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Preparation and adsorption performance of CTMAB-bentonite on landfill leachate

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ABSTRACT

The toxic organic pollutant with high concentration in landfill leachate is increasingly harmful to human health. In order to treat landfill leachate more efficiently, a novel cheap organobentonite (CTMAB-bentonite) was successfully prepared from Na-bentonite modified with cetyltrimethylammonium bromide (CTMAB) as intercalation agent. The CTMAB-bentonite were characterized by X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy, and the effects of contact time, CTMAB concentration, temperature and pH on the adsorption performance were investigated. XRD analysis results showed that CTMAB with concentration of 4 mmol/5 g was successfully intercalated into bentonite, and the layer spacing of CTMAB-bentonite increased by 6 Å than larger that before modification. The adsorption experiment results indicated that the best adsorption time is 60 min, pH and temperature have little effect on the adsorption performance. The adsorption process of landfill leachate conforms to the Freundlich and pseudo-second-order kinetic model, which indicated a multimolecular layer and chemical adsorption, respectively. Thermodynamic parameters confirmed that adsorption process was spontaneous and exothermic. Bentonite modified by CTMAB has a satisfactory adsorption effect on leachate and satisfactory adsorption capacity. CTMAB-bentonite was an excellent adsorbent for removal of landfill leachate which was promising in the field of wastewater treatment.

Keywords: Organic bentonite; CTMAB intercalating; Adsorption; Landfill leachate

1. Introduction

Landfill leachate is a heterogeneous mixture of complex organic and inorganic contaminants, formed by excess water percolating through the waste layers in the landfills. Municipal garbage leachate contains a large number of toxic and harmful substances, whose chemical oxygen demand (COD) and biochemical oxygen demand (BOD) values can reach 10,000 mg/L. So the leachate was difficult to be treated and caused surface water and groundwater pollution [1]. In the current waste management system, landfill is not the best way to dispose of municipal solid waste, but wastes are mainly landfilled in many developing countries. Moreover, after simple biological and mechanical treatment of wastes, the landfill will also be carried out if the corresponding landfill standards are met. In both cases, leachates will inevitably be produced [2]. The characteristics of leachate vary, but the main pollutants are a large amount of refractory organic compounds in leachate [3]. However, the physical adsorption is generally considered to be an effective method because of low-cost and easy operation. The bentonite with large specific surface area and excellent adsorption performance, as

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a cheap and easily available natural clay mineral [4], can be used as the adsorbent of landfill leachate treatment [5].

Sodium bentonite (abbreviated as Na-bentonite), its main component is montmorillonite, often serves as a substrate in landfills [6]. Na-bentonite can be used as a low-permeability landfill liner due to its high swelling [2]. It has a large specific surface area and high cation exchange capacity, which could fix pollutants such as metals by adsorption [7]. Adsorption is an important method of water treatment [8]. The development of water treatment adsorbents with low cost and good adsorption performance is an urgent need of environmental protection industry [9].

Bentonite has the characteristics of low-cost, stable, non-toxic and harmless, excellent adsorption performance, etc. [10]. In recent years, the study of modified bentonite as adsorbent for water treatment has become one of the hot topics in the field of wastewater treatment field [11–13]. The silica structure of natural bentonite has a strong hydrophilicity, resulting poor adsorption ability for hydrophobic organic compounds. However, modified bentonites can be obtained using organic functional groups to replace ions on Na-bentonite. After modification with organic groups, the distance between layers increases, and the specific surface area and microstructure change, providing a larger adsorption space for the removal of organic matter. Most importantly, the organic carbon contents and hydrophobic nature of modified bentonite was increased, which will be beneficial for the removal of hydrophobic organic matter. The hydrophobic nature also increased and the adsorption capacity of modified bentonite was greatly improved [11]. In order to further improved the adsorption capacity of bentonite, Guo and Wang [12] used thermal acid treatment, organic and inorganic modification of surfactants and other modification methods. Hasan and Ahamd [13] used cetyltrimethylammonium bromide (CTMAB) to modify natural bentonite and was used to adsorb Cr(VI) from contaminated groundwater or phenol from water [14]. Therefore, the modified bentonites will be an optimal candidate adsorbent to treat landfill leachate [15].

In this work, a kind of modified bentonite using surfactants as modifier was obtained and used as an adsorbent to treat landfill leachate. The effects of the dosage of modified bentonite, contact time, temperature, and pH on the adsorption capacity of landfill leachate were studied. On the other hand, this study also focused on the adsorption performance and mechanism of landfill leachate with CTMAB-bentonite since the process of combining organic matter with bentonite was much more complicated. It was promising that we can improve the adsorption capacity and efficiency of bentonite to organic matter in leachate by using surfactant.

2. Materials and methods

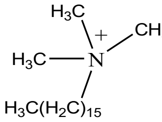
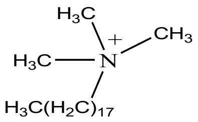
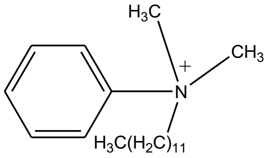
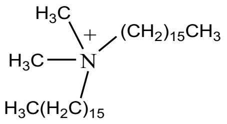
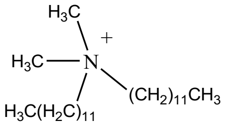
2.1. Details of materials

Ca-Bentonite which used in this experiment was obtained from Yunnan, China. Landfill leachate was taken from Anning Waste Treatment Plant in Yunnan, the composition of leachate was analyzed by ion chromatography, and the results are shown in Table S1. The Ca-bentonite contains about 89.70% montmorillonite, 6.50% quartz, 1.80% feldspar and 1.0% other substances. Its chemical composition was as follows in Table S2: 51.89% SiO_2, 16.91% Al_2O_3, 13.36% Fe_2O_3, 5.14% MgO, 4.31% CaO, 2.21% Na_2O, 0.73% K_2O and 0.23% TiO_2. The names and chemical structures of the five intercalators were shown in Table 1, which were provided by Tianjin Zhiyuan Chemical Reagent Co., Ltd., China Na_2CO_3 and other common reagents were provided by Sinopharm Chemical Reagent Beijing Co., Ltd., China. And all reagents were of analytical grade.

2.2. Preparation of modified bentonite

Briefly, Ca-bentonite was treated with 3 procedures: Na_2CO_3 treatment (sodium treatment), heat and dry in a vacuum drying oven (thermal treatment) and treatment by CTMAB (organic modification). Firstly, for Na_2CO_3 treatment, added 300 g Ca-bentonite into a conical flask with deionized water (volume ratio = 1:10), then, a certain of bentonite was added, and add Na_2CO_3 (4 wt.%) to the conical flask (mass ratio = 1:3). The pH value of the sample solution was adjusted to 7.0 by adding sodium hydroxide. The bentonite suspension were reacted at a frequency of 110 r min^{-1} for 2 h in a vibrating incubator at 60°C. Then the solid was washed residue 3 times with deionized water. The obtained samples were dried overnight at 100°C and sifted through 200-mesh to obtain Na-bentonite. Finally, for organic modification, a series of solution containing different organic solvents were prepared (1631, 1831, 1227, D1621 and D1221

Table 1
Structures and properties of selected modifier

Name (abbrev.)	Chemical structure	Molar mass (F.M.)	CAS
1631 (CTMAB)		328.42	112-02-7
1831		348.5	112-03-8
1227		339.99	139-07-1
D1621		530.4	1812-53-9
D1221		418.19	3401-74-9

from Table 1). 100 g of Na-bentonite and a series of organic solution was added in to 500 mL conical flask and vibrated for 3 h at 60℃. Then, the soil sample was filtered and washed for 3 times with deionized water to remove bromine ions and chloride ions [16]. Afterward, the solid was dried with vacuum drying oven at room temperature for 24 h. Finally, modified bentonite with different intercalation agents was obtained through a 200-mesh sieve.

Organic intercalator (1631, 1831, 1227, D1621, D1221) operating fluid of 10 mmol/L were diluted with ultrapure water. Leachate was treated with modified bentonite in a series of conical bottles. The different concentration of CTMAB (2, 3, 4, 5, 6 mmol/L) was selected to determine the optimal concentration.

2.3. Characterization methods

The crystalline phase and functional groups were characterized using X-ray diffraction (XRD), Fourier-transform infrared (FT-IR), respectively. The XRD data of adsorbents were recorded with a 2SX100e (Rigaku, Japan). A Nicolet iS10 (Thermo Scientific, USA) was used to record FT-IR of adsorbents.

2.4. Adsorption experiments

The solution pH is controlled within the range of 2–11 and the CTMAB-bentonite dosages were limited within 0.1–1.6 g. COD_{cr} was measured by HH-6 chemical oxygen consumption meter (Shanghai Haiheng Mechanical & Electrical Co., China). Adsorption capacity A (mg/g) were calculated by Eq. (1):

$$A = \frac{\left(C_0 - C_e\right)V}{\left(1{,}000D\right)} \tag{1}$$

where C_0 and C_e (mg/L) are the pre-adsorption concentration and post-adsorption concentration of landfill leachate, V (mL) is the volume of sample and D (g) is the dosage of CTMAB-bentonite.

3. Results and discussion

3.1. Selection of intercalating agent

As shown in Table 2, we respectively selected a variety of modifiers to modify bentonite. The adsorption capacity of bentonite modified by CTMAB reached 345.76 mg/g, and its distribution coefficient K_a = 0.2081, was also the largest among all modified bentonite. Compared with other organic bentonite, CTMAB-bentonite has a larger distribution coefficient and a much higher adsorption capacity for landfill leachate [17]. Therefore, CTMAB-bentonite was selected as the research object.

In addition, you can see the effect of concentration of CTMAB on leachate adsorption by CTMAB-bentonite in Fig. 1. When the concentration of CTMAB was 4 mmol/5 g, the adsorption capacity reached the maximum value. At the same time, the organic carbon content and their adsorption removal rate of leachate are shown in Table S3. After CTMAB modification, the organic carbon content of modified bentonite increased from 3.28% to 9.89%, and the removal rate increased from 10% to 85%. The results showed that the adsorption capacity of CTMAB-bentonite was obviously improved. The increase of carbon content also indicated that bentonite were successfully modified with $CTMA^+$ as intercalators.

3.2. Characterization of CTMAB-bentonite

3.2.1. XRD analysis

XRD was used for the characterization of bentonite. Generally, layer spacing is calculated according to Bragg's formula, which is as follows:

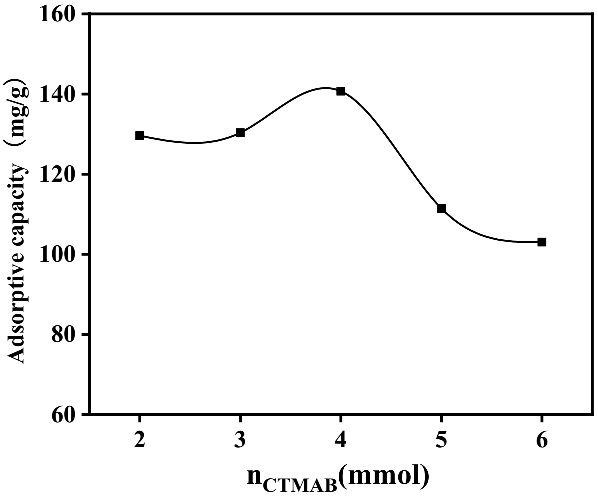


Fig. 1. Effect of molar concentration of cetyltrimethyl ammonium bromide on leachate adsorption by CTMAB-bentonite.

Table 2
Effect of different intercalators on adsorption of bentonite

Modifier	COD_0 (mg/L)	COD_t (mg/L)	q_e (mg/g)	K_a	Removal rate (%)
Na-bentonite	11,244	10,142	59.863	–	9.81
1631 (CTMAB)	11,125	1,646	345.76	0.2181	85.1
1831	11,415	2,383	457.51	0.1999	79.9
1227	11,270	2,294	456.38	0.1929	79.6
D1621	11,160	2,332	454.04	0.1952	79.0
D1221	11,055	2,411	452.67	0.1964	78.2

$$2d\sin\theta = n\lambda \tag{2}$$

XRD analysis (Fig. 2) results indicated that the characteristic diffraction peaks of Na-bentonite and CTMAB-bentonite at 2θ 5.87° and 4.54 ° were observed, respectively. However, compared with Na-bentonite, the characteristic peak of CTMAB-bentonite shifted to the left, and the crystal structure of bentonite did not change after CTMAB modification. And the spacing between the layers has increased significantly, The layer spacing d_{001} of the Na-bentonite is 12.69 Å, and the layer spacing d_{001} of CTMAB-bentonite is 18.94 Å, which is more than 6 Å larger than that of the Na-bentonite, which indicated that the organic cation $CTMA^+$ entered into the layer structure of bentonite and exchanged with the inorganic cation between the layers to form an organic complex dominated by ionic bonds [18]. The adsorption capacity of bentonite will be improved.

3.2.2. FT-IR analysis

FT-IR spectrum characterization of modified bentonite has been widely used [19]. The FT-IR spectra of Na-bentonite and CTMAB-bentonite, which in 4,000–500 cm^{-1} range were seen in Fig. 3. As can be seen from the spectrogram, the significant change after modification is that Si–O–Si antisymmetric stretching vibration peak becomes wider, this phenomenon has been found in previous studies [11]. The main peak shape and frequency of CTMAB-bentonite and Na-bentonite below 1,300 cm^{-1} are basically similar, indicated that the basic skeleton of the two substances is similar. Between 3,620–3,720 cm^{-1}, we could see the stretching vibration of hydroxyl groups in bentonite, between 1,000–1,038 cm^{-1}, Si–O–Si antisymmetric stretching vibration of bentonite, located at around 440–515 cm^{-1}, Si–O–Ca and Si–O–Al and Ca–O and Al–O coupling vibration. At 3,300–3,500 cm^{-1}, there was a strong and wide absorption band, which was the stretching vibration of hydroxyl of interlayer water molecules, suggesting that there was still a small amount of hydrate between CTMAB-bentonite. Obviously different from the Na-bentonite, there were two peaks of stretching vibration of $–CH_3$ and $–CH_2$ at 2,878 and 2,808 cm^{-1}, respectively [20]. The above analysis indicated that organic quaternary ammonium salt had entered the interlayer of bentonite [21]. Organic surfactants had entered the bentonite interlayer to replace Na^+ and formed new complexes.

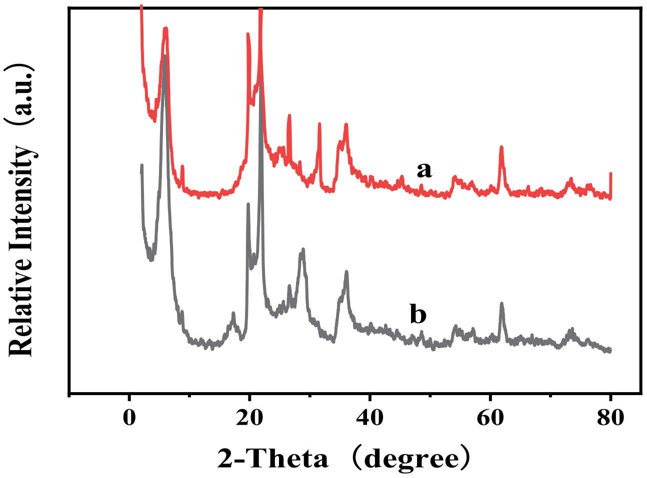


Fig. 2. X-ray diffraction patterns of CTMAB-bentonite (a) and Na-bentonite (b).

3.3. Adsorption experiments

3.3.1. Effect of contact time

Fig. 4a shows the effect of contact time on the adsorption of leachate. It can be seen that the initial adsorption process of leachate on CTMAB-bentonite was very fast, but with the increase of time, the adsorption removal rate decreased gradually. The adsorption capacity reached 32.2 mg/g in the first 10 min. The adsorption time curve of CTMAB-bentonite of leaching solution showed that the adsorption capacity increased slowly and reached equilibrium at 50 min. The amount of adsorption remained unchanged in subsequent experiments. Therefore, in order to ensure the adsorption equilibrium, 60 min is the most appropriate adsorption time [18].

3.3.2. Effect of adsorbent dosage

The influence of CTMAB-bentonite dosage on the adsorption of landfill leachate is shown in Fig. 4b. The adsorption capacity of the CTMAB-bentonite increased with the increasing dosage of adsorbent. The adsorption capacity could reach up to 25.6 mg/g when the adsorption dosage was only 0.3 g, the adsorption capacity rose quickly in the range of 0–0.4 g, then the adsorption reached equilibrium at 0.8 g. The maximum adsorption capacity was 30.8 mg/g. When the dosage of CTMAB-bentonite exceeded 0.5 g/15 mL, the adsorption capacity hardly increased. Therefore, the amount of dosage was determined to be 0.5 g/15 mL. Above results indicated that the adsorption capacity of CTMAB-bentonite for the landfill leachate strongly enhanced after being organic modified [22]. The possible reason was that the surface property of bentonite changes from hydrophilic to hydrophobic, which was more conducive to the adsorption of organic pollutants [23].

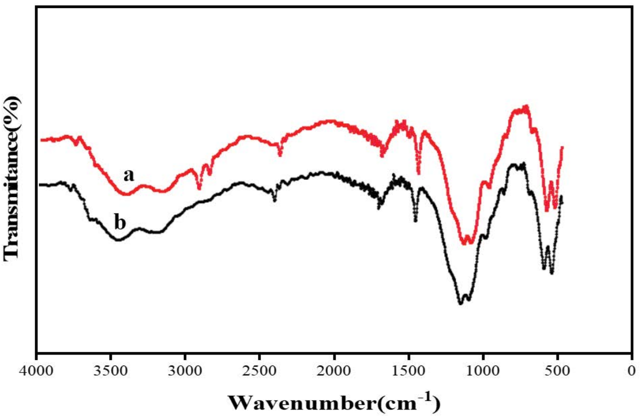


Fig. 3. Fourier-transform infrared spectra of CTMAB-bentonite (a) and Na-bentonite (b).

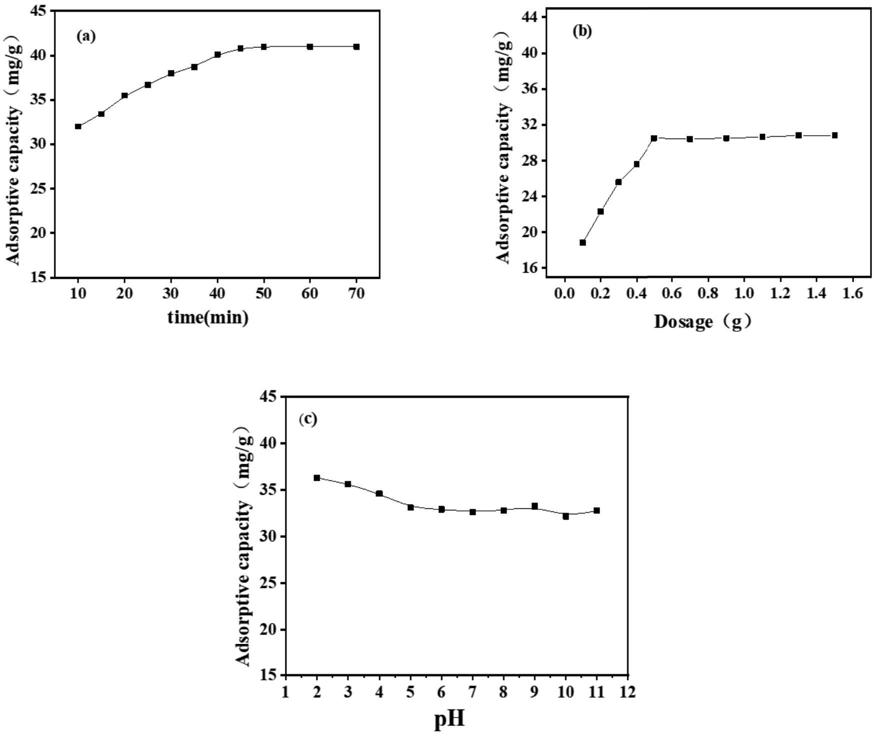


Fig. 4. Effect of contact time (a), dosage (b), and pH (c) on leachate adsorption by CTMAB-bentonite.

3.3.3. *Effect of initial solution pH*

Generally, it is considered that pH value is an important factor determining the process of mass transfer between solid and liquid phases. As can be seen in Fig. 4c, the adsorption capacity decreased slightly with the increase of pH value from 2 to 4, this has been seen in other studies as well [24], and then kept unchanged with further increase of pH value to 10. We can see that, when the pH value was less than 3, the adsorption performance was greatly affected by pH value. But when the pH value ranged from 5 to 10, it had little influence on the adsorption capacity. It has been reported that the pH of landfill leachate was between 6 and 9, which suggested that CTMAB-bentonite adsorbed landfill leachate has strong resistance to acid–base interference and could maintain good performance in a wide range. Therefore, the pH value of the adsorbent can be applied to a wide range of practical life [24].

3.4. *Adsorption kinetics study*

In this experiment, the adsorption of leachate by CTMAB-bentonite was fitted by pseudo-first-order kinetics, pseudo-second-order kinetics and intraparticle diffusion equation.

Pseudo-first-order model equation is:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{3}$$

where, q_e is amount of adsorption when adsorption reaches equilibrium (mg/g); q_t is the amount of adsorption at time t (min). k_1 is the reaction rate constant (min^{-1}).

Pseudo-second-order model equation is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{4}$$

where k_2 is the pseudo-second-order kinetic constant (g/mg·min).

As shown in Fig. S1a and b, the fitting result of leachate on CTMAB-bentonite was ideal and the relevant kinetic parameters are listed in Table 3. The R^2 of pseudo-second-order kinetic model reached 0.9972, and the fitting result was better than that of pseudo-first-order kinetic model (R^2 = 0.83). It can be seen from that the correlation coefficient of the pseudo-first-order model was not satisfactory, which indicated that the quantization calculated by the pseudo-first-order model was inconsistent with the experimental data. However, a better correlation coefficient could be obtained by fitting the experimental data according to Eq. (6), which indicated that the sorption process of leachate on modified bentonite was the pseudo-second-order. In addition, the theoretical adsorption capacity q_e of CTMAB-bentonite on leachate was 44.64 mg/g. Meanwhile, k_2 is often used to describe the pseudo-second-order initial adsorption rate. By calculating ($k_2^* = k_2 q_e$), the adsorption rate of leachate is 0.2049 min^{-1}, which was consistent with the adsorption rate in Fig. 4b. Analysis of the above experimental data indicated that the adsorption of leachate by CTMAB-bentonite conformed to pseudo-second-order kinetic model.

The intraparticle diffusion equation is:

$$q_t = k_3 t^{\frac{1}{2}} + C \tag{5}$$

Table 3
Kinetic parameters of CTMAB-bentonite for leachate removal

Pseudo-first-order model			Pseudo-second-order model			Intraparticle diffusion model		
k_1	q_e	R^2	k_2	q_e	R^2	k_3	C	R^2
–0.0959	0.1369	0.8321	0.0224	0.1091	0.9956	2.5352	23.92	0.9965

where k_3 is the rate constant of the kinetic model of diffusion in particles (g/mg·min$^{1/2}$); C is related to boundary layer thickness, (mg/g). In theory, this type of graph may appear multilinear, which showed that the adsorption process included several steps. The first part (the steeper part) is the outer surface adsorption or transient adsorption stage (State 1). The second part is the gradual adsorption stage (State 2), in which the diffusion inside the particle is rate-controlled. And the third part is the final equilibrium stage (State 3). At this time, due to the extremely low solute concentration, the diffusion velocity inside the particles begins to slow down.

To further investigate the rate-controlling mechanism, the intraparticle diffusion model was employed for discussion. The model relates the adsorption capacity to the square root of time ($t^{1/2}$), the equation of the intraparticle diffusion model is shown in Eq. (5). Its regression graph was a straight line, as shown in Fig. S1c, the figure did not pass through the origin ($C > 0$), so the reaction rate was not completely controlled by intraparticle diffusion. With the increase of time, the dynamics of diffusion in particles is relatively slow. The results showed that intraparticle diffusion and surface adsorption existed simultaneously when CTMAB-bentonite adsorbed leachate. It can be seen from the correlation coefficient that the diffusion model was suitable to describe the adsorption process of leachate on bentonite.

3.5. Adsorption isotherms

It is necessary to describe the experimental data of equilibrium adsorption by adsorption isotherms. The optimum adsorption isotherms were obtained (Fig. 5) through experiments to further determine the adsorption mechanism of bentonite on leachate, and various isotherm models were used to analyze the adsorption data. Some commonly used adsorption isotherm models are listed as Eqs. (6) and (7), such as Langmuir and Freundlich models and their linear form of equation Table S4 [25].

$$q_e = q_m \frac{bC_e}{1+bC_e} \tag{6}$$

$$q_e = k_f C_e^{1/n} \tag{7}$$

where q_e (mg/g) is the adsorption capacity, and C_e (mg/L) is the concentration of the solute left in the solution at the equilibrium concentration, q_m (mg/g) is the maximum adsorption capacity, b (L/mg) is the constant in Langmuir model, k_f (L/g) is the adsorption constant which is related to the adsorption affinity of the adsorbent. n is the Freundlich constant, which is often described as $1/n$ in studies [26].

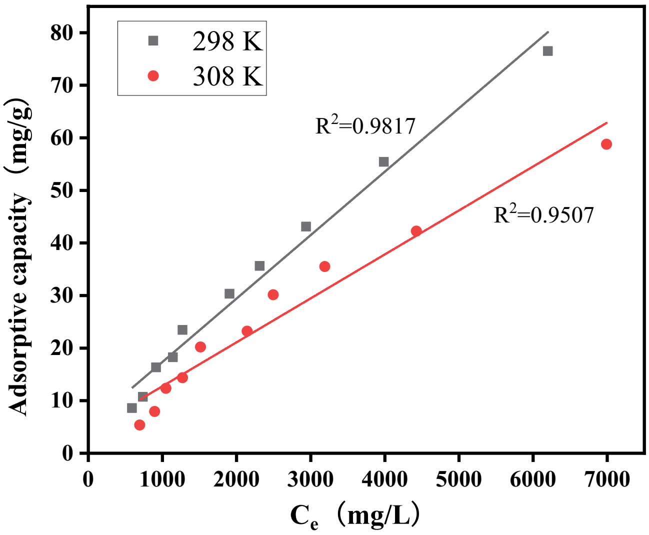


Fig. 5. Effect of temperature on adsorption of leachate by CTMAB-bentonite.

The Freundlich model was widely used, but it applied to highly uneven surface adsorption and multilayer adsorption, the model was more suitable for adsorption data in lower concentration. The constant n was an empirical constant, which was usually used to measure the linearity of adsorption and was used to judge the preference of adsorption. When $n < 1$, the adsorption process was non-preferential adsorption, indicated that the less adsorbents in the adsorbent. When $n \approx 1$, the adsorption was considered to be linear, each molecule occupies only one adsorption site and the adsorption energy of each adsorption site was the same. When $n > 1$, the adsorption was favorable [27].

Langmuir adsorption isotherm was monolayer adsorption on a uniform surface at constant temperature. This model assumed that solid surface was uniform and each adsorption site had the same affinity force for molecules. Therefore, many monomolecular adsorption experimental data often conformed well to this equation. In this experiment, Langmuir equation and Freundlich equation were used to analyze the adsorption data of landfill leachate [28].

The adsorption process could be explained by the Dublin–Radushkevich (D-R) isotherm. The adsorption mechanisms could be drawn from the following equation:

$$\ln q_e = \ln q_m - K\varepsilon^2 \tag{8}$$

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{9}$$

$$E = \frac{1}{\sqrt{2K}} \tag{10}$$

R and T are also related to gas constant (8.314 J/K·mol) and temperature (K), respectively. q_m (mg/g) is the adsorption capacity in the Dublin–Radushkevich (D-R) isotherm. K also represents the adsorption energy constant in this isotherm. ε is the Polanyi potential calculated by Eq. (9).

In the D-R isotherm, the most probable free adsorption energy (E, kJ/mol) is calculated by Eq. (10). $E < 8$ and $8 < E < 16$ kJ/mol show a physical and chemical process [29], respectively.

The value of E can be used to assess the process of adsorption. E is 10.47 kJ/mol according to Eq. (10). When the value is in the range of 8–16 kJ/mol, then the adsorption type can be explained by ion exchange, this implies that the type of adsorption involved in this study is chemical absorption [30] which reveals that the organic pollutants migrated to the bentonite surface by intermolecular polar force, and were "dissolved" by the active center of CTMAB-bentonite.

Parameters obtained by linear fitting calculation of Langmuir, Freundlich and D-R models are shown in Table 4. The fitting results (Fig. S2) show that Freundlich model has the best fitting effect ($R^2 > 0.91$). The similar result was obtained in other work [8] on the adsorption of landfill leachate by loam [31].

3.6. Adsorption thermodynamics

The influence of temperature on adsorption was obtained by experiments at different temperatures. In addition, a series of adsorption thermodynamic parameters including standard enthalpy change ΔH (kJ/mol), the standard entropy change ΔS (kJ/mol·K) and the Gibbs free energy change ΔG (kJ/mol) were obtained through experimental calculation. The results are listed in Table 5 and Fig. S3.

The thermodynamic equation is:

$$\ln k = \frac{\Delta S}{R} - \frac{\Delta H}{R} \times \frac{1}{T} \tag{11}$$

$$\Delta G = \Delta H - T \times \Delta S \tag{12}$$

where T is the reaction temperature of adsorption experiment, K and $\Delta H/R$ and ΔS are the slope and intercept of the line in the graph of $1/T$–ln$K$, respectively. According to the adsorption thermodynamic curve, the adsorption efficiency of bentonite to landfill leachate increases with the decrease of temperature. This may be due to the exothermic nature of the adsorption process.

Based on Table 5, we could see that $\Delta H < 0$, $\Delta S > 0$, and $\Delta G < 0$, with the increase of temperature, the content of ΔG decreased, which indicated that the adsorption effect was better at higher temperature. ΔS was positive, which indicated that the solid–liquid interface increased randomly during the adsorption of leachate by CTMAB-bentonite. In addition, the value of ΔH was negative, which further proved that the adsorption was an exothermic reaction and proceed spontaneously to the direction of chaotic increase, which indicated that the adsorption process was exothermic and physical adsorption properties [32].

Therefore, adsorbents contribute to the diffusion of $CTMA^+$ and accelerate its interaction rate with bentonite [33]. This indicated that room temperature was favorable for the adsorption of landfill leachate on materials [34].

3.7. Possible adsorption mechanism

According to previous studies, the adsorption of leachate by bentonite was a complex multi-stage process, and it was generally believed that the distribution effect was dominant in the treatment of organic pollutants by hydrophobic bentonite [35,36]. Firstly, the ion exchange between CTMAB and Na^+ of bentonite was conducted, and CTMAB filled in the Si–O alkane of bentonite to form hydrophobic organic layers, increasing the layer spacing (from 12.69 to 18.94 Å, Fig. 2) and affinity for organic materials (K_a = 0.208 L/g). it had an excellent treatment property of landfill leachate than that of the Na-bentonite (Table S3).

During the adsorption process of landfill leachate, CTMAB-bentonite firstly dispersed into the solution of landfill leachate to form an organophilic adsorbent. Then the organic pollutants migrated to the bentonite surface by intermolecular polar force, and were "dissolved" by the active center of CTMAB-bentonite. It was reported that the nonlinear isothermal adsorption line reflected that organics interacted with organics mainly by adsorption, while the linear isothermal line reflected that organics interacted with surfactants on organ-bentonite mainly by "extraction" [37,38].

Table 5
Thermodynamic parameters at 289, 308, and 318 K

Temperature (K)	ΔH (J/mol)	ΔS (J/mol·K)	ΔG (kJ/mol)
298	–3.57	32.92	–9.81
308			–10.14
318			–10.47

Table 4
Adsorption isotherm of CTMAB-bentonite for leachate removal

Temperature (K)	Langmuir			Freundlich			Dublin–Radushkevich		
	K_L	q_m^{-1}	R^2	k_f	n	R^2	q_m^{-1}	E	R^2
298	0.0659	0.0181	0.9636	0.3142	1.103	0.9643	0.0176	10.47	0.95
308	0.1344	0.0172	0.8898	0.0893	0.991	0.9105	0.0173	9.86	0.94

According to Fig. 5, the adsorption isotherm presented that the q_e was well lineared with the C_e (500–7,000 mg/L) both at 298 and 308 K, with correlation coefficient > 0.9500. The kinetic study showed that the pseudo-second-order kinetic model could well fit the experimental data ($R^2 = 0.99$), which suggested that chemisorption process existed. Intraparticle diffusion model study showed that the curve did not pass through the origin (the value of C is not 0), indicating intraparticle diffusion was not the rate-control step [39]. In addition, the adsorption heat released by organic distribution was very small ($\Delta H = -3.57$ J/mol). These results were consistent with the distribution effect [40,41].

4. Conclusions

In this work, bentonite modified by CTMAB was successfully prepared to treat landfill leachate. Through a series of characterization of CTMAB-bentonite (XRD and FT-IR), it was found that $CTMA^+$ cations were intercalated into the interlayer spaces of bentonite leading to an increase in the basal spacing d_{001}, resulting to the layer spacing of modified bentonite increased about 6 Å compared with original bentonite. The adsorption test results showed that the adsorption dosage and time were 0.5 g and 60 min and the effect of temperature and pH on the adsorbent will not affect the practical application. The adsorption process of landfill leachate conformed to the Freundlich model. The study of adsorption kinetics showed that the adsorption of leachate by CTMAB-bentonite accorded with pseudo-second-order kinetic model ($R^2 > 0.99$). The model of intraparticle diffusion showed that the adsorption rate of CTMAB-bentonite to leachate was not completely controlled by intraparticle diffusion, and the intraparticle diffusion and surface adsorption coexisted. The adsorption isotherms imply that the type of adsorption involved in this study is chemical absorption. Thermodynamic studies showed that during the adsorption of leachate by CTMAB-bentonite, the interface between solid and liquid increased randomly. The adsorption process was an exothermic reaction, and the adsorbent contributed to the diffusion of $CTMA^+$ and accelerated the interaction rate between $CTMA^+$ and bentonite. Under the optimum conditions, the maximum removal rate could reach 85% which showed that CTMAB-bentonite was an excellent adsorbent for landfill leachate.

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Supporting information

Table S1
Leachate components

Composition	COD	Al^{3+}	Li^{2+}	Ba^{2+}	Mn^{7+}	Cr^{6+}	Be^{2+}	Br^-	I^-
(mg/L)	11249	16.91	4.14	13.36	4.31	0.462	0.23	20.70	0.531

Table S2
Bentonite oxide composition

Composition	SiO_2	Al_2O_3	MgO	Fe_2O_3	CaO	K_2O	TiO_2
(%)	51.89	16.91	4.14	13.36	4.31	0.462	0.23

Table S3
Organic content and removal effect of bentonite before and after modification

	Organic content (%)	Removal rate (%)
Na-bentonite	3.28	9.89
CTMAB-bentonite	21.83	85.06

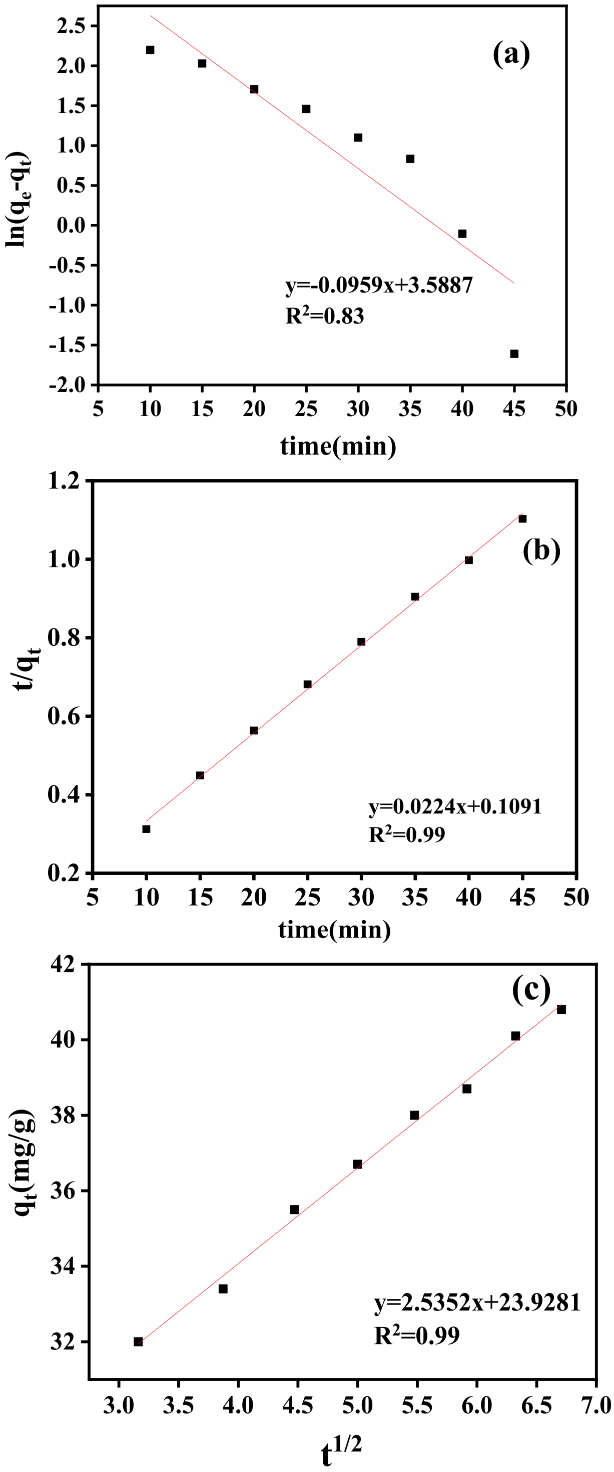

Fig. S1. Pseudo-first-order (a) and pseudo-second-order (b) order kinetic curves of adsorption leachate by CTMAB-bentonite and intraparticle diffusion model (c).

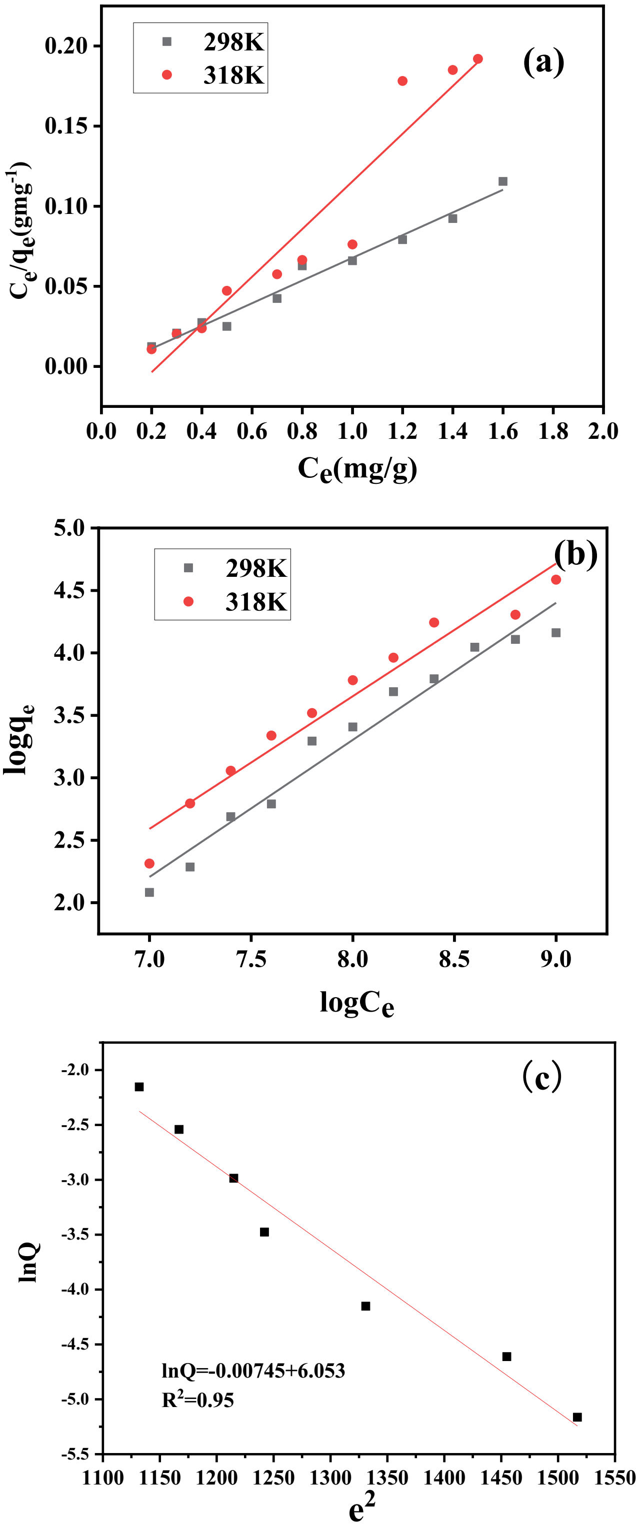

Fig. S2. (a) Langmuir (b) Freundlich and D-R (c) adsorption isotherm at different temperatures.

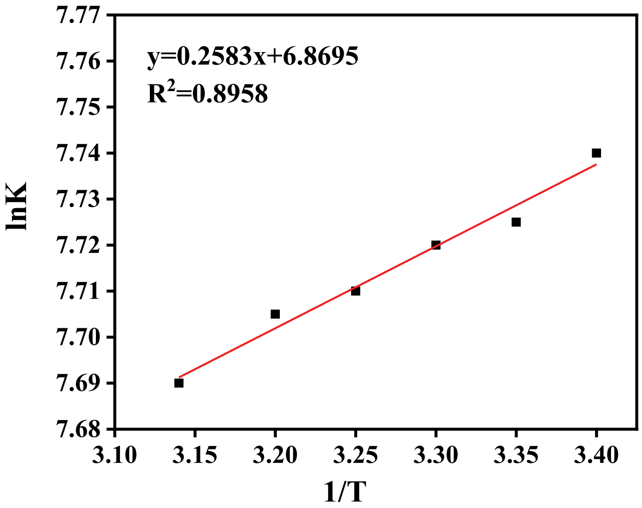

Fig. S3. Adsorption thermodynamic curve.

Table S4
Adsorption isotherm models and their linear forms

Isotherm	Equation	Linear form of equation
Langmuir-I	$q_e = q_m \frac{bC_e}{1+bC_e}$	$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m}$
Freundlich	$q_e = k_f C_e^{1/n}$	$\ln q_e = \ln k_f + \frac{1}{n} C_e$