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Adsorption of 2-methylisoborneol and geosmin from water onto thermally modified attapulgite

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ABSTRACT

This study mainly focused on the adsorption of 2-methylisoborneol (2-MIB) and geosmin (GSM) form water onto a new type of adsorbent (attapulgite) (ATP) and thermally modified attapulgite (T-ATP). The adsorption isotherm and the adsorption kinetics of GSM onto T-ATP were studied in batch experiments. Meanwhile, the effect of temperature and pH on the removal efficiency and the absorbed amount of GSM and 2-MIB was also investigated. Experimental results show that the optimal concentrations of adsorption of GSM and 2-MIB onto ATP and T-ATP were both 1 g/L. The adsorption of GSM onto T-ATP better followed pseudo-second-order model. Freundlich isotherm fit the experimental data (the adsorption of GSM onto T-ATP) better than Langmuir isotherm. Besides, the best operational condition of adsorption of GSM and 2-MIB onto ATP and T-ATP was at lower temperature (5˚C) and under neutral pH (6.5 ~ 7.5). Although the adsorption of GSM onto T-ATP was nonspontaneous, it was an exothermic reaction, in terms of the thermodynamic parameters (positive of ΔG° and negative of ΔH° and ΔS°). The weak adsorption reaction could take place by simply raising shaking speeds.

Keywords: GSM; 2-MIB; T-ATP; Adsorption isotherm; Adsorption kinetics

1. Introduction

Removing taste and odor compounds from drinking water is a significant challenge all over the world. In particular, the compounds of 2-methylisoborneol (2-MIB) and geosmin (GSM) are probably the most commonly natural occurring taste and odor compounds in water supplies. Both of them are metabolites of actinomycetes, and some species of cyanobacteria, and both of them can cause musty–earthy

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Presented at the Fifth Annual International Conference on "Challenges in Environmental Science & Engineering—CESE 2012" Melbourne, Australia, 9–13 September 2012 odor problems even at the concentration of 10 ng/L or less [1–3]. Various techniques based on physical [4,5], chemical [6,7], and biological process [8,9] are widely applied to remove these compounds. The capital and energy costs associated with chemical processes can be significantly high, especially for its large-scale application. There is also a risk of the formation of disinfection byproducts, which are unacceptable due to the health and regulatory concerns. In terms of biological processes, although some bacteria have been identified to remove 2-MIB/GSM, it would be difficult to introduce these micro-organisms into drinking water treatment systems. Physical technique is the most effective and widely used technology in water treatment plants to treat these odorants.

Conventional physical techniques, for example, adsorption of powdered- activated carbon or granular-activated carbon are applied in water treatment plants during severe outbreaks. However, for long time operation, the costs might still be very high. Therefore, alternatively economic adsorbents are widely investigated to reduce the operation cost for high-removal efficiency of these odorants. Successful results have been obtained such as elutrilithe [10], diatomite [11] fly ash and bentonite composition [12], and zeolite [13].

It is noteworthy that there are a great deal of high-quality reserves of attapulgite (ATP) clays in Southeast of China, but some ATP clays are only used as activities in the forge and the fertilizer [14]. Moreover, ATP clays have lower cost than other minerals [14]. ATP is a hydrated aluminum–magnesium silicate crystalline with a fibrous morphology and has a structure composed of parallel ribbons of 2:1 layers. It has been widely used as environmental adsorbents to remove heavy metal cations [15–17] and organic pollutants [18–20], due to its large specific surface area (SSA) and cation-exchange capacity [18]. Nevertheless, the adsorption efficiency of negatively or neutral contaminant by ATP clays are very low due to the permanent negative charges on its surface [21]. In order to improve its adsorption capacity for negatively charged or neutral contaminant, ATP has been widely treated with thermal modification [14,22,23], organic modification [16,24,25], acid modification [23,26,27]. Unfortunately, organic reagents used in the modification processes may bring the secondary pollution [18], a wastewater and it is difficult to adjust the neutral condition in the acid modification. Thermal modification process just changes the pore structure and the surface properties, because different kinds of water located in intracrystalline tunnels can be selectively removed by calcining at different temperatures. Therefore, thermal modification process is simple and economic.

Thermal modification is applied to treat ATP in this research. The adsorption of 2-MIB and GSM onto ATP and thermally modified attapulgite (T-ATP) was studied in this study. The adsorption isotherm and the adsorption kinetic model of GSM onto T-ATP were investigated, and the influencing factors (concentrations of T-ATP, pH, and temperatures) were also researched.

2. Materials and methods

2.1. Preparation of test materials

2-MIB and GSM were purchased from Sigma-Aldrich Co., USA, at a concentration of 10 mg/L in the methanol as stock solutions, stored at −20˚C in the fridge. Media stock solutions of 1 mg/L were prepared by diluting the methanol solution with ultrapure water, stored at 4˚C in the fridge.

2-MIB and GSM were analyzed using the headspace solid-phase microextraction–gas chromatography/mass spectrometry.

ATP clay was purchased from Jiangshu Jiuchuan Nano-material Technology Co., Ltd, China.

ATP was heated at 300˚C in the Electric Blast Drying Oven (DHG-9146, China) for 2.5 h and then stored in the dryer for use (T-ATP).

2.2. ATP surface analysis

The mineral and chemical compositions of ATP and T-ATP were investigated by using the X-ray fluorescence spectrometer (XRF, AXIOS PW4400). The chemical functional groups of ATP and T-ATP were recorded by the Fourier transform infrared spectroscopy (FTIR, Spectrum One B), specimens being examined in form of KBr disks. The BET surface area was measured by the N_2 adsorption—desorption technique using an ASAP 2020M analyzer.

2.3. Adsorption isotherm and adsorption kinetic tests

All batch tests were conducted by varying the dosage of T-ATP clays in the range of 10–500 mg (corresponding to 0.1–5 g/L), so as to evaluate the kinetics and the isotherm behaviors of adsorption of 2-MIB and GSM onto T-ATP. Different amounts of T-ATP clays were added to 100 mL 2-MIB or GSM solution in 150-mL Erlenmeyer flasks. The flasks were covered and immediately placed on the orbital shaker, then shaken for 24 h (160 rpm, 25˚C). Thirty millilitre 2-MIB

Table 1
Mineral and chemical compositions of ATP and T-ATP

(a) ATP									
Composition	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	Fe_2O_3
Ratio (%)	0.239	12.39	10.61	67.42	0.75	1.02	1.13	0.63	5.53
(b) T-ATP									
Composition	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	Fe_2O_3
Ratio (%)	0.196	12.61	10.76	67.95	0.011	1.03	1.16	0.62	5.40

or GSM solution was sampled with a pipettor at different time intervals of adsorption. The sampled solution was first pretreated by 30-min centrifugation and then was filtrated through a 0.45-μm filter membrane. Then 2-MIB and GSM were analyzed according to Section 2.1.

2.4. Effect of pH

PH value in this part referred to the equilibrium pH. The effect of pH on the adsorption of 2-MIB and GSM onto ATP and T-ATP was investigated by varying the equilibrium pH from 2 to 12. 0.1 g T-ATP was added into 100 mL 2-MIB or GSM solution in 150-mL Erlenmeyer flasks. PH of the solution was adjusted by using 0.01 M HCl and 0.01 M NaOH to obtain and keep certain pH value. The flasks were covered and immediately placed on the orbital shaker, then shaken for 24 h (160 rpm, 25℃). At the end of shaking, 2-MIB, and GSM were analyzed as mentioned in Section 2.1.

2.5. Effect of temperature

The adsorption experiments were performed at different temperatures (5, 10, 20, 30, 40, and 50℃). As the same method operated in Section 2.3, 0.1 g T-ATP was added into 100 mL 2-MIB or GSM solution in 150-mL Erlenmeyer flasks. The flasks were covered and immediately put in the temperature shaker incubator, which was controlled at different temperatures and shaken for 24 h (160 rpm). At the end of shaking, 2-MIB, and GSM were analyzed as mentioned in Section 2.1.

3. Results and discussion

3.1. Surface properties

There was no obvious difference in the composition between ATP and T-ATP in Table 1. Only some ingredient content raised due to the loss of partial water in T-ATP.

Fig. 1 shows the FTIR spectra of ATP and T-ATP. Most adsorption bands of ATP were identical to the other researches [28,29] and the locations of adsorption bands between ATP and T-ATP were the same. Moreover, the intensity of five bands at 3,615, 3,583, 3,551, 3,399, and 1,655 cm^{-1} decreased, corresponding to the symmetrical and asymmetrical stretching vibration of O–H connected to the Mg and Al between the tetrahedral and octahedral structure of ATP and the stretching vibration of O–H of bound water and adsorbed water of ATP.

The SSA of ATP and T-ATP was 107.92 and 123.28 m^2/g (increasing by 14%). The total pore volume of ATP and T-ATP was 0.3376 and 0.5570 cm^3/g (increasing by 65%).

So thermal modification did not change the composition of ATP and just partial water was lost [30], and therefore, T-ATP shows better adsorption ability.

3.2. Adsorption kinetics

The removal efficiency of 2-MIB and GSM, as shown in Fig. 2, increased obviously as the concentration of ATP and T-ATP increased (less than 1 g/L)

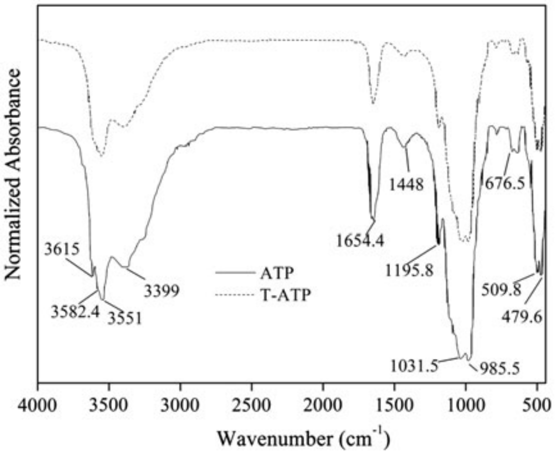


Fig. 1. FTIR spectra of ATP and T-ATP.

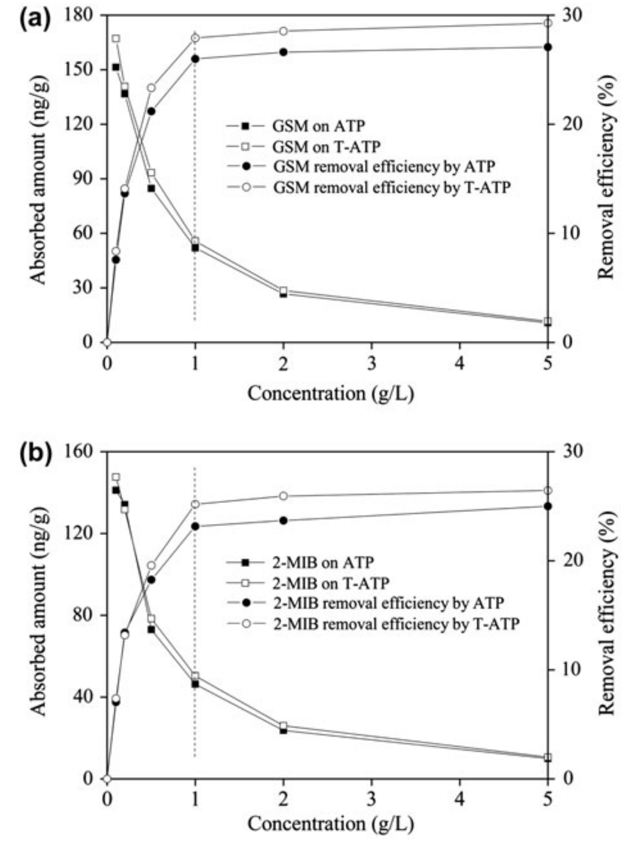


Fig. 2. Absorbed amount and removal efficiency (a: GSM and b: 2-MIB) as a function of the concentration of ATP and T-ATP.

and remained constant, when the concentration of ATP and T-ATP was more than 1 g/L. However, the adsorbed amount of 2-MIB and GSM onto ATP and T-ATP decreased all the time, when the concentration of ATP and T-ATP increased from 0 to 5 g/L.

So the optimal concentration of adsorption of 2-MIB and GSM onto ATP and T-ATP was both 1 g/L. Meanwhile, the removal efficiency (%) and the adsorbed ability (ng/g) of GSM and 2-MIB onto T-ATP, increased by 7.3% and 8.8, 2.8 and 2.7%, respectively, compared with ATP.

Pseudo-first-order and pseudo-second-order models were used to fit the adsorption kinetic data of T-ATP adsorbing GSM and investigate the adsorption rate of T-ATP adsorbing GSM. Two models can be rearranged as follows [31,32].

$$\text{Pesudo-first-order model: } \log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (1)$$

$$\text{Pesudo-second-order model: } \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

where q_e is the adsorbed amount of GSM at the equilibrium time (ng/g), q_t is the absorbed amount of GSM at time t (ng/g), k_1 is the rate constant of pseudo-first-order adsorption (1/min), k_2 is the rate constant of pseudo-second-order adsorption (g/(ng min)).

The fitting results of kinetic data for two models were listed in Table 2. The regression coefficient (R^2) was used to evaluate the fitness of two models. R^2 of pseudo-second-order model (around 0.99) was higher than that of pseudo-first-order model, indicating that the adsorption of GSM onto T-ATP better obeyed pseudo-second-order kinetic model. Similar results of previous studies that the adsorption of naring in onto modified clay [33], the adsorption of bromopropylate onto activated carbons [34], the adsorption of algal odorants (dimethyl trisulfide and β-cyclocitral) onto granular carbon [35], and the adsorption of GSM onto chitosan-coated granular-activated carbon [36] all better followed pseudo-second-order kinetic model.

3.3. Adsorption isotherm

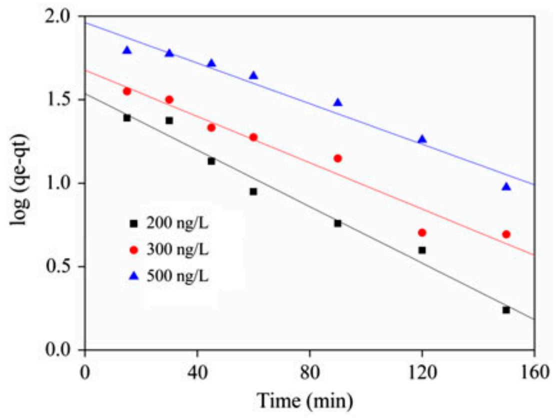
Freundlich and Langmuir equations are the most frequently used models to fit experimental data of adsorption isotherms. These two models are listed as follows:

$$\text{Freundlich equation } q_e = K C_e^{\frac{1}{n}} \quad (3)$$

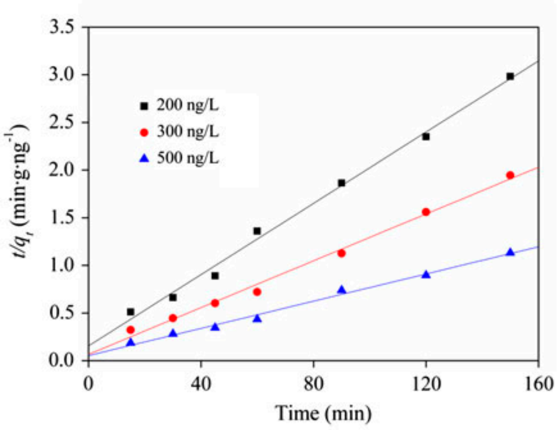
$$\text{Langmuir equation } q_e = \frac{b q_m C_e}{1 + b C_e} \quad (4)$$

Table 2
Parameters of pseudo-first and pseudo-second models (the adsorption of GSM onto T-ATP)

Dosage (ng/L)	q_e (exp) (ng/g)	Pseudo-first-order model			Pseudo-second-order model		
		q_e (ng/g)	$K_1 \times 10^{-2}$ (1/min)	R^2	q_e (ng/g)	$K_2 \times 10^{-3}$ (g/ng min)	R^2
200	54.6	54	1.96	0.9786	53.48	2.25	0.9941
300	82.4	82	1.59	0.9525	81.30	2.28	0.9927
500	142.3	91.64	1.4	0.9653	140.85	0.935	0.9919



a) Pseudo-first order kinetic



a) Pseudo-second order kinetic

Fig. 3. Pseudo-first and pseudo-second-order kinetic of the adsorption of GSM onto T-ATP.

where q_e is the adsorbed amount of GSM at equilibrium (ng/g), q_m is the maximum adsorbed amount of GSM (ng/g), C_e is the equilibrium concentration of GSM in solution (ng/L), K and n are the Freundlich constants, b is the Langmuir constant.

The experimental results of adsorption of GSM onto T-ATP are shown in Fig. 4. Freundlich isotherm fits the experimental data better than Langmuir isotherm. The estimated Freundlich and Langmuir constants are shown in Table 3. Freundlich isotherm is normally used to model the adsorption of taste and odor compounds in water [37–39].

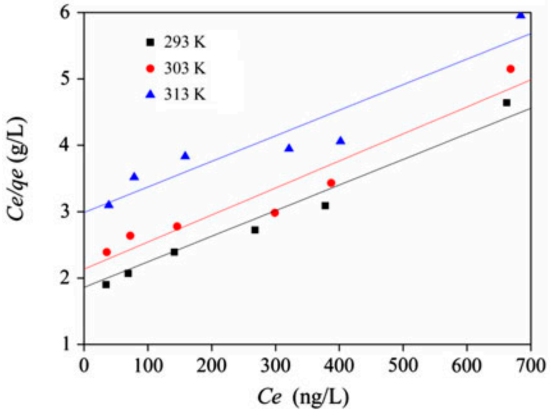
The magnitude of the exponent $1/n$ represents an indication of the favorability and the capacity of the adsorbent/adsorbate system. Normally, it is stated that the value of $1/n$ show good adsorption ability in the range of 0.1–1. Moreover, the smaller the value is, the better adsorption ability it will represent. Especially, in the range of 0.1–0.5, it represents that the adsorbate could be more easily adsorbed by the adsorbent. As shown in Table 3, the values of $1/n$ are all between 0.5 and 1, indicating that the adsorption of GSM onto T-ATP is very weak.

Table 3
Freundlich and Langmuir constants at different temperatures (the adsorption of GSM onto T-ATP)

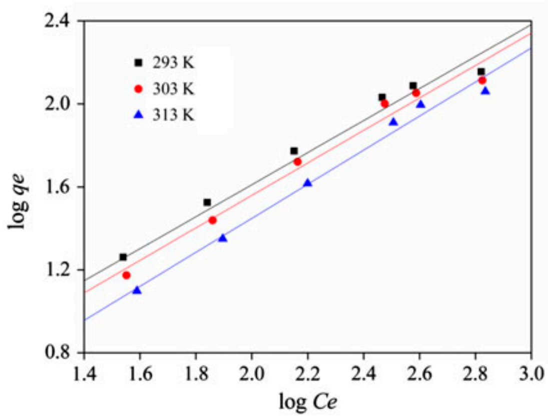
Temperature	Freundlich			Langmuir		
	K	$1/n$	R^2 (%)	q_m	b	R^2 (%)
293	1.19	0.73	97.98	238.10	0.002452	98.16
303	0.99	0.78	97.66	243.90	0.00192	92.87
313	0.83	0.83	98.59	256.41	0.001306	89.33

3.4. Effect of pH

The equilibrium pH obviously had a significant effect on adsorption of GSM and 2-MIB onto T-ATP, as shown in Fig. 5. The removal efficiency of GSM



a) Langmuir adsorption isotherms



b) Freundlich adsorption isotherms

Fig. 4. Langmuir and Freundlich adsorption isotherms at different temperatures (the adsorption of GSM onto T-ATP).

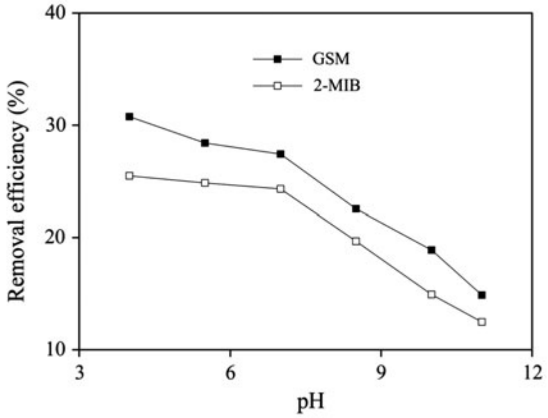


Fig. 5. Effect of pH on the removal efficiency of GSM and 2-MIB (T-ATP).

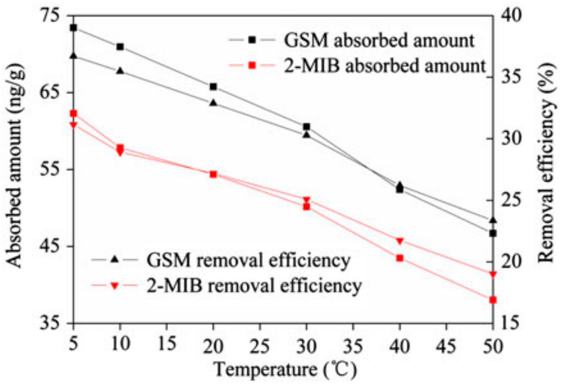


Fig. 6. Effect of the temperature on the removal efficiency and absorbed amount of GSM and 2-MIB (T-ATP).

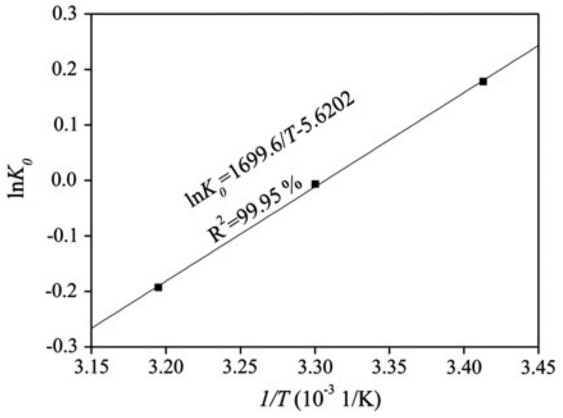


Fig. 7. $\ln K_0$ as a function of $1/T$ (the adsorption of GSM onto T-ATP).

and 2-MIB increased all the time, when the equilibrium pH raised from 3 to 12. GSM and 2-MIB are both hydrophobic micromolecular organics as molecular form without ionization, so pH has little effect on their form in the aquatic environment. ATP clays are known to process a negative surface charge, when pH of the solution is more than 3. In the research of acid activation of a palyporskite with HCl [40], BET of the palyporskite increased with the concentration of HCl increased from 1 to 5 N. So in this research, T-ATP had larger BET and the removal efficiency of GSM and 2-MIB was higher at lower pH when pH was between 3 and 8. When the pH value went on increasing from 8 to 12, there will be a great difference in T-ATP surface characters in terms of activating group and then the surface free energy of T-ATP would increase. So the adsorption ability of GSM, and 2-MIB onto T-ATP reduced, and then the removal efficiency decreased.

However, in view of the fact that practical water treatments were conducted at the neutral pH, the adsorption of GSM, and 2-MIB experiments should be operated at the neutral pH condition (pH 6.5–7.5).

3.5. Effect of temperature

The effect of temperature on removal efficiency of GSM and 2-MIB was carried out at 6 different temperatures (5, 10, 20, 30, 40, and 50℃) (Fig. 6). The removal efficiency and the adsorption ability of GSM and 2-MIB followed the order: 10 > 20 > 30 > 40 > 50℃, that is, the adsorption of GSM and 2-MIB onto ATP and T-ATP was favored to take place at lower temperature. This phenomenon implies that the adsorption of GSM and 2-MIB onto ATP and T-ATP is a natural exothermic reaction. Similar findings were reported that the adsorption of direct acid proof scarlet 4BS onto purified ATP [41], the adsorption of p-nitrophenol onto anion-cation modified ATP [42], the adsorption of uranyl onto modified ATP [43], the adsorption of Methyl Violet cationic dye onto poly (acrylic acid-co-acrylamide)/ATP composite [44] were all exothermic reactions.

Standard Gibbs free energy change (ΔG°) was expressed as followed equation [45]:

$$\Delta G^\circ = -RT \ln K_0 \tag{5}$$

where R is the gas constant (8.314 J/mol/K) and T is the absolute temperature (K). K_0 is the equilibrium constant. Moreover, standard enthalpy and entropy change (ΔH°, ΔS°) are correlated with K_0 according the following Eq. (6) [45].

Table 4
Thermodynamic parameters (adsorption of GSM onto T-ATP)

Temperature	GSM		
	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/(mol K))
293	−0.43	−14.13	−46.73
303	0.02		
313	0.50		

$$\ln K_0 = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{6}$$

The value of ΔH° and ΔS° can be calculated from the slope and the intercept of the linear plot of ln K_0 vs. $1/T$, as shown in Fig. 7. The values of thermodynamic parameters ΔG°, ΔH° and ΔS° are listed in Table 4. The enthalpy change, ΔH° is −14.13 kJ/mol (the adsorption of GSM onto T-ATP). The negative value of ΔH° exhibited that the adsorption of GSM onto T-ATP is exothermic,and it is also the removal efficiency of GSM is improved by reducing the temperature. The entropy change ΔS° was found to be −46.73 kJ/(mol K). The negative value of ΔS° suggests a decrease in the randomness at the solid/solution interface during the absorption of GSM onto T-ATP. Moreover, Standard Gibbs free energy change ΔG° was −0.43, 0.02, and −0.50 kJ/mol, respectively, for the adsorption of GSM onto T-ATP at the temperatures of 293, 303, and 313 K, respectively. Low positive ΔG° values indicated that the adsorption of GSM onto T-ATP was nonspontaneous. But the weak adsorption of GSM onto T-ATP was feasible to take place by simply raising shaking speeds.

4. Conclusions

A new type of adsorbent material (T-ATP) was employed in the adsorption of GSM and 2-MIB from water. The results show that:

(1) The optimal concentrations of adsorption of GSM and 2-MIB onto ATP and T-ATP were both 1 g/L.
(2) The adsorption behavior of GSM onto T-ATP better followed pseudo-second-order model and Freundlich isotherm fit the experimental data better than Langmuir isotherm at the temperature of 293, 303, and 313 K.
(3) The best operational condition of adsorption of GSM and 2-MIB onto ATP and T-ATP was at lower temperature (5℃) and under neutral pH (6.5–7.5).
(4) Although the adsorption of GSM onto T-ATP was nonspontaneous, but it was an exothermic reaction. The weak adsorption reaction could take place by simply raising shaking speeds.

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