, adsorbent, and could be used as bacteria-carrying materials. Two materials were selected: peanut shells, and the synthetic material described in the patent "A sorbent for removing antibiotics in water, preparation method and application" [57]. Peanut shells are a suitable carrier material for immobilized bacteria because they have high particle sizes, absorbency, plentiful, and biodegradability, and are inexpensive [58]. To date, there have been many international reports on the use of peanut shells, which are a waste material, for adsorption of heavy metals [59], dyes [60], organic solvents [61], antibiotics [62], and other pollutants. In this study, we used peanut shells and a synthetic material loaded with sulfonamide-degrading bacteria to prepare composite materials, and compared the removal rates of the original and composite materials. Orthogonal static experiments and dynamic experiments were used to study the adsorption-degradation effects of the materials. Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectrometry (FTIR) and other modern microscopic detection and analysis techniques were used to explore the mechanism of action.

2. Materials and methods

2.1. Materials

2.1.1. Instruments

The following instruments were used in this study: Agilent 1260 Infinity Series (Agilent, USA) for high performance liquid chromatography (HPLC), JSM-6700F (Japan Electronics Co., Ltd.) for SEM, FTIR-2000 (Perkin-Elmer,

Waltham, MA, USA) for FTIR, ESCALAB 250Xi (Thermo Fisher Scientific, USA) for XPS, Bettersize 2000 (Dandong Baxter Instrument Co., Ltd., China) for particle size analysis, and DDBJ-350 (Shanghai Precision Scientific Instrument Co., Ltd., China) for conductivity measurements.

2.1.2. Materials

2.1.2.1. Adsorbent materials and degrading bacteria

Peanut shells were purchased from a local farm in Jilin Province, China. Their composition is shown in Table 1. According to the continuously optimized technical scheme for synthetic materials [57], the mass fraction composition in this study was bentonite 70%, sodium chloride 5.6%, cetyltrimethylammonium bromide 6.4%, and fly ash 18%. The particle size composition of the synthetic material after preparation is shown in Table 2. The particle size of the material was small, with a mass median diameter of 18.38 μm. Sulfonamide-degrading bacteria were obtained from groundwater contaminated by sulfonamides in agricultural and livestock breeding areas.

2.1.2.2. Sulfonamides and main chemical reagents

Four sulfonamides (sulfamethoxazole (ST), sulfamethazine (SM), sulfamethazine (SM2), and SMX) were purchased from Sigma-Aldrich (St. Louis, MO, USA). The main chemical reagents used in the experiment were analytical grade $FeCl_3$, $MnSO_4$, NH_4Cl, $NaNO_3$, $NaNO_2$, NaOH, and HCl. Chromatography grade ethanol and formic acid were used for preparation of microbial cultures and determination of the sulfonamide concentrations.

2.2. Research methods

2.2.1. Adsorption of the supported materials

The peanut shells were washed with distilled water and dried in an oven at 40°C for 5 h. After drying, the peanut shells were crushed using a stainless steel mixer to reduce their particle size to 0.5–0.6 mm. Solutions were prepared of four sulfonamides mixed solution which each of the four sulfonamides at a concentration of 0.5 mg/L in ultrapure water. Next, 50 mL aliquots of the mixed solution were placed in 60 mL brown bottles containing 1.0 g of peanut shells with a particle size larger than 10 mesh. The bottles were placed in a shaking incubator at 100 r/min and 10°C and protected from the light. The pH in each bottle was between 7.0 and 8.0. After shaking for 0.5, 1, 2, 4, 8, 12, 16, 20, 24, or 48 h, a 0.5 mL aliquot of the supernatant was removed, filtered through cellulose membranes (0.22 mm), and then analyzed by HPLC to determine the concentrations of the sulfonamides.

For the experiments with the synthetic material, 20.0 g of synthetic material was prepared and 1.0 g was weighed into a 60 mL brown bottle. Next, 50 mL of the 0.5 mg/L mixed sulfonamide solution was added. The pH in each bottle was between 7.0 and 8.0. The mixture was stirred for 5, 10, 15, 20, or 25 min to allow for precipitation to occur. After precipitation, the supernatant was filtered through a 0.22 μm filter and the concentration of each sulfonamide in the filtrate was measured by HPLC. Blank and replicate samples were run for all experiments, and the average of the results for each set of replicates was taken as the final experimental result.

2.2.2. Preparation of the composite material

To optimize the immobilization conditions, a horizontal orthogonal test was carried out with the following three factors: the mass of the carrier (0.5, 1.0, or 1.5 g), the volume fraction of the inoculum (1%, 3%, or 5%), and the fixation time (24, 36, or 48 h). The orthogonal experiment details are given in Table 3. For each experiment, the sterilized carrier material (0.5, 1.0, or 1.5 g) was placed in a 60 mL brown bottle containing 50 mL of basal medium [63] and then inoculated with the bacterial suspension (1%, 3%, or 5% volume fraction). The bottles were shaken at 100 r/min and 10°C in the dark for 24, 36, or 48 h to allow the bacteria to fix to the carrier material. After the bacteria were sufficiently fixed on the carrier material, the solution was precipitated for 10 min and the supernatant was decanted to isolate the composite material, which was washed twice with physiological saline.

Ultrapure water was used to prepare solutions of the sulfonamides at a concentration of 0.5 mg/L. Fifty milliliters of this solution was placed into separate brown bottles containing the mass of composite material and volume fraction of inoculum detailed in Table 3. The bottles were then placed in a shaking incubator at 100 r/min and 10°C in the dark. The pH in each bottle was between 7.0 and 8.0. After shaking, a 0.5 mL aliquot of the supernatant was removed, filtered through a 0.22 μm filter, and analyzed by HPLC to determine the sulfonamide concentration.

Table 1
Particle sizes in the synthetic material

Particle size (μm)	Particle grading %
<5.314	9.62
5.314–10.77	14.34
10.77–21.82	35.76
21.82–44.23	27.72
>44.23	12.56

Table 2
Composition of the peanut shells

Composition	Mass content (%)
Crude protein	4.8–7.2
Crude fat	1–1.1
Crude fiber	65.7–79.3
Hemicellulose	10.1
Carbohydrates	10.6–21.2
Crude ash	1.9–4.6
Calcium	0.24–0.27
Phosphorus	0.08–0.09

Table 3
Orthogonal experiment investigating bacterial immobilization

Serial number	Attached material (g)	Inoculum volume %	Fixed time (h)
Experiment 1	0.5	1	24
Experiment 2	0.5	3	36
Experiment 3	0.5	5	48
Experiment 4	1.0	1	36
Experiment 5	1.0	3	48
Experiment 6	1.0	5	24
Experiment 7	1.5	1	48
Experiment 8	1.5	3	24
Experiment 9	1.5	5	36

The effects of the different factors on immobilization of degrading bacteria on the carrier material.

2.2.3. Dynamic experiments

2.2.3.1. Design and filling of the column for simulation

A miniature column (height: 10 cm, diameter: 3 cm) was used for the simulation. There was a water inlet at the top and a water outlet at the bottom of the column. Nylon mesh (30 μm pore size) was placed on the top of the column to prevent fine particles from entering the column and blocking the inlet and outlet. The column was filled with the composite material, which contained the degrading bacteria. The column was sterilized before filling and then washed with distilled water and allowed to air dry. After filling, the column was covered completely with black plastic film to simulate the underground environment. The experimental device is shown in Figs. 1a and b. A constant pressure bottle was used for the water supply.

The column was filled to a height of 10 cm with 22.3 g of peanut shells. To ensure the density in the column was uniform, the column was filled in layers of 2 cm at a time, making sure that each layer contained no voids or cracks. After filling, the inorganic salt culture solution [63] was used to saturate the water. After the column was completely immersed in water, the water supply was continued for 24 h.

2.2.3.2. Tracer experiment

The column was saturated with ultrapure water for 24 h before 0.1 mol/L NaCl was introduced for the tracer experiment. The conductivity was measured at the water outlet using a portable conductivity meter (DDBJ-350). The water flow rate was also measured at the water outlet, and the diffusion coefficient and the dispersion degree were calculated.

2.2.3.3. Dynamic adsorption of sulfonamides

A mixed solution containing the four sulfonamides at 0.5 mg/L was prepared in ultrapure water and injected into a constant pressure elution bottle. After the experiment, samples were taken from the water outlet every 20 min and tested by HPLC until the sulfonamide concentrations stabilized.

2.2.3.4. Experimental study on sulfonamide degradation

Purified and isolated degrading bacteria were inoculated into the basal medium [63], and an appropriate amount of Fe^{3+} was added to allow for stable growth of the bacteria. A stable phase was reached after 4 d of culture. The degrading bacteria were fixed on 1.5 g of peanut shell in 50 mL of medium with a 5% inoculum volume fraction and fixation time of 36 h. The column was then filled with the composite material, and basic medium containing glucose and yeast extract was supplied to the column. To reduce experimental test error and determine the instrument detection limit, sulfonamide concentrations of 0.05, 0.5, 1.0, and 5.0 mg/L were investigated. Samples were collected from the water outlet for HPLC analysis to evaluate the effect of the column on comprehensive removal of the four sulfonamides.

2.2.4. Determination of the sulfonamide concentrations

A 1260 Infinity Series HPLC (Agilent) equipped with an Eclipse XDB-C18 column (4.6 mm × 150 mm, 5 mm) was used to determine the sulfonamide concentrations. The column temperature was 30°C and the samples were detected with a UV detector at 270 nm. The mobile phase was a mixture of methanol and 0.1% formic acid (30:70, v/v) with a flow rate of 1 mL/min. The sample injection volume was 20 mL.

2.2.5. Adsorption mechanism on the composite material

2.2.5.1. Point of zero charge measurement of the surface of the composite material

The PZC on the surface of the peanut shell composite material was determined by the salt titration method [64]. In several 50 mL centrifuge tubes, add 0.1 g of composite material each, add an appropriate amount of distilled water and 0.01 mol/L HCl or NaOH, so that the final volume of the solution in the tube is 10 mL, and make the pH distribution in an appropriate range (1–6). After equilibration at 10°C for 3–4 d with shaking each day for 1 h, the $pH_{initial}$ of the suspension in each tube was recorded. Next, 0.5 mL of a 0.2 mol/L NaCl solution was added to each tube, the tube was shaken for 4 h, and the pH was recorded as pH_{final}. The change in pH was calculated as $DpH = pH_{final} - pH_{initial}$. The $pH_{initial}$ was plotted on the *x*-axis and DpH on the *y*-axis.

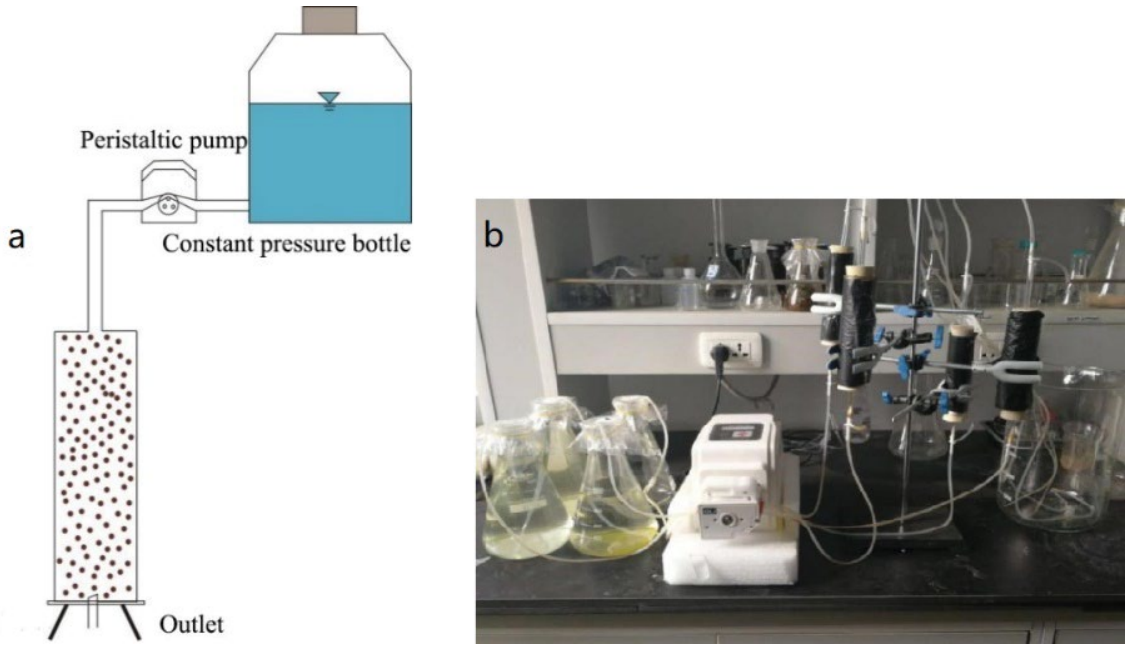


Fig. 1. (a) Schematic of the column for the simulation and (b) photograph of the device.

The pH value corresponding to ΔpH = 0 is the point of zero charge (PZC) of the sample.

2.2.5.2. Microstructural characteristics of the composite material

SEM was used to analyze the sulfonamide-degrading bacteria loading of the adsorbent material from a microscopic perspective, and changes in the microstructure before and after adsorbent loading were evaluated to characterize the microstructure of the medium. Energy dispersive X-ray spectroscopy (EDX) was used to determine the elemental composition. XPS was used to analyze changes in the surface elements and chemical bonds before and after adsorption of the sulfonamides. FTIR was used to analyze changes in the functional groups before and after adsorption of the sulfonamides to determine whether a chemical reaction occurred.

3. Results and discussion

3.1. Adsorption of sulfonamides on the materials

Adsorption of the four sulfonamides by peanut shells and the synthetic material was investigated (Figs. 2a and b). The adsorption rates of the peanut shells for the four sulfonamides were 72.81% (ST), 46.98% (SM), 45.08% (SM2), and 32.84% (SMX). The adsorption equilibrium was reached in about 12 h. The adsorption rates of the four sulfonamides by the synthetic material were 78.31% (ST), 12.77% (SM), 31.60% (SM2), and 21.38% (SMX). With the synthetic material, the adsorption reached a maximum value within 5 min

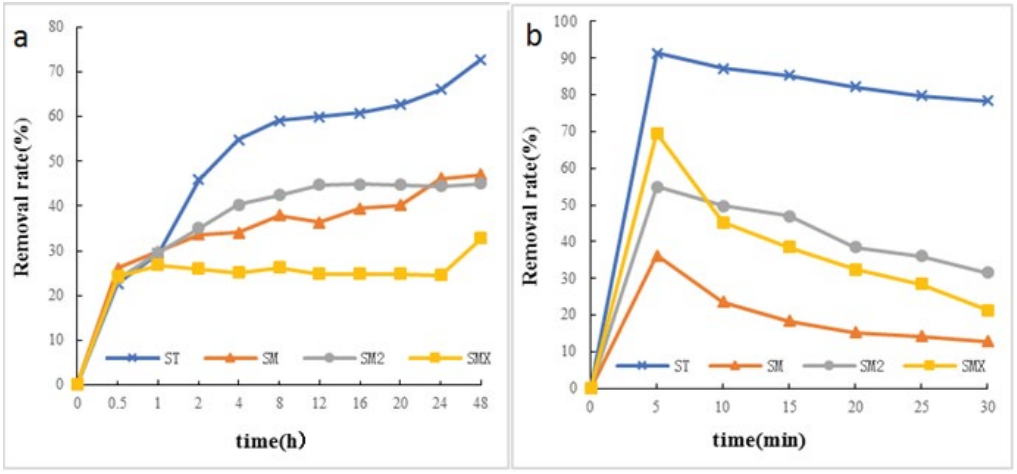


Fig. 2. Adsorption of sulfonamides with peanut shells (a) and synthetic material (b).

and then decreased slightly between 15 and 30 min. These results show that the synthetic material provides rapid adsorption but the adsorption decreases over time. Overall, the peanut shells provide better and more stable adsorption than the synthetic material.

3.2. Adsorption of sulfonamides on the composite material

Degradation of the four sulfonamides with the degrading bacteria was evaluated in nine experiments. The results of the degradation experiments with the peanut shell composite material are shown in Table 4. The average removal rates of the four sulfonamides with this material were 93.10% (ST), 66.22% (SM), 60.20% (SM2), and 62.95% (SMX). The maximum degradation rate for each sulfonamide was obtained in a different experiment, as follows: ST, experiment 3 (96.61%); SM, experiment 6 (80.91%); SM2, experiment 4 (75.96%); and SMX, experiment 9 (88.55%). The degradation results obtained with the synthetic material composite are shown in Table 5. The average removal rates of the four sulfonamides with this material were 90.61% (ST), 53.33% (SM), 61.82% (SM2), and 66.67% (SMX). These results showed that the synthetic material composite had no obvious advantage over the peanut shell composite. This may be because the synthetic material itself is a highly efficient adsorption medium and not suitable for immobilization of degrading bacteria. Attachment of the bacteria to the synthetic material could both reduce its adsorption effect and result in the degrading bacteria failing to exert their degradation effect. Therefore, peanut shells are more suitable as a supporting material for degrading bacteria than the synthetic material, and the synthetic material is more suitable as an adsorption medium for removing sulfonamides.

The effects of three factors in the preparation of the peanut shell composite were investigated using average degradation rates of the four sulfonamides (Table 6). The highest average adsorption rate for the four sulfonamides was obtained in experiment 9. The results indicated that the order of the factors in terms of their effects on the degradation rate was peanut shell mass > inoculum volume fraction > fixation time. Among the factors, the mass of peanut shell had the greatest influence on the degradation rate. This is because when the inoculum volume fraction was constant and the mass of peanut shell was low, there were fewer spaces available on the surface of the peanut shells for adsorption of bacteria. In this case, adsorption of the bacteria is incomplete and the quantity fixed on the peanut shells is low. This means that some of the degrading bacteria are present in a free form, the advantage of immobilization is not obvious, and the degradation rate is low. When the

Table 4
Orthogonal test results for the peanut shell composite material for degradation of sulfonamides

Serial number	Peanut shell g	Inoculum volume %	Fixed time h	ST degradation rate %	SM degradation rate %	SM2 degradation rate %	SMX degradation rate %
Experiment 1	0.5	1	24	96.31	55.69	48.71	46.45
Experiment 2	0.5	3	36	96.31	62.75	54.50	55.16
Experiment 3	0.5	5	48	96.61	58.71	46.08	46.75
Experiment 4	1	1	36	93.87	59.47	75.96	35.10
Experiment 5	1	3	48	90.20	48.77	42.30	52.68
Experiment 6	1	5	24	92.34	80.91	72.05	61.99
Experiment 7	1.5	1	48	92.68	70.82	68.26	85.42
Experiment 8	1.5	3	24	93.26	68.30	51.39	68.89
Experiment 9	1.5	5	36	89.69	78.39	71.38	88.55

Table 5
Orthogonal test results for the synthetic material composite for degradation of sulfonamides

Serial number	Synthetic material g	Inoculum volume %	Fixed time h	ST degradation rate %	SM degradation rate %	SM2 degradation rate %	SMX degradation rate %
Experiment 1	0.5	1	24	89.43	40.23	59.06	53.69
Experiment 2	0.5	3	36	87.15	44.65	59.13	57.98
Experiment 3	0.5	5	48	78.36	41.91	44.98	51.62
Experiment 4	1	1	36	94.26	58.96	53.43	46.93
Experiment 5	1	3	48	90.10	55.07	62.17	66.23
Experiment 6	1	5	24	91.26	52.68	61.79	71.90
Experiment 7	1.5	1	48	94.48	69.56	73.51	86.94
Experiment 8	1.5	3	24	95.78	66.25	66.33	75.81
Experiment 9	1.5	5	36	94.63	50.68	75.94	88.96

Table 6
Orthogonal test for degradation of sulfonamides by peanut shell immobilized bacteria

Serial number	Peanut shell g	Inoculum volume %	Fixed time h	Average degradation rate %
Experiment 1	0.5	1	24	61.79
Experiment 2	0.5	3	36	67.18
Experiment 3	0.5	5	48	62.00
Experiment 4	1.0	1	36	66.10
Experiment 5	1.0	3	48	58.50
Experiment 6	1.0	5	24	76.82
Experiment 7	1.5	1	48	79.30
Experiment 8	1.5	3	24	70.46
Experiment 9	1.5	5	36	82.00
Average value 1	63.66%	69.06%	69.69%	
Average value 2	67.14%	65.38%	71.76%	
Average value 3	77.25%	73.61%	66.60%	
Standard deviation	48.01%	17.00%	6.74%	

inoculum volume fraction is too high, the degradation rate may decrease because fewer sulfonamides are adsorbed by the peanut shell per unit area, and the available carbon source of the bacteria is reduced, which affects the growth of bacteria and reduces the degradation rate of the sulfonamides. The effect of the inoculum volume fraction was mainly related to the fact that when the inoculum volume fraction was low, there were fewer fixed bacteria, which naturally resulted in low degradation rates. By contrast, when the inoculum volume fraction was high, there would be a high density of bacteria on the peanut shells and the bacteria would compete for nutrients, which will affect their growth and result in a low degradation rate [65]. The fixation time had little effect on the degradation rate, which may be because immobilization of bacteria on the peanut shells is a slow process. Initially, there would be sufficient channels on the surface of the peanut shells to adsorb the degrading bacteria. Over time, many bacteria would become immobilized on the surface of the peanut shells and a saturation point would be reached. When this point was reached, further increases in the fixation time would have a minimal effect and changing the fixation time would have little effect on the degradation rate. Removal of the four sulfonamides was optimized in experiment 9 and the optimum conditions for fixation of the degrading bacteria were a peanut shell mass of 1.5 g, inoculum volume fraction of 5%, and fixation time of 36 h. Because the effects of the inoculum volume fraction and fixation time on the fixation of degrading bacteria were minimal, the inoculum volume fraction could be varied between 1% and 5% and the fixation time between 36 and 48 h without greatly affecting the results.

3.3. Dynamic experiments

3.3.1. Tracer experiment results

The tracer experiment was carried out using 0.1 mol/L NaCl with a flow rate of 1 mL/min. Fig. 3a shows the standard curve of the relationship between the NaCl solution concentration and conductivity. The linear equation was $y = 0.5634x - 136.06$ with $R^2 = 0.9995$. The solution concentration was calculated from the measured conductivity and the results are shown in Fig. 3b. The column effluent concentration reached that of the influent at 137 min. The diffusion coefficient and the dispersion were calculated using the measured data and the one-dimensional convection dispersion model (Eqs. (1) and (2)), and the results were $D_L = 8.04$ cm^2/min and $\alpha = 8.04$ cm.

$$D_L = \frac{1}{8}\left[\frac{x - vt_{0.16}}{\sqrt{t_{0.16}}} - \frac{x - vt_{0.84}}{\sqrt{t_{0.84}}}\right]^2 \quad (1)$$

$$\alpha = \frac{D_L}{V}\ldots, \quad (2)$$

where D_L is the longitudinal diffusion coefficient; α is the degree of dispersion; x is the distance from the tracer inlet to the monitoring point; and $t_{0.16}$ and $t_{0.84}$ are the times when the tracer concentration in the effluent solution is 16% and 84% of the initial concentration, respectively.

3.3.2. Analysis of the dynamic adsorption experiment results

With a water supply flow rate of 1 mL/min, migration of the four sulfonamides through the peanut shell medium reached equilibrium at 10 h (Fig. 4). SMX was first detected in the effluent, about 2 h after starting the simulation with the column, and this was followed by detection of SM at about 2.5 h and ST and SM2 at about 2.8 h. The migration abilities of the four sulfonamides were in the order SMX > SM > SM2 > ST. SMX penetrated the column first at 6 h and ST penetrated the column at 10 h.

3.3.3. Degradation experiments

The concentrations of the four sulfonamides detected at the column outlet in the simulation are shown in Fig. 5.

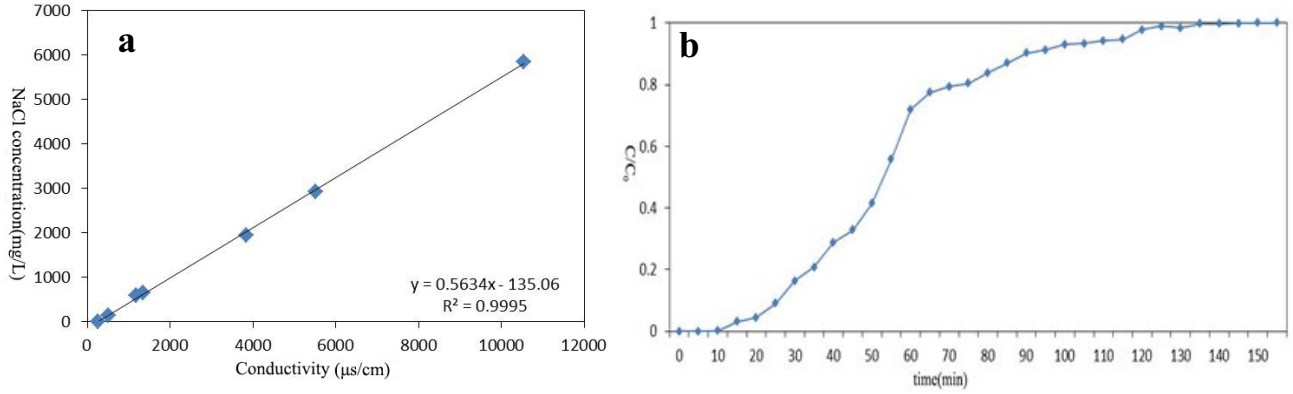


Fig. 3. (a) Tracer test standard curve and (b) tracer curve with column used in simulation.

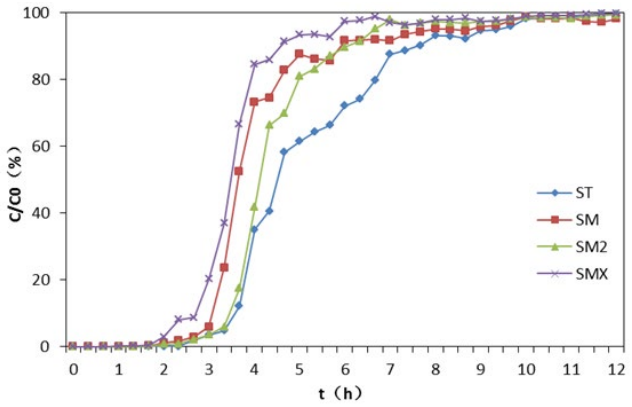


Fig. 4. Changes in the concentrations of the four sulfonamides in the simulation experiment over time.

ST had the highest removal rate (³90.00%) at all concentrations, followed by SM (>80.00%) (Fig. 6). For SM2 and SMX, removal was better at low concentrations. When the sulfonamide concentration was 0.05 mg/L, the removal rates for SM2 and SMX were 64.25% and 75.03%, respectively. When the sulfonamide concentration was increased to 5 mg/L, the removal rates for SM2 and SMX decreased to 31.75% and 39.75%, respectively. The average removal rate of the four sulfonamides on the column in the simulation was 79.89% with a low sulfonamide concentration (0.05 mg/L) and 61.53% with a high sulfonamide concentration (5.0 mg/L).

The peanut shell composite material showed good removal at both low and high sulfonamide concentrations. The method is inexpensive and is not easy to cause secondary pollution, and can remove sulfonamides from water.

3.4. Analysis of the adsorption mechanism

3.4.1. Surface electrostatic force analysis

The PZC is the value when the variable charge on the colloidal surface is zero. When the pH value in the system is less than the PZC, the variable charge on the surface is positive; when the pH is greater than the PZC, the variable charge on the surface is negative; and when the pH is equal to the PZC, the total net charge is zero [66]. Unlike other organic molecules, sulfonamides have dissociable amino and amido groups in their structures [67]. Under certain pH conditions, the amino group can acquire a proton to make the structure positively charged and the amide group can release a proton to make the structure negatively charged [67,68]. At $pH_{PZC} < 2$, the amino group gradually dissociates and the sulfonamides are mainly cationic. At $pH_{PZC} > 8$, the amino group gradually dissociates, and the sulfonamides are mainly anionic. When the pH_{PZC} is between 3 and 5, sulfonamides is dominated by molecular states. At pH_{PZC} ranges of 2–3 and 5–8, 50% is in each of the ionic and molecular states [69]. The PZC of peanut shells is around $pH_{PZC} = 3.9$ (Fig. 7). In a neutral sulfonamide solution, the surface of the peanut shells is negatively charged, and half of the sulfonamide solution is in each of the ionic and molecular states. Peanut shells adsorb dissociated amino groups. Because of the low ion content in the solution, the electrostatic adsorption effect of peanut shells toward sulfonamides is very small.

3.4.2. Microstructural characteristics of the composite materials

SEM was used to characterize the morphology of the material before and after the immobilization of the degrading bacteria on the peanut shells (Fig. 8). Before immobilization of the bacteria, the surface of the original peanut shell was covered with folds and porosity, which increased its surface area. These folds and porosity could adsorb sulfonamides and provide sites for immobilization of the degrading bacteria. After the degrading bacteria were immobilized on the peanut shells, mixed flora appeared in clusters. The morphology of the bacteria was uniform, and extracellular polymers produced by the cells enhanced the adhesion of the bacteria to the carrier material. The activity of the bacteria was not affected, indicating that the carrier had good bioaffinity.

Fig. 9 shows the results from EDX elemental analysis of the peanut shell composite material. The main elements in the composite material were C, N, and O, and it contained small amounts of Ca, Mg, S, P, and K. The empirical molecular formula of microbial cells is $C_5H_7O_2N$, with C accounting for about 50% of the cell dry weight and N accounting

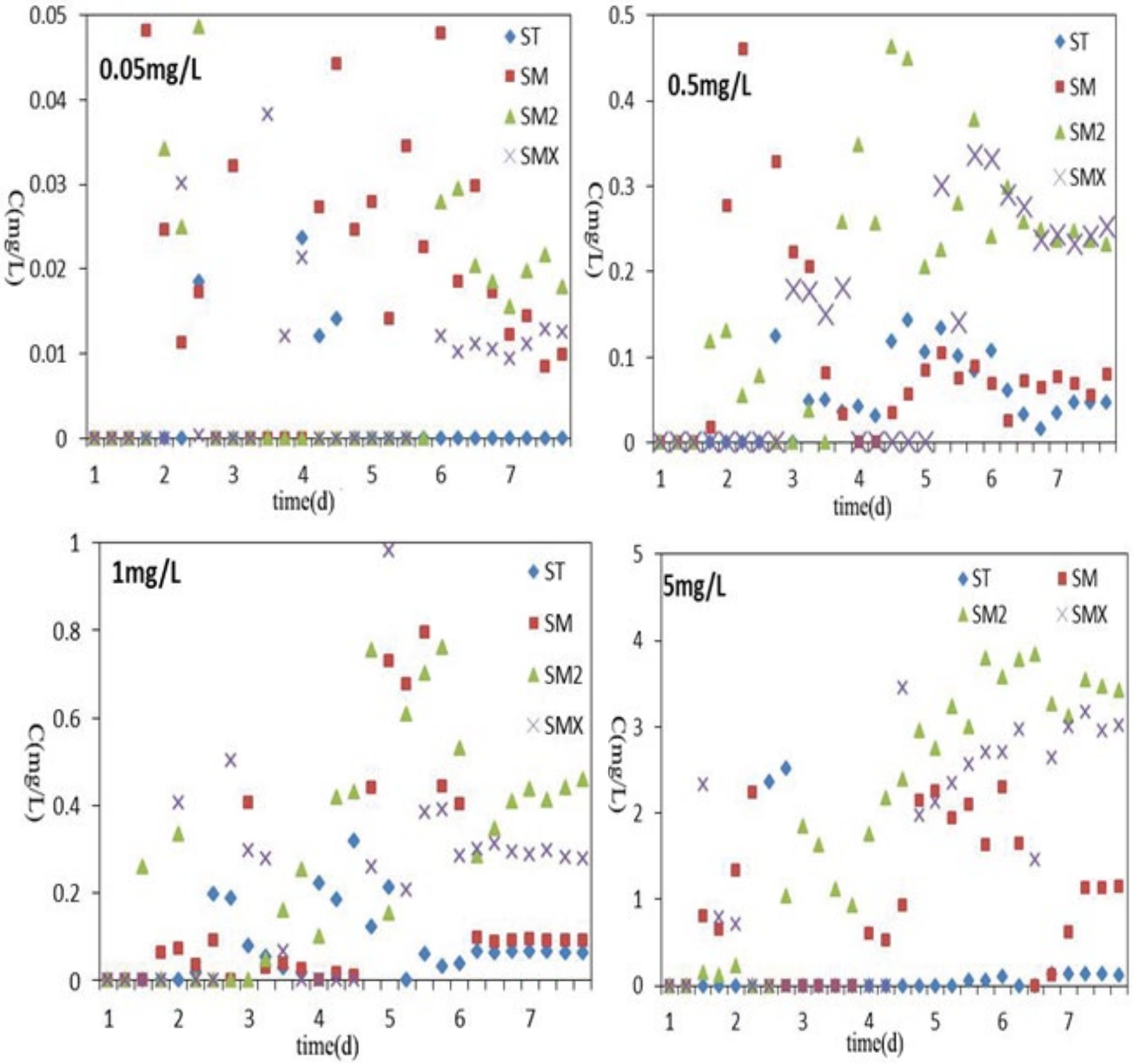


Fig. 5. Detected concentrations of sulfonamides at the column outlet in the simulation.

for about 9% of the cell dry weight [70]. Microbial cells also contain trace amounts of P, K, Ca, and Mg, among which P accounts for 1.4%–4.7% of the cell dry weight and K accounts for 0.1%–0.4% of the cell dry weight [70]. The peanut shell contained C, O, Ca, and P. The types of elements and their contents on the surfaces of the peanut shells and synthetic material basically conformed to the elemental composition of microbial cells.

The XPS spectrum and high-resolution spectrum of the peanut shell composite material are shown in Fig. 10a. The spectrum of the peanut shell showed three peaks for C1s, N1s, and O1s (Fig. 10a). High-resolution spectra of C1s, N1s, and O1s are shown in Figs. 10b–g. In the high-resolution XPS spectra of C1s (Figs. 10b and c), three peaks were observed at 284.5, 285.4, and 288 eV, which could be attributed to C–H, C–OH, and C=O [71,72], respectively. The N1s spectra (Figs. 10d and e) contained two peaks at 399.8 and 401.1 eV, corresponding to N–C and NH–C=O [73,74], respectively. The high-resolution XPS spectra of O1s (Fig. 10f and g) had peaks at 533.4 and 531.5 for C–O and –OH, respectively [75–78]. The C1s score level spectrum showed that the ratio of C–H to C=O groups in the peanut shell before adsorption–degradation of the sulfonamides was larger than that afterwards. The N1s spectrum showed that the N=C–H peak was larger before adsorption–degradation of the sulfonamides than that afterwards. In the O1s spectrum, the ratio of C–O to –OH before adsorption–degradation of the sulfonamides was larger than that afterwards. Therefore, C–O, –OH, N=C–O, C–H, and C=O are involved in the adsorption and degradation of the sulfonamides.

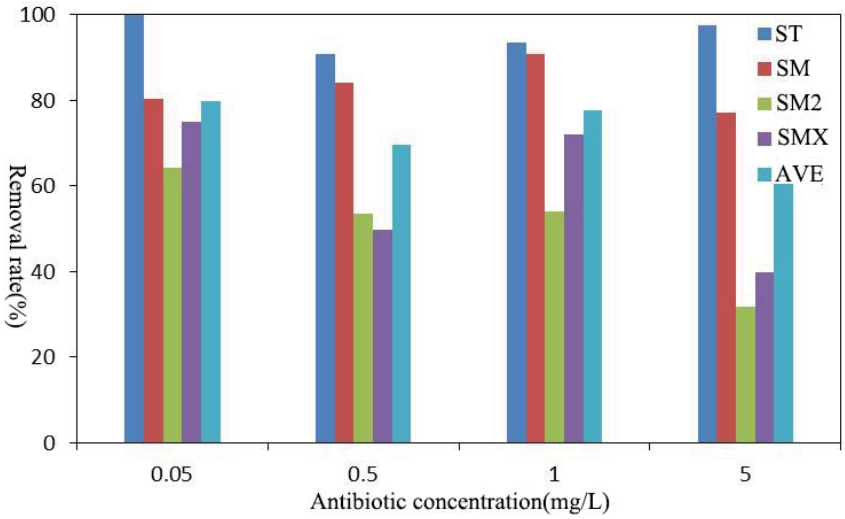


Fig. 6. Removal rates of the sulfonamides at different concentrations using the column in the simulation.

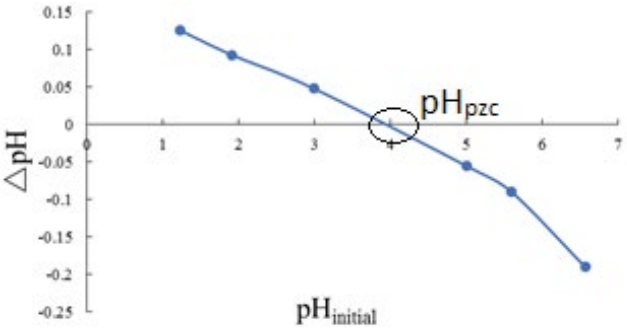


Fig. 7. Point of zero charge results for the peanut shells.

The adsorption mechanism was analyzed using FTIR spectra. Comparison of the results for the peanut shell composite before and after adsorption of sulfonamides (Fig. 11) showed that the main absorption peaks of the peanut shell composite were at 650; 1,000–1,050; 1,500–1,550; 1,600–1,700; 2,300–2,400; 2,800–3,000; and 3,300–3,600 cm^{-1}. The functional group region had a wavenumber range of 1,300–4,000 cm^{-1} and could be divided into four main bands. The first band at 2,500–4,000 cm^{-1} was for stretching vibrations of groups containing a hydrogen atom (i.e., *x*–H where *x* is O, N, or C) [79–81]. The first two absorption peaks of the peanut shells are located in this band. The band at 3,300–3,600 cm^{-1} could be ascribed to N–H of peanut shell composite [82]. There was a large increase in the size of this band after adsorption, which indicates it plays an important role in adsorption of the sulfonamides. The band at 2,800–3,000 cm^{-1} could be ascribed to C–H of peanut shell composite [73,83]. The $–CH_3$ of peanut shell composite peak at 2,875 cm^{-1} increased slightly and the $–CH_2–$ of peanut shell composite [84,85] peak at 2,850 cm^{-1} decreased after adsorption of the sulfonamides.

The band from 2,000 to 2,500 cm^{-1} is for triple bond and cumulative double bond stretching vibrations, which mainly includes the stretching vibrations of –C≡C–, –C≡N, C=C=C, C=C=O, and other asymmetric stretching vibrations of double bonds. Stretching vibrations for S–H, Si–H, P–H, and B–H are also observed in this region. A peak at

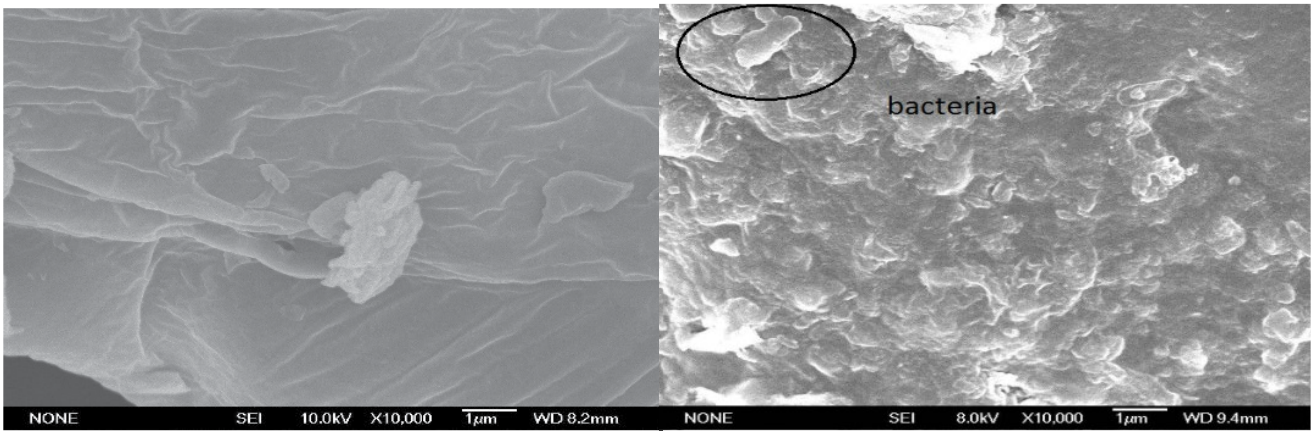
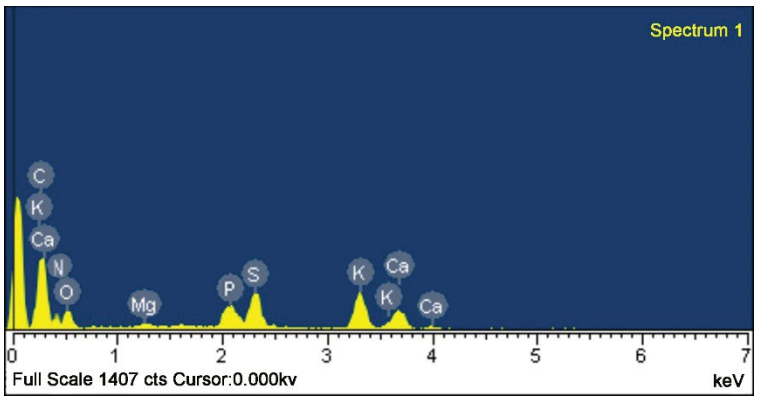


Fig. 8. SEM images before (left) and after (right) immobilization of degrading bacteria on the peanut shells.



元素	含量/%
C	54.01
N	15.24
O	0.50
Mg	6.44
P	9.25
S	5.11
K	4.32
Ca	5.13

Fig. 9. EDX elemental analysis results for the peanut shell composite material.

2,300–2,400 cm^{-1} in this region was for the peanut shell composite and did not show any obvious changes, which indicates it did not participate in adsorption of the sulfonamides. The region from 1,500 to 2,000 cm^{-1} was for double bond stretching vibrations. The peak at 1,600–1,700 cm^{-1} was for the peanut shell composite C=O stretching, and this increased slightly after adsorption. The peak at 1,500–1,550 cm^{-1} was for stretching vibrations of C=N [86,87], C=C, and N=O [88,89]. The C=C skeleton vibration (breathing) of mononuclear aromatic hydrocarbons usually exhibits between two and four characteristic absorption peaks at around 1,600 and 1,500 cm^{-1}. In the present study, a peak was observed at 1,500 cm^{-1}, which confirmed that the peanut shell composite contained C=C bonds. This peak did not change much after adsorption of the sulfonamides, so it is not the main chemical bond involved in the adsorption. The region from 1,300 to 1,500 cm^{-1} is for the saturated C–H deformation. The peanut shell peak in this region showed no obvious change after adsorption of the sulfonamides. The region from 1,000 to 1,050 cm^{-1} is for the C–O single bond vibration [90,91], and the peak in this region increased slightly after adsorption. The peak at 650 cm^{-1} is located in the fingerprint region. The peak at 650 cm^{-1} is for six unsubstituted C–H single bonds, and decreased slightly after adsorption of the sulfonamides. In summary, the adsorption of sulfonamides by peanut shell composite resulted in changes to N–H, $–CH_3$, $–CH_2–$, C=O, and C–H bonds on the surface of the peanut shell composite.

4. Conclusions

In this study, peanut shells and a synthetic material were compared for adsorption of four kinds of sulfonamides. The results showed that the overall adsorption effect of the peanut shells was better than that of synthetic material. With the synthetic material, the adsorption rates of the four sulfonamides were 78.31% (ST), 12.77% (SM), 31.60% (SM2), and 21.38% (SMX), and the maximum rates were reached within 5 min. In this case, although the adsorption rates were good, but the subsequent adsorption rate will decrease. With the peanut shells, the adsorption rates of the four sulfonamides were 72.81% (ST), 47.98% (SM), 45.08% (SM2), and 32.84% (SMX), the adsorption equilibrium was reached in about 12 h, and the adsorption performance was stable. Comparison and analysis of the degradation effects of the two kinds of composite materials on the degradation of the four sulfonamides showed that the synthetic material composite had no obvious advantage over the peanut shell composite for the overall degradation effect. Therefore, peanut shells are a more suitable carrier material for degrading bacteria. The optimum experimental conditions from the orthogonal experiment were a basic medium volume of 50 mL, peanut shell:bacteria inoculum ratio of 1.5 g/2.5 mL (5% inoculum volume fraction), and fixation time of 36 h. The average removal rate of the four sulfonamides was 82.00%. The effects of the inoculum volume fraction and fixation time on fixation of the bacteria were relatively small and they could be varied within ranges of 1%–5% and 36–48 h, respectively, without greatly affecting the results. The degradation rates of the four sulfonamides on the composite material were higher than those on the synthetic material, as shown by the following comparisons: 90.61% > 78.31% for ST, 53.33% > 12.77% for SM, 61.82% > 31.60% for SM2, and 66.67% > 21.38% for SMX. The average adsorption rates for the four sulfonamides on the of peanut shell composite material were higher than those on peanut shell, as shown by the following comparisons: 89.69% > 72.81% for ST, 78.39% > 47.98% for SM, 71.38% > 45.08% for SM2, and 88.55% > 32.84% for SMX. These results showed that the composite material had the best removal efficiency for the sulfonamides. Addition of sulfonamide-degrading bacteria to the peanut shells increased the sulfonamide removal rate by about 20%. The removal rate of sulfa antibiotics by peanut shell composites is greater than that of similar types of biochar [43], powdered activated carbon [44], composite material CoFeM48 [45] and single microorganism degradation [49–53].

The dynamic effects of the composite material were studied in a micro-simulation with a column. In this simulation, the highest removal rate was obtained for ST (>90.00%), followed by SM (>80.00%). The removal rates for SM2 and SMX were better at low concentrations than at high concentrations. The average removal rate of the four kinds of sulfonamides by the column was 79.89% at a low concentration (0.05 mg/L) and 61.53% at a high concentration (5.0 mg/L).

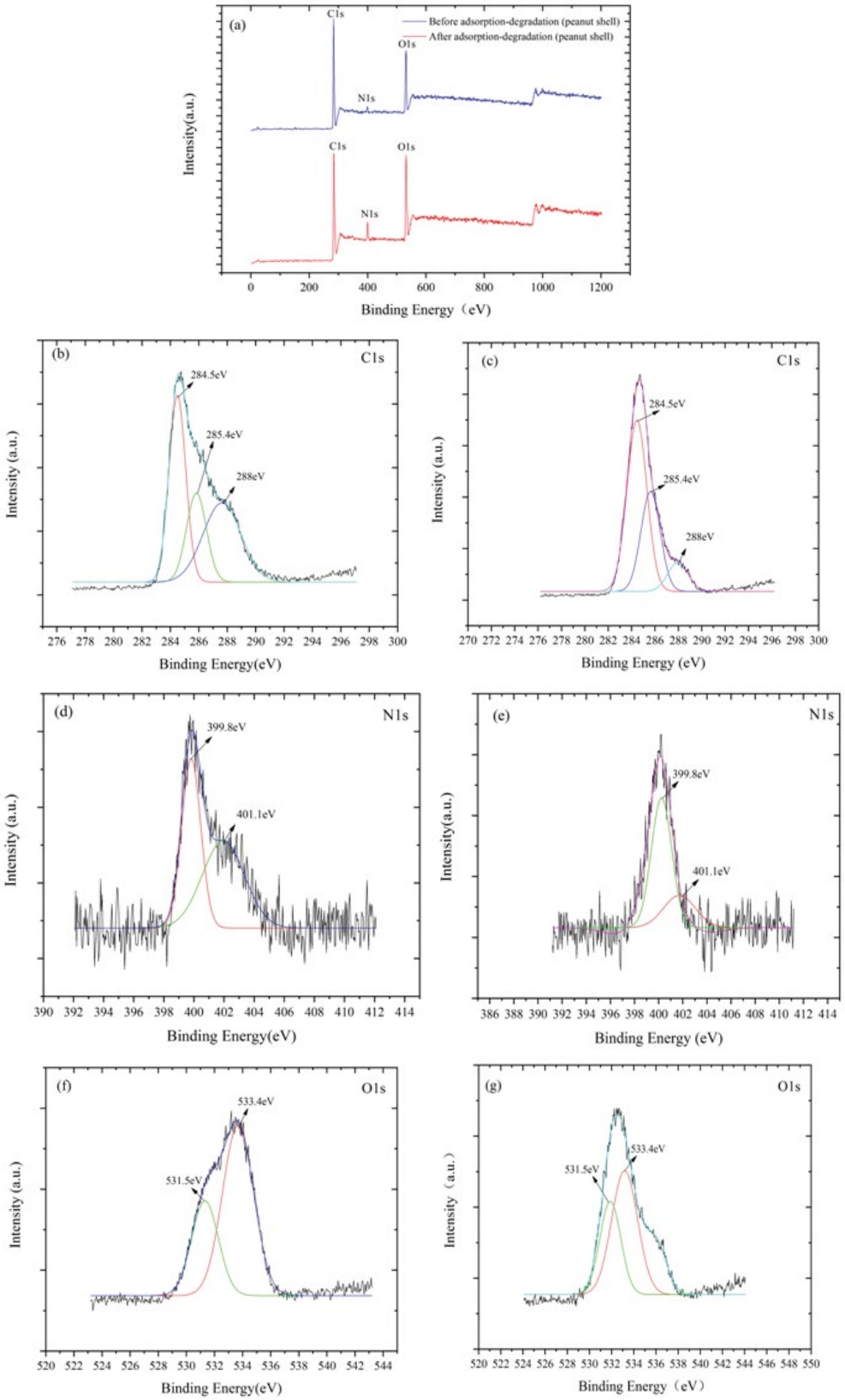


Fig. 10. (a) XPS wide scan spectra, (b, d, and f) high-resolution XPS spectra for C1s, N1s, and O1s, respectively, in the peanut shell material before adsorption of the sulfonamides; (c, e, and g) C1s, N1s, and O1s, respectively, in the peanut shell material after adsorption of the sulfonamides.

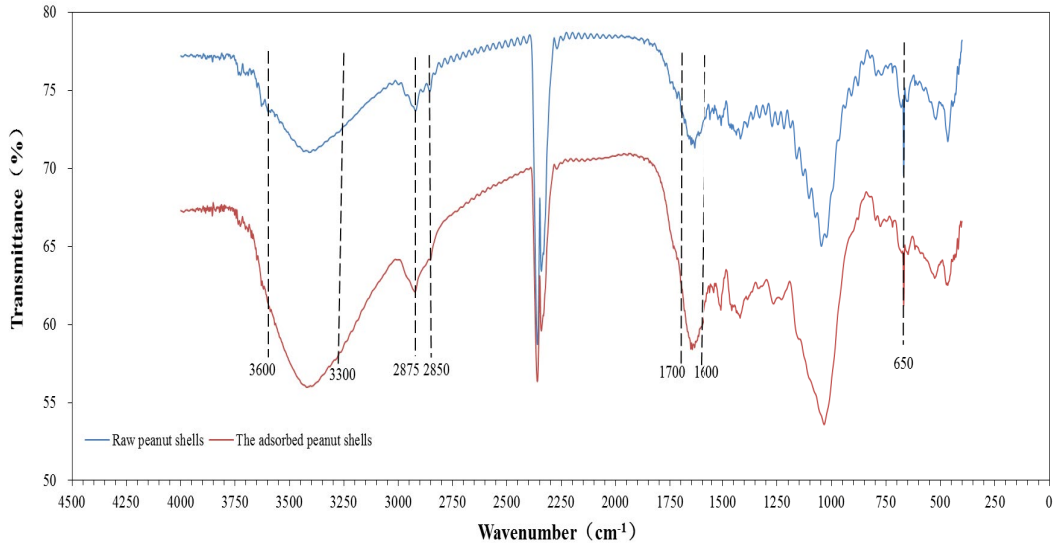


Fig. 11. Comparison of the Fourier-transform infrared spectra of the peanut shell composite material before and after adsorption of sulfonamides.

SEM was used to analyze immobilization of bacteria on the peanut shells from a microscopic perspective. Microstructural changes in the medium were evaluated by comparing the results obtained before and after loading of the bacteria on the adsorbent. The surface of the original peanut shell was covered with folds and porosity that could absorb sulfonamides and provide sites for fixation of the degrading bacteria. Mixed flora grew in clusters and extracellular polymeric substances produced by the cells enhanced their adhesion to the carrier material. The peanut shells had good bioaffinity. EDX was used to analyze the elemental composition of the peanut shell composite, and the results showed that the element types and contents on the peanut shell composite surface were basically in accordance with the elemental composition of the bacterial cells. XPS was used to analyze the mechanism of sulfonamide removal by adsorption–degradation. The main components of the peanut shell involved in adsorption of the sulfonamides were C, N, O, C–O, –OH, N=C–O, CH, and C=O. Further study using FTIR revealed that C=O, C–H, N–H, $–CH_3$, and $–CH_2–$ functional groups changed during adsorption of the sulfonamides by the peanut shell composite.

The removal of sulfonamides from water by peanut shells occurs mainly via physical and chemical adsorption, and biological effects. The physical and chemical adsorption are mainly related to the porous structure and active functional groups on the surface of the peanut shells. Biodegradation mainly involved metabolism by sulfonamide-degrading bacteria immobilized on the peanut shells. There are two main stages in this process. The first stage is the main adsorption process where adsorption on the composite material rapidly reduces the concentration of sulfonamides in water. The second stage is the biodegradation process where bacteria immobilized on the carrier degrade sulfonamides with the adsorbate as a carbon source, and are finally mineralized to carbon dioxide and water. This restores the adsorption capacity of the carrier material. The two stages form a short-term dynamic equilibrium, which is consistent with the adsorption-associated biodegradation model proposed by Wang et al. [92].

Fixation of degrading bacteria on peanut shells is a simple method for producing a material that has high degradation rates for sulfonamides. Because peanut shells are a readily available raw material, they could easily be applied to treatment of antibiotic pollution in water. This method has good application prospects because it provides both remediation of environmental pollution and improves the overall economic benefits of peanuts.

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