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Adsorption Behaviors of Benzonic Acid by Carboxyl Methyl Konjac Glucomannan Gel Micropheres Cross-Linked with Fe^{3+}

Bi Wang,*[†,‡] Limin Liao,[†,‡] Qihui Huang,[†] and Yongxiang Cheng[†]

[†]College of Chemistry and Chemical Engineering, Neijiang Normal University, Sichuan 641112, China

[‡]Key Laboratory of Fruit Waste Treatment and Resource Recycling, Sichuan 641112, China

ABSTRACT: Ferric carboxylmethyl konjacglucomannan gel microspheres (CMKGM-Fe) were prepared by cross-linking carboxyl methyl konjac glucomannan (CMKGM) with ferric ions (Fe^{3+}). The complex of CMKGM-Fe/benzoic acid was characterized by IR spectroscopy. The adsorption capacity of CMKGM-Fe for benzoic acid was studied by UV−vis spectroscopy. Several parameters including the adsorption time, temperature, microsphere size, and the concentrations of CMKGM, $FeCl_3$, and benzoic acid were investigated. The results showed that adsorption equilibrium could be established in about 11 h. When the temperature was 298 K, the CMKGM concentration was 1.5 % (w/v), the mass ratio of Fe^{3+} was 2.5 % (w/v), and the initial concentration of benzoic acid was 1000 $mg \cdot L^{-1}$ and the adsorption capacity attained 0.4954 $mmol \cdot g^{-1}$. According to the adsorption isotherms of benzoic acid on CMKGM-Fe, the thermodynamic parameters of adsorption process were calculated. The experimental data were fitted with the Freundlich equation, and it was found that the equation was suitable for the study of the investigated adsorption system. The entropy value of the system is negative, and cooling is beneficial for the adsorption, suggesting that the system is a spontaneous exothermic process.

1. INTRODUCTION

Benzoic acid and its derivatives are important raw materials and are widely used in production of dyes, medicines, and so forth. On the other hand, these chemicals are toxic compounds. They may be carcinogenic, mutagenic, and teratogenic. Therefore, the pollution in the water, soil, and air caused by wastewater produced during the production and applications of benzoic acid and its derivatives poses a “serious public health threat”.[1] In the past decade, studies on the application of sorbents to reduce and eliminate environmental organic pollutants or metal ions have become active. Micro-organisms, chitosan, agricultural solid waste, and other substances used for the adsorption of metal ions in water have been widely reported.[2−13] The applications of sorbents to reduce and eliminate environmental pollution of the benzoic acid and its derivatives have attracted more and more attention. Materials such as resin, silica gel, and chitosan have been used for the adsorption of benzoic acid.[14−17] However, to the authors' knowledge, there is no report of using glucomannan and its derivatives to adsorb benzoic acid so far.

Konjac glucomannan (KGM) as reserve polysaccharide is stored in konjac tuber. It is a class of polysaccharides which can be obtained by linking β-D-glucose and β-D-mannose through a β-1,4-glycosidic bond. Compared with other polysaccharide compounds, KGM, with specific physical and chemical properties, has been widely used in food, packaging, coatings, and biomedical fields.[18,19] However, the natural KGM has some drawbacks such as the poor rheology, poor stability of its aqueous solution, ease to degrade, and difficulty of storage. KGM microspheres are formed under near-neutral conditions, and they swell and decompose in water rapidly. All of these shortcomings limit its applications. To improve the physical chemical and biological properties of KGM, certain methods have been used to modify KGM.[20−22] Carboxyl methyl konjac glucomannan (CMKGM) is the carboxymethylation product of glucomannan.[20] It is easily soluble in water because of its strong hydrophilic nature. The stability of its colloidal solution and the ability for microsphere formation are greatly improved compared with KGM. Also, its resistance to mold is significantly enhanced. Therefore, compared with KGM, CMKGM has a broader field of applications. Some researchers modified KGM for the absorption of tannins,[21] copper, lead,[22] cadmium, and other heavy metal ions in water.[23−27] There are also some reports on the preparation of strong acid ion-exchange resin (SHPCMKGM) based on modified KGM.[28,29] It was also found that KGM microspheres coupled with diethyl aminoethyl (DEAE) groups can prepare a new type of anion exchange media which with has excellent performance and is less costly.

Fe^{3+} can be precipitated with benzoic acid in water, but the direct use of iron salts may produce secondary pollution. In the present study, based on the fact that Fe^{3+} can gelatinize CMKGM and it also has an affinity for the carboxyl group, CMKGM was prepared from the carboxymethylation of glucomannan first. Then ferric carboxyl methyl konjac glucomannan gel microspheres (CMKGM-Fe) were produced via the cross-linking ferric ion (Fe^{3+}) and CMKGM. Digital microscope and scanning electron microscopy were used to characterize the morphology of the microspheres. The performance of CMKGM-Fe as an absorbent for benzoic acid was studied. The effects of adsorption time, temperature, microsphere size, and concentrations of $FeCl_3$, CMKGM, and benzoic acid were investigated. This study provides the data for adsorption and separation of environmental pollutant benzoic acid.

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2. EXPERIMENTAL SECTION

2.1. Instruments and Materials. A digital microscope (Motic SMZ-168 digital microscope equipped with a Moticam2506 digital camera, from China Motic) and a scanning electron microscope (SEM, JSM-5900LV from JEOL Corporation of Japan) were used for the studies on the morphology of the microspheres. The UV−vis spectra were collected on a Hitachi 4600 UV−vis spectrophotometer (Hitachi, Japan). pH measurements were conducted using a pHS-3C precision pH meter (China Shanghai Precision Instrument Factory).

KGM was provided by China Chengdu Xieli Corporation with a concentration > 98 % and an average molecular weight of 220 kD; chloroacetic acid, anhydrous ethanol, sodium hydroxide, benzoic acid, and other chemicals were provided by China Chengdu Kelong Chemical Reagent Factory and with purity of > 99 %. Double-distilled water was used in this study.

2.2. Experimental Methods. *2.2.1. Preparation of CMKGM.* CMKGM was prepared according to the method described in literature,[20] and its degree of etherification was 0.78. In this method, 30 mL of 80 % (v/v) ethanol, 6.0 g of KGM, and 4.00 g of $ClCH_2COOH$ were put into a three-necked flask. The mixture was stirred for 2 h at 293 K and then heated to 328 K. After 20 mL of 80 % (v/v) ethanol and 5.00 g of NaOH were added, the mixture was continuously stirred for 3 h and then filtered by a filter paper of 11 μm. The filtrate was repeatedly washed with 85 % ethanol until the solution was neutral. The filtrate was soaked with ethanol and kept at 277 K overnight. Then it was filtered again, and the filtrate was vacuum-dried at 333 K and milled to get the desired CMKGM.

2.2.2. Preparation of CMKGM-Fe. CMKGM solution of certain concentrations was prepared first. Under stirring, a certain amount of CMKGM was injected into $FeCl_3$ solution with a syringe. After a solidification process of 12 h, the resulted gel was filtered and dehydrated in double-distilled water for 3 h. The prepared ferric carboxylmethyl konjacglucomannan gel microspheres (CMKGM-Fe) were filtered and stored in a dry conical flask for further use.

2.2.3. Study of CMKGM-Fe Adsorption Behaviors for Benzoic Acid. The CMKGM-Fe (dry weight 0.03 g) was placed in a 100 mL conical flask, then 50 mL of benzonic acid solution of a set concentration was added. Double-distilled water was used as a reagent blank. Under a set temperature, the CMKGM-Fe was put in the water bath oscillator at 150 $r \cdot min^{-1}$ for a set time. Then, the concentration of benzoic acid in the residual solution was estimated using the UV−vis absorbance at 227 nm.[15] The concentration difference between original solution and residual solution was used to calculate the adsorption capacity ($mmol \cdot g^{-1}$) according to the following equation: $q_e = [C_0 - C_e] \cdot V/m]$, in which q_e is the equilibrium adsorption capacity ($mmol \cdot g^{-1}$); C_0 and C_e are initial concentration and equilibrium concentration ($mmol \cdot L^{-1}$); V is the volume of solution (L), and m is the weight gel microsphere (g). Five parallel tests were conducted on each sample.

2.2.4. Mechanical Strength of Gel Microspheres. The gel microspheres were placed between two glass slides, and then weights were added on the upper slide until the gel microsphere was crushed. The final weight of the weights was used to represent the strength of the microspheres. Three parallel tests were carried out on gel microspheres of similar sizes.[30]

2.2.5. Structure Characterization of CMKGM-Fe. CMKGM, iron-cross-linked CMKGM gel, and a complex of CMKGM-Fe/benzoic acid were compressed into pellets using KBr, respectively, and the pellets were analyzed using Fourier transform infrared (FTIR) spectroscopy. The morphological structure of the CMKGM-Fe was illustrated applying a JSM-5900LV scanning electron microscope.

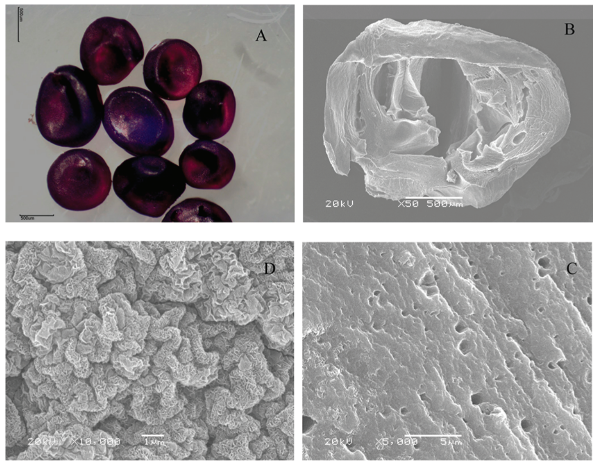

Figure 1. Images of CMKGM-Fe microspheres (shown clockwise from the top left): (A) digital microscope photograph of the CMKGM-Fe microspheres; (B) SEM photograph of the CMKGM-Fe cross section 1; (C) SEM photograph of the CMKGM-Fe cross section at a larger magnification; (D) SEM photograph of the CMKGM-Fe surface.

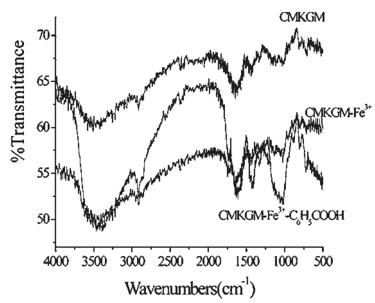

Figure 2. FTIR spectra of CMKGM, CMKGM-Fe^{3+}, and CMKGM-Fe^{3+}-C_6H_5COOH.

3. RESULTS AND DISCUSSION

3.1. Morphology of a Microsphere. Digital micrographs and scanning electron micrographs of microspheres are shown in Figure 1. The CMKGM-Fe's are brown hollow spheres with particle size between (0.8 to 0.90) mm and a smooth surface (Figure 1A). The surface and cross section of the material was further observed by scanning electron microscopy (Figure 1B, C, and D). A hollow was observed in the material. There are holes in the inside of gel microspheres, but the surface is uniform with no holes (Figure 1D).

3.2. FTIR Spectra. FTIR spectra of CMKGM, CMKGM-Fe^{3+}, and CMKGM-Fe^{3+}-C_6H_5COOH are shown in Figure 2. The absorption peak of the CMKGM at 3369 cm^{-1} was from the hydroxyl's absorption peak of the carboxymethyl group. At 1602 cm^{-1} and 1456 cm^{-1}, there were two characteristic absorption peaks of the carboxyl group. When CMKGM reacted with Fe^{3+}, the absorption peak near 1750 cm^{-1} was shifted to 1704 cm^{-1}, and the absorption peak near 1650 cm^{-1} shifted to 1635 cm^{-1}. All of the facts showed above indicate that the coordination of COO^- and Fe^3

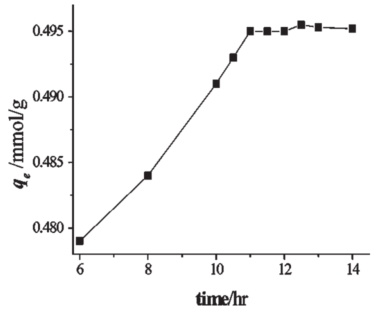

Figure 3. Effect of time on the adsorption capacity of benzoic acid by CMKGM-Fe.

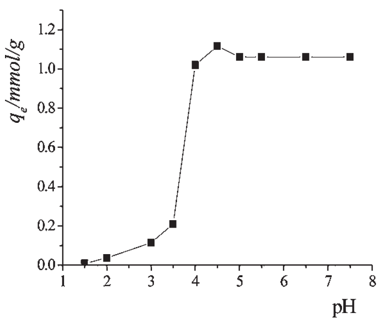

Figure 4. Effect of pH on the adsorption capacity of benzoic acid on CMKGM-Fe.

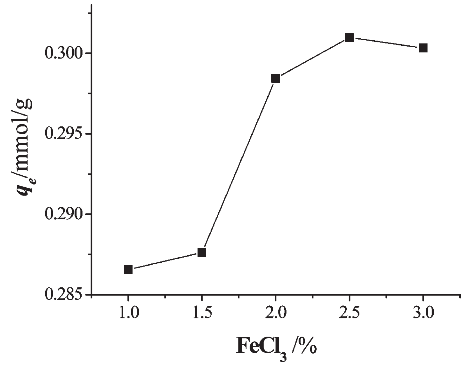

Figure 5. Effect of concentrations of $FeCl_3$ on adsorption capacity.

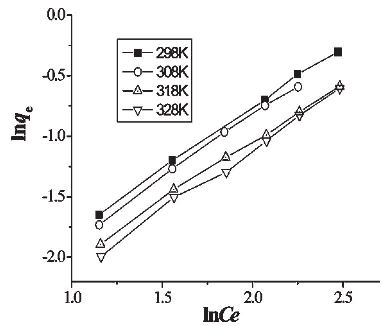

Figure 6. Freundlich isotherm of adsorption of CMKGM-Fe for benzoic acid.

$^+$ has occurred. In the vicinity of 1024 cm^{-1}, there was a strong C═O stretching vibration. After the adsorption of benzoic acid, in the IR of CMKGM-Fe, three benzene skeleton vibration peaks appeared in the range of (1650 to 1450) cm^{-1}. Near 1024 cm^{-1}, there was a strong C═O stretching vibration. These results also indicate the coordination of COO^- and Fe^{3+}.

3.3. Factors Affecting Adsorption Capacity. *3.3.1. Effect of Time on Adsorption Capacity.* The initial concentration of benzoic acid was controlled to be 1000 $mg \cdot L^{-1}$. At 298 K, the effect of adsorption time on adsorption capacity was studied following the procedure described in the Experimental Section (2.2.3). The results (Figure 3) showed that the adsorption capacity increased with the increase of adsorption time. When the process of adsorption lasted for 11 h, the adsorption capacity achieved the maximum, and the adsorption capacity was 0.4954 $mmol \cdot g^{-1}$.

3.3.2. Effect of pH on Adsorption Capacity. Figure 4 showed that, when the pH value of the tested solution was controlled by dilute HCl or NaOH solution, the equilibrium adsorption capacity for benzoic acid increased with the increase of pH until the pH was 4.5. When the pH was lower than 1.5, almost no benzoic acid was adsorbed by CMKGM-Fe microspheres. The concentration of benzoic acid was controlled as 1000 $mg \cdot L^{-1}$; when the pH was 1.50, 2.00, 3.00, 3.50, 4.00, 4.50, 5.00, 5.50, 6.50, and 7.50, the adsorption capacity of CMKGM-Fe microspheres for benzoic acids was 0.0089 $mmol \cdot g^{-1}$, 0.03715 $mmol \cdot g^{-1}$, 0.1145 $mmol \cdot g^{-1}$, 0.2090 $mmol \cdot g^{-1}$, 1.0206 $mmol \cdot g^{-1}$, 1.1165 $mmol \cdot g^{-1}$, 1.0606 $mmol \cdot g^{-1}$, 1.0605 $mmol \cdot g^{-1}$, 1.0605 $mmol \cdot g^{-1}$, and 1.0606 $mmol \cdot g^{-1}$, respectively. Other experiments in this paper were carried out in benzoic acid without the addition of diluted HCl or NaOH solution.

3.3.3. Effects of Concentrations of $FeCl_3$ and CMKGM on Adsorption Capacity. The addition weights of CMKGM and $FeCl_3$ solution were kept constant. At 298 K, the $FeCl_3$ concentrations of 1.0 %, 1.5 %, 2.0 %, 2.5 %, and 3.0 % (w/v) were used to prepare gel microspheres. The initial concentration of benzoic acid was 600 $mg \cdot L^{-1}$. The results are given in Figure 5. It was shown that the adsorption of benzoic acid increased with the increase of $FeCl_3$ concentration. But when the $FeCl_3$ concentration is 2.5 % (w/v) or above, the adsorption of benzoic acid decreased slightly with the increase of $FeCl_3$ concentration. Fe^{3+} may be excessive cross-linking with −COOH and −OH of CMKGBM.

The addition amounts of CMKGM solutions were 0.03 g, and CMKGBM solutions of 0.5 %, 1.0 %, 1.5 %, 2.0 % and 2.5 % (w/v) were used to prepare gel microspheres with 2.5 % (w/v) $FeCl_3$, respectively. The initial concentration of benzoic acid was 600 $mg \cdot L^{-1}$. At 298 K, the effect of CMKGM concentration on adsorption capacity was studied, and the results showed that a CMKGM of 0.5 % (w/v) could not form a good gel microsphere. When CMKGM concentration increased from 1.0 % to 1.5 % (w/v), the adsorption capacity changed gradually from 0.2944 $mmol \cdot g^{-1}$ to 0.3010 $mmol \cdot g^{-1}$. When the CMKGBM concentration was increased to 2 % (w/v), the adsorption of benzoic acid decreased to 0.2879 $mmol \cdot g^{-1}$. This may be because when the concentration of CMKGM was too high and the number of microspheres was small, the chance of the microsphere to contact benzoic acid was reduced. Therefore, the following experiments described below used CMKGM concentrations of 1.5 % (w/v) and $FeCl_3$ concentrations of 2.5 % (w/v) for gel microsphere preparation.

3.3.4. Effect of Microsphere Size on Adsorption Capacity. The initial concentration of benzoic acid was 1000 $mg \cdot L^{-1}$. At 298 K, the effect of microsphere size on adsorption capacity was studied.

Table 1. Freundlich Parameters of Adsorption of Benzoic Acid by CMKGM-Fe

temperature		Freundlich parameters		
K	fitting equations	k	n	R^2
298	$\ln q_e = 1.0232 \ln C_e - 2.8117$	0.060103	0.9773	0.9993
308	$\ln q_e = 1.0442 \ln C_e - 2.9138$	0.054269	0.9577	0.9986
318	$\ln q_e = 0.9814 \ln C_e - 3.0081$	0.049385	1.0190	0.9984
328	$\ln q_e = 1.3064 \ln C_e - 3.1809$	0.041548	0.9649	0.9968

The results showed that when the size of microspheres was 0.45 mm, 0.5 mm, and 1.2 mm, the adsorption capacity was 0.4954 $mmol \cdot g^{-1}$, 0.4925 $mmol \cdot g^{-1}$, and 0.4924 $mmol \cdot g^{-1}$, respectively. Therefore, microsphere size had no significant effect on the adsorption.

3.4. Adsorption Isotherms of Benzoic Acid on CMKGM-Fe. The effect of the benzoic acid concentration on the adsorption capacity under different temperatures was studied with a concentration range between (400 and 1500) $mg \cdot L^{-1}$ for benzoic acid as shown in Figure 6. It indicated that, at the same temperature, the adsorption capacity increased with the increase of initial benzoic acid concentration. When the initial benzoic acid concentration was the same, the adsorption capacity decreased with the increase of temperature. At 298 K, when the initial benzoic acid concentration was 400 $mg \cdot L^{-1}$, 600 $mg \cdot L^{-1}$, 1000 $mg \cdot L^{-1}$, 1200 $mg \cdot L^{-1}$, and 1500 $mg \cdot L^{-1}$, the adsorption capacity of CMKGM-Fe for benzoic acid was 0.1921 $mmol \cdot g^{-1}$, 0.3010 $mmol \cdot g^{-1}$, 0.4954 $mmol \cdot g^{-1}$, 0.6141 $mmol \cdot g^{-1}$, and 0.7373 $mmol \cdot g^{-1}$, respectively.

The adsorption isotherm of benzoic acid on CMKGM-Fe was analyzed using the classical Freundlich equation (eq 1):[9−11,15]

$$\ln q_e = \ln k + (1/n)\ln C_e \quad (1)$$

in which q_e is the equilibrium adsorption capacity in $mmol \cdot g^{-1}$; C_e is the equilibrium concentration in $mmol \cdot L^{-1}$; k and n are constants obtained from curve fitting.

Constants (k, n) and correlation coefficient (R^2) were obtained through the linear fitting of least-squares method and are listed in Table 1. The fitting results of Freundlich equation were good, and all of the correlation coefficients were greater than 0.99, indicating that the Freundlich equation was suitable for the adsorption system. According to the theory of Freundlich, the value of constant k indicates the relative magnitude of adsorption capacity. As shown in Table 1, n changed slightly with the increase of temperature, while k gradually decreased with the increase of temperature. Overall, the equilibrium adsorption capacity decreased with the increase of temperature, which is similar to general physical adsorption phenomenon.[11,15] Generally, the process of adsorption tends to be easy when $1/n = 0.1$ to 0.5, and the process of adsorption tends to be difficult when $1/n > 2$. n values of the adsorption material developed in this study were close to 1, indicating a moderate adsorption capacity of the investigated adsorption system.

3.5. Thermodynamic Analysis of Adsorption of CMKGM-Fe for Benzoic Acid. *3.5.1. Enthalpy Change of Adsorption (ΔH).* The linear relationship of $\ln C_e$ and $1/T$ is shown in Figure 7. The correlation coefficients were greater than 0.99 when the values of q_e in the range of (0.065 to 0.28) $mmol \cdot g^{-1}$, and the correlation coefficient was 0.9835 when the value of q_e was 0.4 $mmol \cdot g^{-1}$. According to the Clausius−Clapeyron equation (eq 2), the slope ($\Delta H/R$) and adsorption enthalpy ΔH, corresponding to different levels of adsorption, were calculated, and the results are given in Table 2.

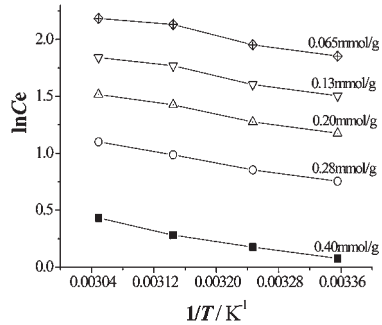

Figure 7. Adsorption isosters of benzoic acid on CMKGM-Fe.

$$\ln C_e = \Delta H/RT + K \quad (2)$$

in which R is the gas constant (8.314 $J \cdot K^{-1} \cdot mol^{-1}$); T is the absolute temperature in K; C_e is the adsorption equilibrium concentration corresponding to q_e (obtained through the Freundlich equation) in $mol \cdot L^{-1}$; ΔH is the adsorption enthalpy, $J \cdot mol^{-1}$; K is the adsorption equilibrium constant.

Thermodynamic parameters of adsorption enthalpy directly reflect the nature of adsorption. Table 2 shows that ΔH values were negative, and the CMKGM-Fe equilibrium adsorption capacity of benzoic acid decreased with the increase of temperature. These facts indicated that an exothermic reaction occurred during the adsorption process. The values of q_e were in the range of (0.065 to 0.4) $mmol \cdot g^{-1}$, and ΔH decreased with the increase of q_e, although the change was slight. The absolute values of ΔH were less than 10 $kJ \cdot mol^{-1}$. These results suggested that the adsorption of benzoic acid by CMKGM-Fe mainly was physical adsorption. It can be inferred that the adsorption of benzoic acid on CMKGM-Fe may rely mainly on the electrostatic attraction of Fe^{3+} and the COO^- group of benzoic acid.

3.5.2. Free Energy Change of Adsorption (ΔG). According to Garcia−Delgado equation (eq 3),[20] combined with the Freundlich equation of this research, results of ΔG can be obtained. According to $\Delta G = -nRT$, ΔG of different temperatures could be calculated (eq 3), and the results are listed in Table 2.

$$\Delta G = \int_0^x y \, dx/x \quad (3)$$

in which x represents the mole fraction of adsorbate in equilibrated solution; y is the equation of adsorption isotherm.

As shown in Table 2, ΔG values were negative. It indicates that the adsorption process was spontaneous and irreversible. The absolute value of ΔG increased slightly when the temperature increased from 298 K to 318 K, suggesting that the spontaneous trend of the adsorption process increased slightly with the increase of temperature. When the temperature increased to 328 K, the absolute value of ΔG became slightly less than that of 318 K, indicating that the spontaneous trend of the adsorption process decreased slightly with the increase of temperature in this temperature range. In the adsorption reaction, the effect of enthalpy on the ΔG change is opposite to that of entropy, and there was a complementary phenomenon. The microscopic nature of this relationship of compensation may be related to the intermolecular interaction and freedom of molecular motion.[15,16]

3.5.3. Entropy Change of Adsorption (ΔS). According to Gibbs−Helmholtz equation (eq 4), the entropy change (ΔS)

Table 2. Enthalpy Change of Adsorption of CMKGM-Fe for Benzoic Acid

equilibrium adsorption (q_e)		enthalpy change of adsorption (ΔH)	free energy change of adsorption (ΔG)/ kJ·mol^{-1}				entropy change of adsorption (ΔS)/ J·mol^{-1}·K^{-1}			
mmol·g^{-1}	correlation coefficient (R)	kJ·mol^{-1}	298 K	308 K	318 K	328 K	298 K	308 K	318 K	328 K
0.065	0.9911	−9.4711	−2.421	−2.452	−2.694	−2.631	−23.66	−22.79	−21.31	−20.85
0.13	0.9964	−9.4951	−2.421	−2.452	−2.694	−2.631	−23.74	−22.87	−21.39	−20.93
0.20	0.9956	−9.5359	−2.421	−2.452	−2.694	−2.631	−23.87	−23.00	−21.52	−21.05
0.28	0.9910	−9.5540	−2.421	−2.452	−2.694	−2.631	−23.94	−23.06	−21.57	−21.10
0.40	0.9835	−9.5766	−2.421	−2.452	−2.694	−2.631	−24.01	−23.13	−21.64	−21.17

values under different temperatures and adsorption capacities (q_e) were estimated and listed in Table 2.

$$\Delta S = (\Delta H - \Delta G)/T \quad (4)$$

The results listed in Table 2 show that ΔS were negative when q_e was in the range of (0.065 to 0.28) mmol·g^{-1}; ΔS slightly increased with the increase of q_e at the same temperature, and ΔS decreased with the temperature increase at the same q_e.

During the adsorption process, the major factors affecting ΔS include solute adsorption, solvent desorption, solute partial ionization, different conformations of solute molecules on the surface of gel microspheres, and electrostatic force (such as that from Fe^{3+} on the microsphere). In the adsorption process of the system, the entropy change (ΔS) was negative, which was unfavorable to the adsorption. Therefore, the adsorption driving force for this adsorption process was mainly enthalpy change (ΔH).

3.6. Effect of CMKGM Concentration on the Mechanical Strength of Gel Microspheres. The effect of CMKGM concentration on the mechanical strength of gel microspheres was investigated according the method of section 2.2.4. When the CMKGM mass fraction was 1.0 %, 1.5 %, 2.0 %, 2.5 %, and 3.0 % (w/v), the maximum weight that the gel microsphere could bear was 5.7 g, 18.3 g, 32.3 g, 52.5 g, and 67.0 g. Thus, the mechanical strength of CMKGM-Fe increased with the increase of CMKGM mass fraction. In the present study, CMKGM with a mass fraction of 1.5 % (w/v) was used to prepare gel microspheres, and each gel microsphere could bear the weight of 18.3 g.

3.7. Desorption and Reapplication of CMKGM-Fe. The total amount of adsorptive benzoic acid was determined using an initial concentration of benzoic acid of 1000 mg·L^{-1}. After static saturated adsorption by CMKGM-Fe microspheres was achieved, the water phase was separated, and then CMKGM-Fe microspheres were washed four times with double-distilled water. CMKGM-Fe microspheres were washed by different concentrations of hydrochloric acid and sodium hydroxide. The results showed that the elution rate attained 96 % when the concentration of HCl or NaOH was 0.020 mol·L^{-1}. After elution, the CMKGM-Fe microspheres were washed several times with double-distilled water, and then the CMKGM-Fe microspheres were used for readsorption experiments for 1, 2, and 3 times, the static saturated adsorption capacity was (0.4805, 0.4632, and 0.4459) mmol·g^{-1}, respectively. The results showed that the CMKGM-Fe microspheres can be repeatedly reused with slightly reduced adsorption capacity.

The adsorption behaviors of benzoic acid on some natural product-based polymeric materials, for example, chitosan resin, have been reported in literature.[15] The adsorption capacity of CMKGM-Fe microsphere for benzoic acid is slightly lower than that of chitosan resin. However, the synthesis procedure of CMKGM-Fe microsphere is simpler and does not involve toxic reagents and organic solvents. KGM is a low-cost and widely available raw material. Therefore, the application of CMKGM-Fe has very positive future applications for the removal of benzoic acid or its derivatives.

4. CONCLUSIONS

CMKGM gel microspheres cross-linked with Fe^{3+} (CMKGM-Fe) were prepared based on a natural product, KGM. The adsorption capacity of CMKGM-Fe for benzoic acid depends on the adsorption time, $FeCl_3$ concentration, CMKGM concentration, temperature, and initial concentration of benzoic acid. When the temperature was 298 K, the CMKGM concentration was 1.5 % (w/v), the $FeCl_3$ concentration was 2.5 % (w/v), the initial concentration of benzoic acid was 1000 mg·L^{-1}, the adsorption equilibrium could be established in about 11 h, and the adsorption capacity reached 0.4954 mg·g^{-1}. Thermodynamic parameters of the adsorption were determined, and the adsorption reaction was dominated by physical adsorption.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: wangbi05@126.com.

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