

Article

Bisphenol A and 17 α -Ethinylestradiol Removal from Water by Hydrophobic Modified Acicular Mullite

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Abstract: The hydrophilicity and hydrophobicity of adsorbents have an important influence on organic pollutants adsorption. To effectively remove bisphenol A (BPA) and 17-acetylene estradiol (EE2) from water, acicular mullite was modified by cetyl trimethyl ammonium bromide (CTMAB) to increase the hydrophobicity of the mullite. The adsorption process and mechanism of BPA and EE2 by modified acicular mullite were studied in detail. Results indicated that the concentration of CTMAB solution was related to the contact angle of CTMAB-modified mullite (CTMAB-M). The optimal concentration of CTMAB was 4 mmol/L. The CTMAB-M could adsorb more hydrophobic organic pollutants than virgin acicular mullite. Due to the electrostatic attraction and hydrophobic partitioning, the adsorption amount of BPA and EE2 on CTMAB-M increased with increasing pH. The adsorption amounts of BPA and EE2 on CTMAB-M increase with increasing ionic strength. The adsorption kinetics of BPA and EE2 adsorption on CTMAB-M could be best described by the pseudo second-order kinetics model. Thermodynamic analysis showed that the low temperature favored the adsorption of BPA and EE2 on CTMAB-M, and the adsorption was driven by entropy increase. Site energy studies indicated that BPA and EE2 firstly occupy high-energy adsorption sites and then switch to low-energy sites during the adsorption process. The average adsorption site energy $\mu(E^*)$ of EE2 on CTMAB-M is smaller than BPA. CTMAB modification can significantly improve the removal efficiency of ceramsite on EDCs.

Keywords: adsorption; bisphenol A; 17 α -ethinylestradiol; acicular mullite; CTMAB



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1. Introduction

Endocrine disrupting chemicals (EDCs) have the capacity to cause reproductive disorders and damage to the nervous system and other metabolic systems of both humans and animals, especially during pregnancy and adolescence. More and more attention is being paid to EDCs by researchers from all over the world [1]. BPA and EE2 are two typical endocrine disruptors that have been widely detected in surface water [2], sediment [3], sewage plant effluent [4], and even waterworks effluent in recent years [5]. Water sources are contaminated by BPA and EE2 through both untreated industrial wastewater and aquaculture wastewater [6]. The traditional water treatment process cannot effectively remove BPA and EE2 from water [6]. The emerging water treatment technologies, such as chemical precipitation, electrodialysis, ion exchange, membrane and advanced oxidation

processes [7–9] have the disadvantages of high cost and application infeasibility in industrial processes. Therefore, it is necessary to improve the removal efficiency of BPA and EE2 by modifying traditional water treatment technology. For example, by modifying the filter material, the removal effect of the filter tank on EDCs can be improved.

Due to the low cost, easy operation (at room temperature and under normal pressure) and reusability [10], adsorption technology is considered one of the most competitive and promising technologies in this field. In recent years, various adsorbents have been developed and tested to remove BPA and EE2 from water [11]. Previous studies have shown that the hydrophilic/hydrophobic balance of adsorbents had an important impact on the adsorption capacity of organic pollutants [12]. According to the similarity intermiscibility theory, the hydrophobic character favors the adsorption of the hydrophobic organic molecules. However, it is also important for adsorbents to have certain hydrophilicity, which could help them to break the interface barrier of adsorbents in the aqueous solution during the adsorption process. The octanol–water distribution coefficient ($\log K_{ow}$) is often used to characterize the hydrophobicity of substances. Usually, at $\log K_{ow} < 1$, the substance is considered relatively hydrophilic and more water-soluble, while the compound is very hydrophobic at $\log K_{ow} > 4$. The $\log K_{ow}$ of EE2 and BPA are 3.90 and 3.64, which indicated that they are both hydrophobic [13]. Therefore, the hydrophobic modification of the adsorbent can promote the adsorption removal of BPA and EE2 from water.

Cetaletyl trimethylated ammonium bromide (CTMAB) is a cationic surfactant of which the head is a positively charged quaternary ammonium group and the tail is a hydrophobic alkyl chain. Due to the unique structure and physicochemical properties, CTMAB is often used for adsorbent modification to increase the removal performance of adsorbents [14]. Wang et al. modified graphite with CTMAB to remove BPA from water [15]. The equilibrium adsorption capacity of BPA by CTMAB-modified graphite was 125.01 mg/g. The adsorption mechanism could be explained with electrostatic interaction and hydrophobic interaction [15]. Evans Dovi et al. synthesized CTMAB-modified walnut to enhance the uptake for BPA and Congo red. The adsorption equilibrium results showed that CTMAB-modified walnut exhibited a huge potential for use in the treatment of waste water, and its maximum adsorption quantity of BPA was 38.5 mg/g [16].

Mullite is a porous ceramicsite with a needle-like structure, a highly developed open hole structure, a large specific surface area, and a high mechanical strength, which makes it an ideal material for adsorbent support material and filter material for water treatment [17]. Herein, CTMAB was used to modify acicular mullite to increase the hydrophobicity of mullite in order to improve the removal efficiency of BPA and EE2 by the filter unit in the traditional water treatment process. Various characterization technologies and the site energy distribution model were used to analyze the surface properties of CTMAB-modified acicular mullite and reveal the adsorption mechanism of EDCs.

2. Materials and Methods

2.1. Materials and Reagents

Acicular mullite (M) ceramicsite with a diameter of 0.8–1.2 mm was laboratory synthesized, and the synthetic method was listed in the Supporting Information. Unless otherwise specified, all chemical reagents were analytical and purchased from Sinopharm Group Chemical Reagents Co., LTD. The standard substances of BPA (99%) and EE2 (99%) were purchased from Dr. Ehrenstorfer GmbH (Dr. E, Germany).

2.2. BPA and EE2 Analysis Methods

BPA and EE2 in water samples were firstly enriched by solid phase extraction (SPE, Oasis HLB, 3cc/60 mg, Water, USA), with the following steps: 10 mL of CH₃OH and 10 mL of HCl solution ($\text{pH} = 3.0 \pm 0.5$) flowed through the SPE column to activate the columns. Then, 80 mL water sample with a drop of the HCl solution (the volume ratio of HCl: H₂O = 1:3) was passed through the SPE column. The extraction rate was 1–2 mL/min. After extraction, 10 mL HCl solution ($\text{pH} = 3.0 \pm 0.5$) was passed through the SPE column

to remove the impurities. Finally, 10 mL of CH₃OH was used to be eluted by the BPA or EE2 molecules. The samples were gently dried by purging N₂. The samples were dissolved with 1 mL of CH₃OH and filtered with a 0.22 µm membrane. The concentrations of BPA and EE2 in the samples were detected by high performance liquid chromatography (HPLC, 1260 Infinity HPLC System, Agilent, Santa Clara, CA, USA). The operating conditions were detailed as follows: the injection volume was 10 µL, 100% CH₃OH was used as the mobile phase with the flow rate of 1 mL/min at the column temperature of 30 °C, the UV detector wavelength was 230 nm, and each sample was measured twice. The standard samples and blanks were used for quality control. The recovery for BPA was 92.56~100.06% and the recovery for EE2 was 93.50~107.37%. EE2 and BPA were quantified according to a calibration curve (the coefficient of determination greater than 0.999), which was performed within the range of experimental concentrations in this study. Please refer to the previous literature for more details [18,19].

2.3. Material Synthesis and Characterization

2.3.1. CTMAB-Modified Acicular Mullite

A series of CTMAB solution 100 mL with different concentrations (0, 1, 4, 10, 20, 40, 60 and 100 mmol/L) was prepared, and 3 g acicular mullite was added to the solution and stirred for 24 h with a rotation rate of 120 r/min at 25 °C. Then, all samples were washed with pure water until no foam was visible. Finally, the samples were dried at 80 °C in an oven and were labeled as CTMAB-M.

2.3.2. Characterizations

The Zeta potential was measured under different pH conditions by using a Zeta potential analyzer (Malvin, Worcestershire, England). Thermal weight analysis was performed on a TGA /DSC1 (Mettler, Gießen, Germany) in a range of 25 to 700 °C under air and a heating rate of 10 °C /min. The hydrophobicity was evaluated by a dynamic contact angle meter DSA100 (KRÜSS, Hamburg, Germany) in pure water at 25 °C and measured at least ten points per sample.

2.4. Batch Adsorption Experiment

2.4.1. Optimization of CTMAB Modification Methods

A series of 100 mL (1 mg/L) of BPA and EE2 solutions (pH = 6.5 ± 0.2) was prepared in 250 mL conical flasks. Then, 1 g CTMAB-M was added and the conical flasks were shaken for 24 h at 120 r/min, after which the samples were filtered through a 0.45 µm membrane and 80 mL filtrate was concentrated to 1 mL by solid phase extraction. The concentrations of BPA and EE2 were measured by HPLC.

2.4.2. Adsorption Equilibrium

A series of 100 mL BPA and EE2 aqueous solution (pH = 6.5 ± 0.2) at different concentrations (0~8 mg/L) were prepared. After adding 1 g CTMAB-M, the samples were stirred at 120 r/min for 24 h at 288, 298 and 308 K. After filtering through 0.45 µm membrane, 80 mL filtrate was collected to determine the concentrations of BPA and EE2 in the samples.

2.4.3. Kinetic Study

Then, 1 g CTMAB-M was added into 100 mL BPA or EE2 aqueous solution (pH = 6.5 ± 0.2) with a concentration of 1 mg/L. The concentration of BPA and EE2 of the samples were measured at a series of time points (5 to 1500 min).

2.4.4. Effect of Solution Environment

The effect of ionic strength on the adsorption of BPA and EE2 over the CTMAB-M was evaluated by adding different concentrations of NaCl (0.01, 0.1, 0.3 and 0.5 mol/L) during the adsorption experiment. The effect of solution pH value on the adsorption of BPA and

EE2 by CTMAB-M was explored by preparing 100 mL of BPA and EE2 aqueous solution (1 mg/L) with a series pH value (3.0~11.0), where 0.1 M HCl and 0.1 M NaOH were used to adjust the pH value.

2.5. Data Analysis

Adsorption isotherms were conducted to study the adsorption behavior of BPA and EE2 on CTMAB-M. The experimental equilibrium data were fitted by Freundlich (Equation (1)), Langmuir (Equation (2)), and Langmuir–Freundlich model (Equation (3)).

The Freundlich model:

$$q_e = K_F C_e^{1/n} \quad (1)$$

where q_e is the equilibrium adsorption capacity (mg/g), C_e is the concentration in solution at equilibrium moment (mg/L), K_F is the Freundlich constant related to the sorption affinity, $1/n$ is the Freundlich exponential coefficient.

The Langmuir model:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

where q_m is the maximum adsorption capacity (mg/g), K_L is the Langmuir constant refer to the adsorption affinity (L/mg).

The Langmuir–Freundlich model:

$$q_e = \frac{Q_g (K_{LF} C_e)^n}{1 + (K_{LF} C_e)^n} \quad (3)$$

where Q_g is the maximum adsorption capacity (mg/g), K_{LF} is the Langmuir–Freundlich constant related to the adsorption affinity, n is the relating to the heterogeneity of adsorbent surface.

Adsorption kinetics

Kinetic models (pseudo-first-order model (Equation (4)), pseudo-second-order (Equation (5)) and intraparticle diffusion model (Equation (6)) were applied to describe the different steps involved in the adsorption process.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

$$q_t = k_{pi} t^{1/2} + c \quad (6)$$

where q_e and q_t are the adsorption capacity (mg/g) at equilibrium moment and time t (min), k_1 and k_2 are the rate constant of the pseudo-first-order (1/min) and pseudo-second-order model (g/(mg min)) [20]. k_{pi} (mg/(g min^{1/2})) is the rate constant of intraparticle diffusion, and c is associated with the thickness of the boundary layer at each adsorption stage.

Adsorption thermodynamic

The thermodynamic parameters such as free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) for the adsorption reaction are estimated using the following equations:

$$\Delta G^0 = -RT \ln K_C \quad (7)$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (8)$$

$$K_C = M_W \times 55.5 \times 1000 \times K_L \quad (9)$$

$$K_C = \frac{K_F \times \rho}{1000} \left(\frac{10^6}{\rho} \right)^{(1-\frac{1}{n})} \quad (10)$$

$$K_C = K_{LF} \left(\frac{10^6}{\rho} \right)^n \quad (11)$$

where R is the gas constant = $8.314 \text{ J}/(\text{mol}\cdot\text{K})$; T is the absolute temperature (K); K_c is the equilibrium constant, the Equations (9)–(11) is the unit conversion formula of K_c ; M_W is the molecule weight of BPA or EE2 (g), 55.5 is the moles of per liter of pure water (1000 g/L divided by 18 g/mol), ρ is the density of water (g/cm^3), K_F , K_L and K_{LF} are the parameters of isothermal adsorption models.

The site energy distribution model is shown in the Supporting Information.

3. Results and Discussion

3.1. CTMAB-M Feature Analysis

3.1.1. Adsorbent Optimization

The CTMAB loading could affect its morphology on the adsorbent. Previous studies have shown that the assembling structures of surfactants on the adsorbent were in various forms, such as hemispheres, hemicylinders, saturated monolayer, bilayer, adsorption micelles [15]. Surfactant micelle is formed in the solution when the concentration of surfactant exceeds the critical micelle concentration, and the adsorption hemimicelle can be formed when the surfactant concentration is slightly less than the critical micelle concentration. Therefore, the CTMAB loading is related to the hydrophobicity of CTMAB-modified ceramsite, which may affect its adsorption of target pollutants.

Considering that the CTMAB loading may be related to the concentration of CTMAB in the precursor solution, the contact angles of the CTMAB-M modified by various concentrations of CTMAB solution and their removal efficiency for BPA and EE2 were studied. The contact angle of adsorbent is related to its hydrophilic hydrophobicity. Usually, the larger the contact angle, the stronger the hydrophobicity [21]. As shown in Figure 1, the concentration of the CTMAB precursor solution increased from 0 mmol/L to 100 mmol/L, the contact angle of the CTMAB-M increased from 16.3° to 130.22° , and the acicular mullite also changed from hydrophilic to hydrophobic. Acicular mullite was negatively charged in neutral aqueous solution and preferred to bind to the head of the CTMAB molecules, while the hydrophobic tail of CTMAB covered the surface of the acicular mullite and resulted in the contact angle increasing rapidly. When the concentration of CTMAB solution increased due to the hydrophobic interaction, the hydrophobic tail of CTMAB would bind to the tail of the CTMAB in solution to form a bilayer, which tended to decrease the contact angle. The adsorption capacity of BPA and EE2 by CTMAB-M increased initially and then dropped. BPA and EE2 are hydrophobic organic materials, and the hydrophobicity of the adsorbent has a significant effect on the adsorption amount. The adsorption capacities of virgin acicular mullite for BPA and EE2 were 0.004 mg/g and 0.0035 mg/g , respectively. After modification with 4 mmol/L CTMAB solution, the adsorption capacities of CTMAB-M for BPA and EE2 reached 0.061 mg/g and 0.071 mg/g , which were increased by about 15- and 20-fold, respectively.

In addition, it can be seen that the adsorption of BPA by virgin acicular mullite was greater than that of EE2, and the adsorption of EE2 was greater than that of BPA by CTMAB-M, which may be because the octanol–water partition coefficient ($\log K_{ow}$) of EE2 is 3.9, while the value for BPA is 3.64, indicating that EE2 is more hydrophobic. The CTMAB-modified acicular mullite exhibited hydrophobicity, which could favor the adsorption of EE2. When the concentration of CTMAB solution was 4 mmol/L, the contact angle of modified mullite was the largest, and the adsorption capacity of BPA and EE2 was also the greatest. Therefore, the optimal concentration of CTMAB solution was determined as 4 mmol/L.

3.1.2. Thermogravimetric Analysis

Studies [22] have shown that CTMAB generally begins to decompose at 220°C , and a strong decomposition peak appears at 248°C . The decomposition of CTMAB in the interlayer always occurs at 300°C . Due to the existence of intermolecular bonds of the surfactant, the decomposition temperature could be further increased to 350°C . Another study showed that CTMAB molecules were entirely removed by calcination at 550°C .

for 5 h [23]. To estimate the loading of CTMAB, the TGA curves of acicular mullite and CTMAB-M were analyzed, and the results were shown in Figure 2. It can be seen that the weight loss of CTMAB-M was faster during 150–550 °C, which was presumed to be caused by the decomposition of CTMAB. During this period, the weight loss of CTMAB-M was 0.74%, and the weight loss of virgin acicular mullite was 0.23%. The difference between them was 0.59%, which was the amount of CTMAB loaded on mullite.

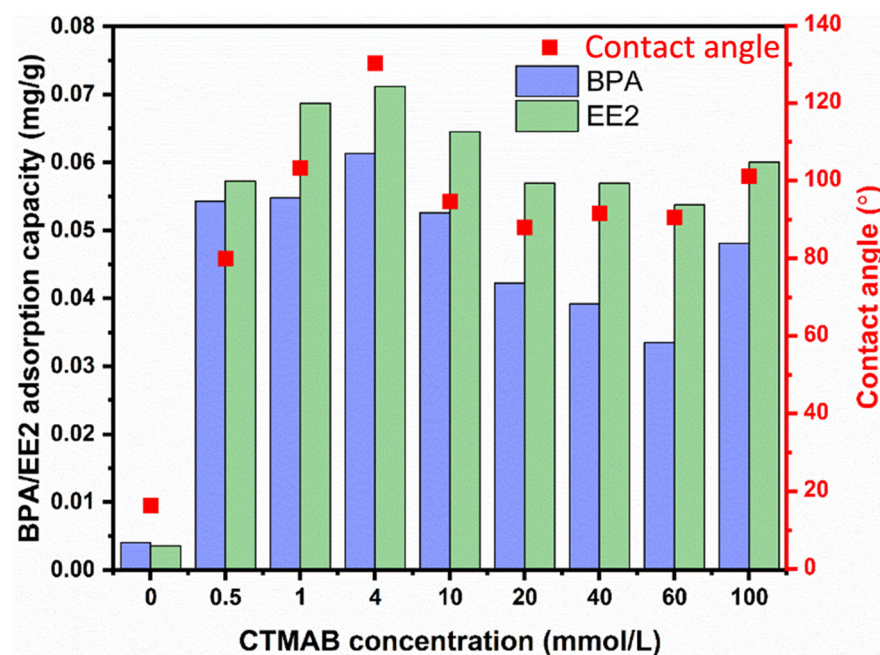


Figure 1. The contact angles of acicular mullite modified by different concentrations of CTMAB and the adsorption amount of BPA and EE2 on CTMAB-M.

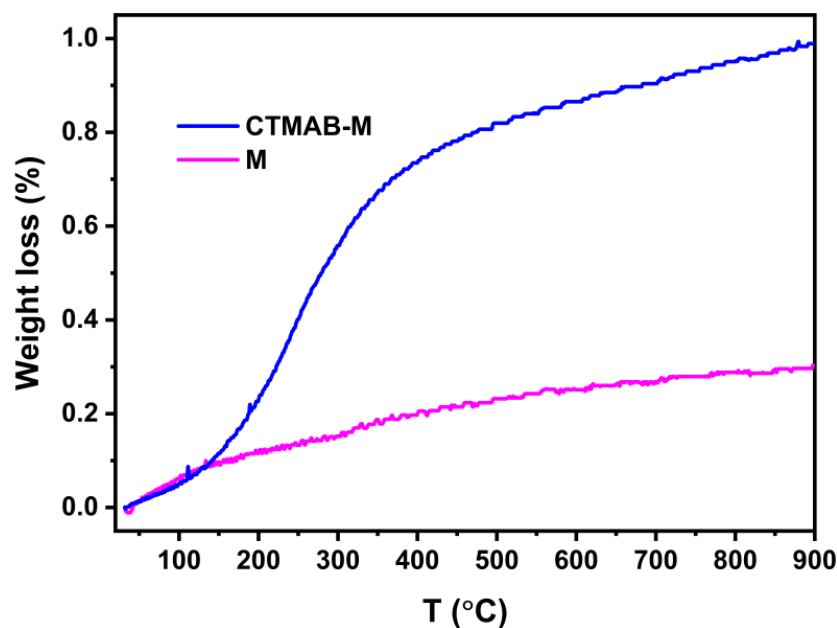


Figure 2. Thermogravimetric analysis of acicular mullite and CTMAB-M.

3.1.3. The Surface Charge Analysis

The surface charge of the adsorbent is one of the most important factors affecting the adsorption of charged pollutants in water. The point of zero charge (pH_{pzc}) is defined as the pH value at which the net charge on the adsorbent surface is zero [24]. pH_{pzc} is related

to the charge type and charge density on the adsorbent surface [25]. When the solution pH is less than the pH_{pzc} , the adsorbent surface is positively charged; otherwise, the adsorbent is negatively charged. As shown in Figure 3, the pH_{pzc} of acicular mullite was 6, while it rose to 7.82 after CTMAB modification. The enhancement of positive charge after CTMAB modification was mainly due to the formation of CTMAB bilayers on the surface of acicular mullite, as shown in Figure 3b.

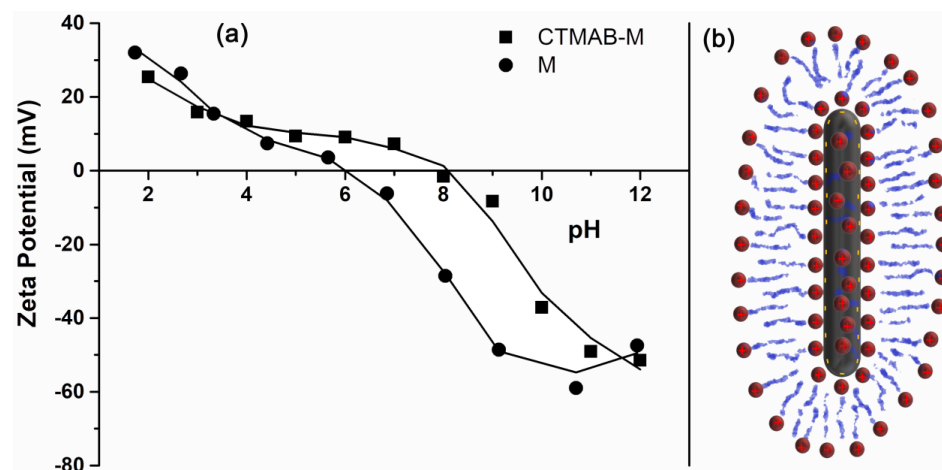


Figure 3. (a) The Zeta potential of acicular mullite and CTMAB-M, (b) Schema diagram of CTMAB-loaded acicular mullite.

3.2. Adsorption Kinetics

The removal efficiency of BPA and EE2 by CTMAB-M as a function of time is depicted in Figure 4. The adsorption amount of BPA and EE2 by CTMAB-M rapidly increased within 120 min, followed by a slow increase process, until it reached equilibrium at 500 min. The adsorption equilibration time in this study was longer than that reported in the literature [26]. The particle size of acicular mullite ceramicsite used in this study was 0.8–1.2 mm. Unlike fine particles that could directly contact the aqueous solution, acicular mullite has a well-developed pore structure inside. The aqueous solution and the BPA and EE2 it carried could be adsorbed only when they reached the inner pores of acicular mullite, and only a small amount could be adsorbed on the outer surface of acicular mullite.

The adsorption kinetic data of BPA and EE2 on CTMAB-M were fitted with pseudo-first-order model, pseudo-second-order model and intraparticle diffusion model, and the fitting parameters were shown in Table 1. It can be seen that the correlation coefficient (R^2) of the pseudo-second-order model of CTMAB-M for BPA and EE2 was the greatest. The equilibrium adsorption capacity ($q_{\text{e,exp}}$) is more similar to the data calculated by the pseudo-second-order model ($q_{\text{e,calculated}}$). Thus, the adsorption of BPA and EE2 by CTMAB-M conforms to a pseudo-second kinetic process, indicating that the adsorption of BPA and EE2 on CTMAB-M was mainly chemical adsorption. A recent study [15] proved that the positively charged quaternary ammonium group on the head of CTMAB could form π -electron interactions with the benzene ring in the BPA molecule. There is likely the same interaction between an EE2 molecule and CTMAB, which also contains a benzene ring. An intraparticle diffusion model was utilized on the data of adsorption of BPA and EE2 by CTMAB-M. As shown in Figure 4c,d, the adsorption process was staged, with a rapid increase at the beginning, probably because the adsorption firstly occurred on the surface of CTMAB-M and the BPA and EE2 molecules prior to occupying the high-energy adsorption sites, and then they slowly diffused into the particle interior. Since $q_t-t^{1/2}$ did not pass through the zero point, which indicated that intraparticle diffusion was not the only factor controlling the adsorption, the adsorption was caused by the combination of intraparticle diffusion and other adsorption forces.

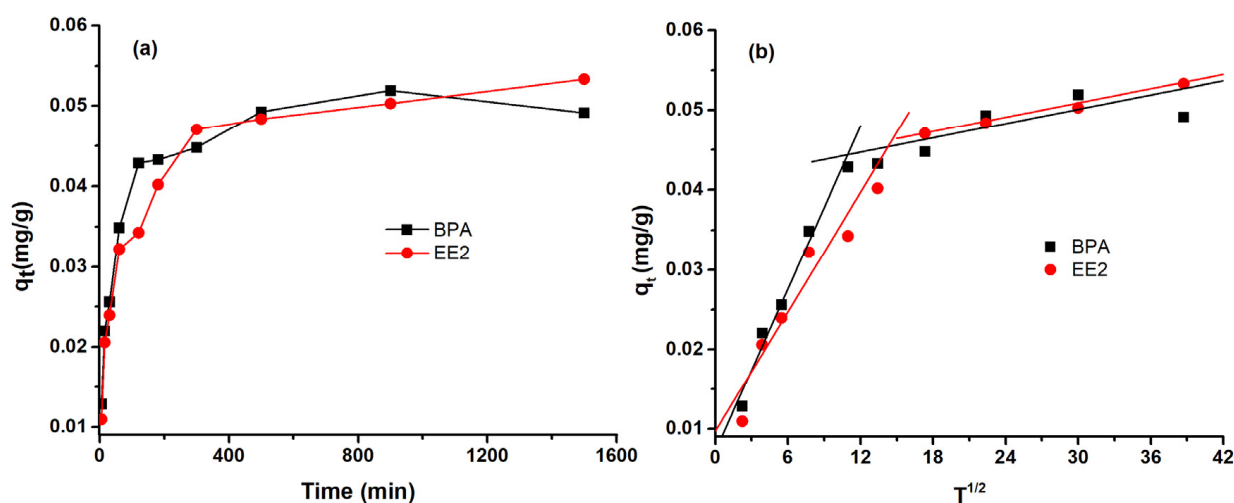


Figure 4. (a) Kinetic study of BPA and EE2 adsorption on CTMAB-M; (b) the relationship between q_t and $t^{1/2}$ of intraparticle diffusion model.

Table 1. Kinetic model parameters for the adsorption of BPA and EE2 on CTMAB-M.

Adsorbates	$q_{e, \text{exp}}$ mg/g	Pseudo-First-Order Model			Pseudo-Second-Order Model			Intraparticle Diffusion Model		
		K_1 min^{-1}	q_e mg/g	R^2	$K_2/$ $\text{g}/(\text{mg} \cdot \text{min})^{1/2}$	q_e mg/g	R^2	k_{pi} $\text{mg}/(\text{g} \cdot \text{min}^{1/2})$	c	R^2
BPA	0.052	0.030	0.047	0.91	0.869	0.050	0.97	0.91	23.76	0.68
EE2	0.055	0.021	0.047	0.84	0.581	0.051	0.94	1.06	20.13	0.77

3.3. Adsorption Isotherms

Figure 5 showed the adsorption isotherms of BPA and EE2 on virgin acicular mullite and CTMAB-M, and it can be seen that the unmodified acicular mullite had little adsorption of both BPA and EE2. After being modified by CTMAB, the adsorption amount of BPA and EE2 significantly increased. The adsorption amounts of BPA and EE2 on CTMAB-M increased with their concentrations in solution, which may be caused by high concentrations of BPA and EE2 in solution accelerating the molecular diffusion of BPA and EE2 [27]. The Langmuir model and Freundlich model are the most commonly used isothermal adsorption models to study the adsorption at the solid–liquid interface. The Langmuir model assumes that adsorption occurs on the solid adsorbent surface, and the adsorption is monolayer adsorption. The Freundlich model is an empirical model that usually describes multilayer adsorption, and the adsorbent surface is inhomogeneous. The Langmuir–Freundlich model combines the Langmuir model and Freundlich model and has three fitting coefficients that can be applied to both homogeneous adsorbent and heterogeneous adsorbent surfaces [28]. In this study, the Langmuir model, the Freundlich model and the Langmuir–Freundlich model were used to fit the isothermal adsorption data, and the fitting parameters were shown in Table 2.

Comparing the R^2 , the three isothermal adsorption models all fitted well with the isothermal adsorption data. The Langmuir–Freundlich model has the highest correlation coefficients (R^2 99.5 > 0) (Figure 5) and the Langmuir model was second, which indicated that CTMAB could uniformly load on the acicular mullite, and the adsorption of BPA and EE2 by CTMAB-M tended toward monolayer adsorption. The Langmuir–Freundlich model was used to analyze the site energy distribution on the surface of CTMAB-M.

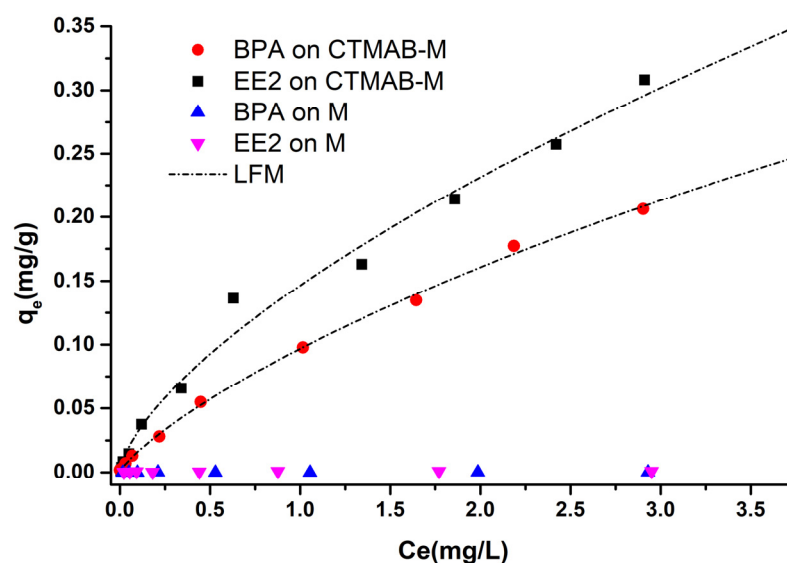


Figure 5. Isothermal adsorption curves of BPA and EE2 on M and CTMAB-M.

Table 2. Equilibrium parameters for the BPA and EE2 adsorption on CTMAB-M.

Adsorbate	Temperature (K)	Langmuir			Freundlich			Langmuir–Freundlich			
		K_L (L/mg)	q_m (mg/g)	R^2	$1/n$	K_F (L/g)	R^2	Q g (mg/g)	K_{LF} (L/mg)	n	R^2
BPA	288	0.276	0.592	0.998	0.712	0.124	0.997	0.887	0.128	0.870	0.999
	298	0.255	0.483	0.997	0.736	0.096	0.998	0.399	0.039	0.802	0.998
	308	0.608	0.235	0.995	0.611	0.081	0.977	0.194	0.909	1.221	0.997
EE2	288	0.169	1.818	0.994	0.835	0.248	0.989	0.862	0.592	1.489	0.999
	298	0.212	1.428	0.984	0.808	0.232	0.972	0.649	0.790	1.930	0.998
	308	0.801	0.339	0.998	0.552	0.129	0.972	0.301	1.062	1.168	0.999

The maximum adsorption capacities (q_m) at 298 K of the BPA and EE2 on the CTMAB-M were 0.483 mg/g and 1.428 mg/g, respectively (Table 2). The removal efficiency of BPA and EE2 was better than that of virgin acicular mullite. The q_m of BPA and EE2 was lower than the values reported in the literature [29]. The main reason is because the diameter of the ceramsite used in this study is 0.8–1.2 mm, while the adsorbent is usually found in fine particles in the literature [30]. As the temperature increases, the adsorption amount of BPA and EE2 on CTMAB-M decreases, indicating that the temperature increase is not conducive to the adsorption of BPA and EE2.

3.4. Effect of Solution pH

Solution pH significantly affects the adsorption of BPA and EE2 [31]. The pH not only affects the charge distribution on the surface of adsorbent but also affects the morphology of the adsorbate in the solution. The adsorption amount of BPA and EE2 on CTMAB-M at different pH values is shown in Figure 6. It is obvious that pH values affect the BPA and EE2 adsorption significantly. The adsorption amount of BPA was less than 0.02 mg/g at $pH < 4$, then increased with the increasing pH value in the range from 4 to 12. Similarly, the adsorption amount of EE2 was also very low at $pH < 4$, less than 30 mg/g, and then increased with pH value in the range of 4 to 10, while the EE2 adsorption amount decreased with pH value when $pH > 10$. Similar results were reported by Ribeiro-Santos et al. [32].

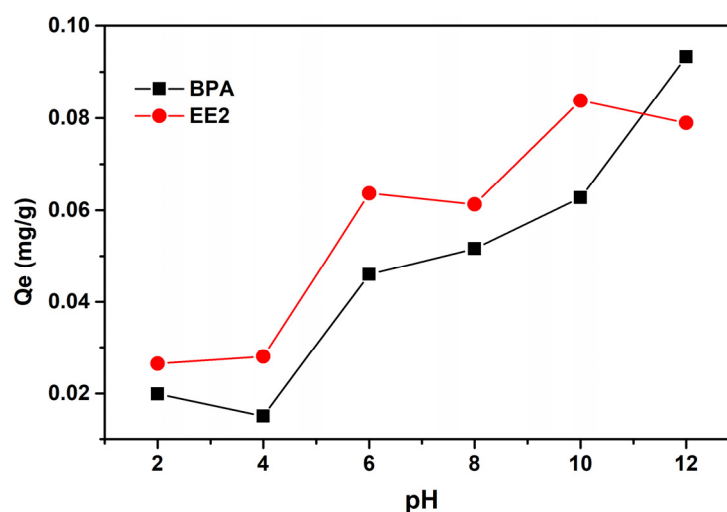


Figure 6. Effects of solution pH value on BPA and EE2 adsorption by CTMAB-M.

The CTMAB ($\text{Si-C-C-C-[N}^+(\text{CH}_3)_3]$) contains quaternary ammonium groups, which can not only provide a large number of adsorption sites and potential electrostatic interaction but can also increase the hydrophobicity of the adsorbent surface, which is favorable for the adsorption of hydrophobic organic pollutants. BPA and EE2 mainly exist in molecular form at $\text{pH} < 4$, while the surface of CTMAB-M was protonated at $\text{pH} < 4$, and H^+ could compete with BPA or EE2 for adsorption sites of CTMAB-M, resulting in quite a low adsorption capacity of BPA and EE2. The molecular structure of BPA remained unchanged at $4 < \text{pH} < 9.6$, and the adsorption amount of BPA on CTMAB-M slowly increased with pH value, probably due to the hydrophobic interaction between BPA and the alkyl chains of CTMAB. At $\text{pH} > 9.6$ (the pK_a value of BPA is $9.6\sim 10.2$) [33], the increase in the adsorption of BPA by CTMAB-M was mainly due to the combined effects of electrostatic attraction and hydrophobic partition between BPA^{1-} , BPA^{2-} and CTMAB.

When $\text{pH} > 10.47$ (the pK_a value of EE2 is 10.47), the adsorption capacity of EE2 decreases. Previous studies [32] have shown that the adsorption of EE2 mainly occurred in the hydrophobic cavity formed by the agglomeration of the CTMAB tail. On the one hand, EE2 is ionized and its hydrophobicity is weakened at $\text{pH} > 10.47$ [15]. On the other hand, when EE2 ionized an H^+ ion and became negative charged, it competed with the negatively charged OH^- in the water for the positively charged adsorption site on the head of CTMAB. Since the concentration of OH^- is higher at $\text{pH} > 10.47$, it is easier for OH^- to occupy the adsorption site on CTMAB than EE2 molecules.

3.5. Effect of Ionic Strength

NaCl was used as the model ion to study the effect of ionic strength on the adsorption of BPA and EE2 by CTMAB-M. As shown in Figure 7, with the increase of NaCl concentration, the adsorption amount of both BPA and EE2 on CTMAB-M increased gradually, which was mainly due to the salting-out effect caused by high ionic strength. On the other hand, the charge shielding effect formed by high ion concentration enhanced the intermolecular London dispersion force [34], which promoted the occurrence of adsorption. With the increase of ionic strength, the amount of BPA adsorbed by CTMAB-M gradually exceeded that of EE2. The solubility of BPA in water was 230 mg/L, and for EE2 the solubility was 9.2 mg/L. Therefore, the effect of increased ionic strength on BPA is greater than EE2 due to the salting-out effect.

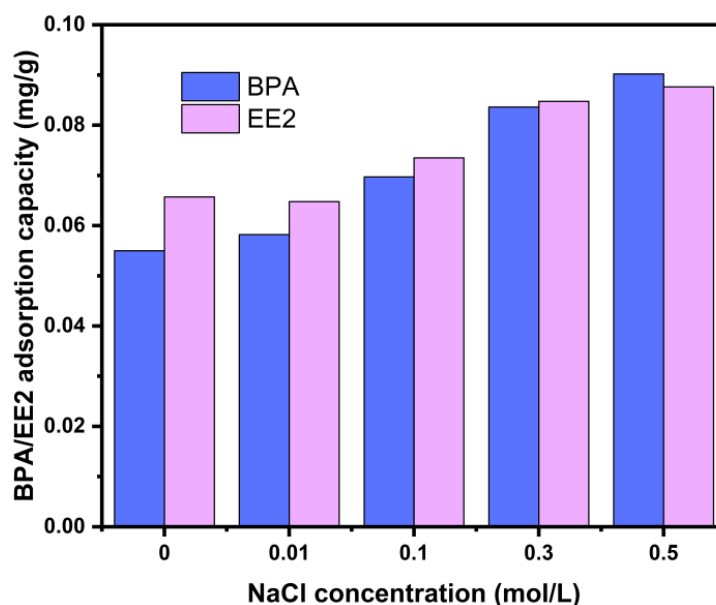


Figure 7. The effects of the ionic strength on the adsorption of BPA and EE2 by CTMAB-M.

3.6. Thermodynamic Study

The adsorption isotherms of EE2 and BPA at 288, 298 and 308 K were shown in Figure 8, and it can be seen that the adsorption amount of EE2 and BPA on CTMAB-M showed a strong correlation with temperature. The adsorption amount of EE2 and BPA both decreased with increasing temperature, indicating that the low temperature favors the adsorption of EE2 and BPA, which was consistent with the results reported in the literature [33].

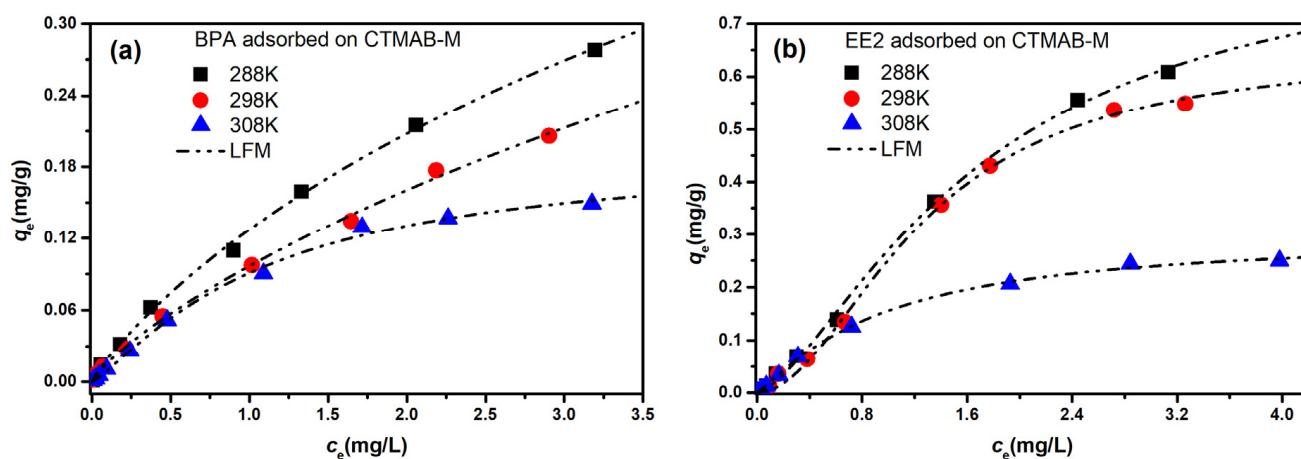


Figure 8. The adsorption isotherms of BPA (a) and EE2 (b) by CTMAB-M at different temperature.

Table 3 shows that the Langmuir–Freundlich model fitted the isothermal adsorption data for BPA and EE2 on CTMAB-M well; thus, this model was further used for thermodynamic analysis. The standard Gibbs free energy variation (ΔG^0), standard enthalpy change (ΔH^0) and the standard entropy variation (ΔS^0) were calculated in this study during the adsorption process of BPA and EE2 by CTMAB-M.

Table 3. Thermodynamics parameters of EE2 and BPA adsorbed on CTMAB-M.

Adsorbent	Adsorbates	Temperature K	ΔG^0 kJ/mol	ΔH^0 kJ/mol	ΔS^0 J/(mol·K)
CTMAB-M	BPA	288	−34.245	70.376	357.379
		298	−32.495		
		308	−41.636		
	EE2	288	−38.532	21.546	208.565
		298	−40.585		
		308	−42.705		

The thermodynamic parameters of the adsorption of EE2 and BPA by CTMAB-M were listed in Table 3. The $\Delta G^0 < 0$ indicated that the adsorption reaction could proceed spontaneously. The $\Delta H^0 > 0$ indicated that the adsorption was an endothermic reaction, and the $\Delta S^0 > 0$ suggested that the system disorder increased during the adsorption process. When the value of ΔS^0 was large enough, the reaction could proceed spontaneously. In this study, the ΔS^0 values of CTMAB-M for BPA and EE2 adsorption were 315.949 J/(mol·K) and 206.638 J/(mol·K), respectively, indicating that the process of CTMAB-M adsorption of two organic pollutants was mainly driven by the increase of entropy. The increase of entropy may be due to the existence of multi-level energy adsorption sites on CTMAB-M. However, the adsorption amount decreased as the temperature increased, which did not conform to the law of endothermic reaction. It is necessary to further analyze the adsorption mechanism to clarify this phenomenon.

3.7. Sites Energy Distribution

Previous studies [35] have shown that the adsorbent's performance was related to the site energy distribution on the adsorbent surface. Carter et al. [36] have shown that the affinity between the adsorbent and the adsorbate was associated with the average site energy on the adsorbent surface. The heterogeneity of the adsorbent surface could be evaluated by the width of the site energy distribution. The site energy distribution curve could provide information on the energy distribution of the high-energy and low-energy sites adsorbed by a specific adsorbate on the adsorbent surface. Therefore, site energy analysis can provide important information for studying the adsorption mechanisms.

In this study, based on the Langmuir–Freundlich model, the site energy distribution of CTMAB-M for adsorption of BPA and EE2 were calculated [37]. The calculation processes were given in the Supporting Information and the results are summarized in Table 4 and Figure 9. It can be seen from Figure 9b,d that with the increased of adsorption amount, E^* gradually decreased, indicating that BPA and EE2 first occupy high-energy adsorption sites during the adsorption process and then turn to low-energy adsorption sites. It can also be seen that the adsorption mainly occurred at high-energy sites at 308 K. When the adsorption energy was less than 12 kJ/mol, BPA was not adsorbed, and when the adsorption energy was less than 3.3 kJ/mol, EE2 was no longer adsorbed. At 298 K and 288 K, the adsorption mainly occurred at low-energy adsorption sites.

Table 4. Site energy distribution parameters for BPA and EE2 adsorbed on CTMAB-M.

Adsorbate	Temperature K	E_m^* kJ/mol	$F(E_m^*)$ mg·mol/(kg·kJ)	$\mu(E^*)$ kJ/mol	σ_e^* kJ/mol
BPA	288	6.55	80.55	6.12	2.86
	298	5.45	113.18	4.34	3.16
	308	14.36	23.07	14.41	2.52
EE2	288	2.50	134.03	3.16	0.98
	298	4.91	126.35	5.22	1.92
	308	6.74	34.35	6.82	4.00

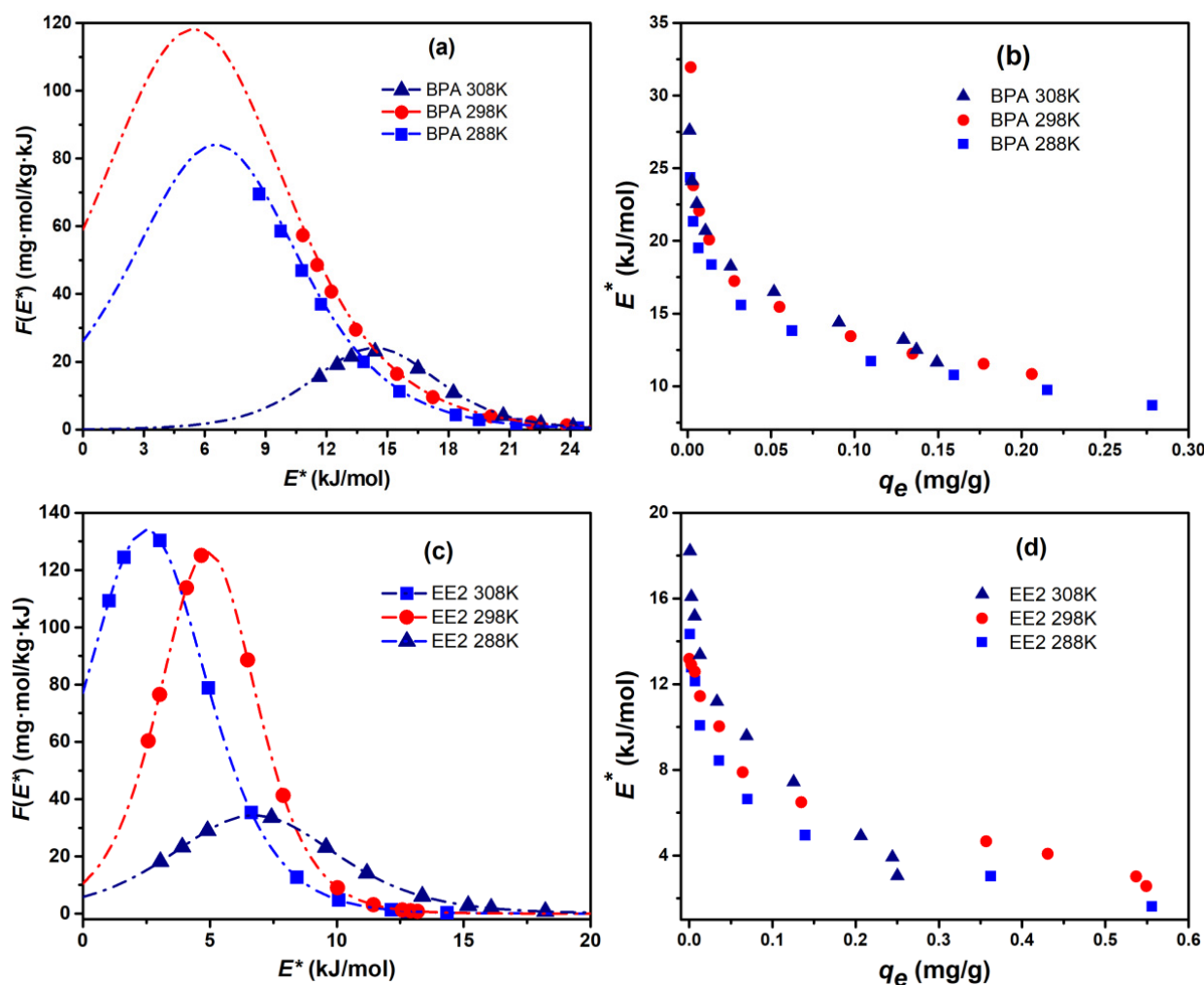


Figure 9. Site energy distribution of BPA and EE2 on CTMAB-M, (a) site energy distribution of BPA; (b) dependence of site energy E^* on q_e of BPA adsorption; (c) site energy distribution of EE2; (d) dependence of site energy E^* on q_e of EE2 adsorption.

Figure 9a,c showed the site energy distribution curves of BPA and EE2 on CTMAB-M calculated based on the Langmuir–Freundlich model. The width of the curve indicated the heterogeneity of the adsorbent surface, and the area under the curve indicated the maximum possible adsorption capacity [19]. Compared with the adsorption of BPA on CTMAB-M at different temperatures, there were more adsorption sites at a low temperature, but the site energy was lower. The site energy was higher at higher temperature, but there are fewer adsorption sites. Figure 9c,d showed that EE2 adsorption on the CTMAB-M had a similar pattern. These results could explain why the BPA and EE2 adsorption amounts decreased with increasing temperature, although the adsorption process was endothermic.

Previous studies [38] have shown that the higher the average site energy on the adsorbent surface ($\mu(E^*)$), the greater the adsorption affinity between the adsorbent and the adsorbate. The standard deviation (σ_e^*) of the site energy distribution indicated the heterogeneity of the adsorbent surface, and the specific parameters were shown in Table 4. With the increasing temperature, the adsorption affinity of CTMAB-M for BPA and EE2 increased, and the distribution amount of the adsorption sites tended to decrease. According to the previous analysis, CTMAB was the only adsorption active site on CTMAB-M. The main driving forces on BPA and EE2 include hydrophobic interactions, electrostatic attraction, and interaction between the positive charge on the quaternary ammonium group of CTMAB molecules and the π electrons of the benzene ring of BPA or EE2 molecules.

The hydrophobic interactions tended to increase with the increase of temperature, the electrostatic attraction was less affected by the temperature, and the temperature had little effect on the interaction between the quaternary ammonium group and the π electrons of the benzene ring. It was speculated that when the temperature was higher, there may be a loss of modifier, so the use of CTMAB-M was limited by temperature, which was more suitable when used at low temperature. The acicular mullite had open-pore structure extending in all directions, with a multi-level distribution of super-large pores, macropores, meso-pores, and micro-pores [17,39]. CTMAB may form different semi-micelles or adsorption hemimicelles on its surface and in the micro-pores. Therefore, the surface of CTMAB-M was heterogeneous.

4. Conclusions

To enhance the removal efficiency of BPA and EE2, the acicular mullite ceramsite was modified with CTMAB. When the concentration of the CTMAB precursor solution was 4 mmol/L, the largest CTMAB-M contact angle was observed, and it also had the highest adsorption amount of BPA and EE2. Before the modification, the adsorption of BPA by nano-acicular mullite was greater than EE2, and the adsorption of BPA by CTMAB-M was less than that of EE2, indicating that the CTMAB modification has a better adsorption effect on highly hydrophobic organic pollutants. The adsorption dynamics showed that the adsorption of BPA and EE2 by CTMAB-M reached equilibrium at 500 min. CTMAB-M for BPA and EE2 fits well with the pseudo-second model. The maximum adsorption amounts of BPA and EE2 by CTMAB-M are 0.483 mg/g and 1.482 mg/g, respectively. Thermodynamic analysis showed that the adsorption amounts of BPA and EE2 on CTMAB-M decreased with increasing temperature, and the low temperature favored the adsorption reaction. The site energy distribution showed that BPA and EE2 first occupy the high-energy adsorption site during initial adsorption process, and after high-energy adsorption site saturation they turn to the low-energy adsorption sites. At 308 K, adsorption occurred mainly at high-energy sites, and at 298 K and 288 K, adsorption occurred mainly at low-energy adsorption sites. The average site energy of BPA and EE2 adsorption on CTMAB-M increases with the rising temperature, while the adsorption sites are greatly reduced, suggesting a possible loss of modifying agents. The average adsorption site energy of EE2 on CTMAB-M (E^*) is less than that of BPA, but the number of active adsorption sites is more than BPA, leading to an adsorption amount that was greater than BPA. Under the combination of electrostatic interaction and hydrophobic distribution, the amount of BPA adsorption on CTMAB-M increased with the pH value. The amount of EE2 adsorption on CTMAB-M increases with pH at pH < 10 and decreases with pH at pH > 10, mainly due to electrostatic interactions. The adsorption amount of both BPA and EE2 by CTMAB-M increased with increasing ionic strength.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/su142114248/s1>. Supporting information Refs [40–42].

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References

1. Al Sharabati, M.; Abokwiek, R.; Al-Othman, A.; Tawalbeh, M.; Karaman, C.; Orooji, Y.; Karimi, F. Biodegradable polymers and their nano-composites for the removal of endocrine-disrupting chemicals (EDCs) from wastewater: A review. *Env. Res.* **2021**, *202*, 111694. [\[CrossRef\]](#) [\[PubMed\]](#)
2. Kasonga, T.K.; Coetzee, M.A.; Kamika, I.; Ngole-Jeme, V.M.; Momba, M.N.B. Endocrine-disruptive chemicals as contaminants of emerging concern in wastewater and surface water: A review. *J. Env. Manag.* **2021**, *277*, 111485. [\[CrossRef\]](#)
3. Hadibarata, T.; Kristanti, R.A.; Mahmoud, A.H. Occurrence of endocrine-disrupting chemicals (EDCs) in river water and sediment of the Mahakam River. *J. Water Health* **2020**, *18*, 38–47. [\[CrossRef\]](#) [\[PubMed\]](#)
4. Liu, Z.-H.; Dang, Z.; Yin, H.; Liu, Y. Making waves: Improving removal performance of conventional wastewater treatment plants on endocrine disrupting compounds (EDCs): Their conjugates matter. *Water Res.* **2021**, *188*, 116469. [\[CrossRef\]](#) [\[PubMed\]](#)
5. Wee, S.Y.; Aris, A.Z.; Yusoff, F.M.; Praveena, S.M. Tap water contamination: Multiclass endocrine disrupting compounds in different housing types in an urban settlement. *Chemosphere* **2021**, *264*, 128488. [\[CrossRef\]](#) [\[PubMed\]](#)
6. Shokoohi, R.; Gillani, R.A.; Mahmoudi, M.M.; Dargahi, A. Investigation of the efficiency of heterogeneous Fenton-like process using modified magnetic nanoparticles with sodium alginate in removing Bisphenol A from aquatic environments: Kinetic studies. *Desalin. Water Treat* **2018**, *101*, 185–192. [\[CrossRef\]](#)
7. Shahid, M.K.; Kashif, A.; Fuwad, A.; Choi, Y. Current advances in treatment technologies for removal of emerging contaminants from water—A critical review. *Coord. Chem. Rev.* **2021**, *442*, 213993. [\[CrossRef\]](#)
8. Wang, S.; Li, L.; Yu, S.; Dong, B.; Gao, N.; Wang, X. A review of advances in EDCs and PhACs removal by nanofiltration: Mechanisms, impact factors and the influence of organic matter. *Chem. Eng. J.* **2021**, *406*, 126722. [\[CrossRef\]](#)
9. Samarghandi, M.R.; Ansari, A.; Dargahi, A.; Shabanloo, A.; Nematollahi, D.; Khazaei, M.; Nasab, H.Z.; Vaziri, Y. Enhanced electrocatalytic degradation of bisphenol A by graphite/ β -PbO₂ anode in a three-dimensional electrochemical reactor. *J. Environ. Chem. Eng.* **2021**, *9*, 106072. [\[CrossRef\]](#)
10. Ahmed, M.B.; Zhou, J.L.; Ngo, H.H.; Johir, M.A.H.; Sornalingam, K. Sorptive removal of phenolic endocrine disruptors by functionalized biochar: Competitive interaction mechanism, removal efficacy and application in wastewater. *Chem. Eng. J.* **2018**, *335*, 801–811. [\[CrossRef\]](#)
11. Mpatani, F.M.; Han, R.; Aryee, A.A.; Kani, A.N.; Li, Z.; Qu, L. Adsorption performance of modified agricultural waste materials for removal of emerging micro-contaminant bisphenol A: A comprehensive review. *Sci. Total Env.* **2021**, *780*, 146629. [\[CrossRef\]](#) [\[PubMed\]](#)
12. Mashkoor, F.; Nasar, A. Carbon nanotube-based adsorbents for the removal of dyes from waters: A review. *Environ. Chem. Lett.* **2020**, *18*, 605–629. [\[CrossRef\]](#)
13. Huang, Y.; Guo, J.; Yan, P.; Gong, H.; Fang, F. Sorption-desorption behavior of sulfamethoxazole, carbamazepine, bisphenol A and 17 α -ethinylestradiol in sewage sludge. *J. Hazard Mater* **2019**, *368*, 739–745. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Belachew, N.; Hinsene, H. Preparation of cationic surfactant-modified kaolin for enhanced adsorption of hexavalent chromium from aqueous solution. *Appl. Water Sci.* **2020**, *10*, 38. [\[CrossRef\]](#)
15. Wang, L.-C.; Ni, X.-J.; Cao, Y.-H.; Cao, G.-Q. Adsorption behavior of bisphenol A on CTAB-modified graphite. *Appl. Surf. Sci.* **2018**, *428*, 165–170. [\[CrossRef\]](#)
16. Dovi, E.; Kani, A.N.; Aryee, A.A.; Jie, M.; Li, J.; Li, Z.; Qu, L.; Han, R. Decontamination of bisphenol A and Congo red dye from solution by using CTAB functionalised walnut shell. *Env. Sci. Pollut. R* **2021**, *28*, 28732–28749. [\[CrossRef\]](#)
17. Zhou, Q.; Long, T.; He, J.; Guo, J.; Gao, J. Cadmium removal from water by enhanced adsorption on iron-embedded granular acicular mullite ceramic network. *J. Taiwan Inst. Chem. E* **2020**, *106*, 92–98. [\[CrossRef\]](#)
18. He, J.; Zhou, Q.; Guo, J.; Fang, F. Characterization of potassium hydroxide modified anthracite particles and enhanced removal of 17 α -ethinylestradiol and bisphenol A. *Env. Sci. Pollut. R* **2018**, *25*, 22224–22235. [\[CrossRef\]](#)
19. He, J.; Guo, J.S.; Zhou, Q.H.; Yang, J.X.; Fang, F.; Huang, Y. Analysis of 17 α -ethinylestradiol and bisphenol A adsorption on anthracite surfaces by site energy distribution. *Chemosphere* **2019**, *216*, 59–68. [\[CrossRef\]](#)
20. Zhang, J.; Stanforth, R. Slow adsorption reaction between arsenic species and goethite (a-FeOOH): Diffusion or heterogeneous surface reaction control. *Langmuir* **2005**, *21*, 2895–2901. [\[CrossRef\]](#)
21. Peng, C.; Min, F.; Liu, L. Effect of pH on the adsorption of dodecylamine on montmorillonite: Insights from experiments and molecular dynamics simulations. *Appl. Surf. Sci.* **2017**, *425*, 996–1005. [\[CrossRef\]](#)
22. Hashemi, M.S.H.; Eslami, F.; Karimzadeh, R. Organic contaminants removal from industrial wastewater by CTAB treated synthetic zeolite Y. *J. Env. Manag.* **2019**, *233*, 785–792. [\[CrossRef\]](#)
23. Bueno, V.; Ghoshal, S. Self-assembled surfactant-templated synthesis of porous hollow silica nanoparticles: Mechanism of formation and feasibility of post-synthesis nanoencapsulation. *Langmuir* **2020**, *36*, 14633–14643. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Li, J.; Jiang, L.; Liu, X.; Lv, J. Adsorption and aerobic biodegradation of four selected endocrine disrupting chemicals in soil–water system. *Int. Biodeterior. Biodegrad.* **2013**, *76*, 3–7. [\[CrossRef\]](#)
25. Kosmulski, M. Isoelectric points and points of zero charge of metal (hydr) oxides: 50 years after Parks’ review. *Adv. Colloid. Interfac.* **2016**, *238*, 1–61. [\[CrossRef\]](#)

26. Krishna, L.S.; Soontarapa, K.; Asmel, N.K.; Kabir, M.A.; Yuzir, A.; Zuhairi, W.Y.W.; Sarala, Y. Adsorption of acid blue 25 from aqueous solution using zeolite and surfactant modified zeolite. *Desalin. Water Treat* **2019**, *150*, 348–360. [\[CrossRef\]](#)
27. Cui, L.; Wei, J.F.; Du, X.; Zhou, X.Y. Preparation and Evaluation of Self-Assembled Porous Microspheres-Fibers for Removal of Bisphenol A from Aqueous Solution. *Ind. Eng. Chem. Res.* **2016**, *55*, 1566–1574. [\[CrossRef\]](#)
28. Umpleby, R.J.; Baxter, S.C.; Chen, Y.Z.; Shah, R.N.; Shimizu, K.D. Characterization of molecularly imprinted polymers with the Langmuir-Freundlich isotherm. *Anal. Chem.* **2001**, *73*, 4584–4591. [\[CrossRef\]](#)
29. Dargahi, A.; Samarghandi, M.R.; Shabanloo, A.; Mahmoudi, M.M.; Nasab, H.Z. Statistical modeling of phenolic compounds adsorption onto low-cost adsorbent prepared from aloe vera leaves wastes using CCD-RSM optimization: Effect of parameters, isotherm, and kinetic studies. *Biomass Convers. Biorefinery* **2021**. [\[CrossRef\]](#)
30. Zhou, G.; Cao, Y.; Jin, Y.; Wang, C.; Wang, Y.; Hua, C.; Wu, S. Novel selective adsorption and photodegradation of BPA by molecularly imprinted sulfur doped nano-titanium dioxide. *J. Clean. Prod.* **2020**, *274*, 122929. [\[CrossRef\]](#)
31. Jun, B.-M.; Hwang, H.S.; Heo, J.; Han, J.; Jang, M.; Sohn, J.; Park, C.M.; Yoon, Y. Removal of selected endocrine-disrupting compounds using Al-based metal organic framework: Performance and mechanism of competitive adsorption. *J. Ind. Eng. Chem.* **2019**, *79*, 345–352. [\[CrossRef\]](#)
32. Ribeiro-Santos, T.A.; Henriques, F.F.; Villarroel-Rocha, J.; de Castro, M.C.M.; Magalhaes, W.F.; Windmoller, D.; Sapag, K.; Lago, R.M.; Araujo, M.H. Hydrophobic channels produced by micelle-structured CTAB inside MCM-41 mesopores: A unique trap for the hazardous hormone ethinyl estradiol. *Chem. Eng. J.* **2016**, *283*, 1203–1209. [\[CrossRef\]](#)
33. Liu, X.C.; Hu, Y.; Huang, J.; Wei, C.H. Detailed characteristics of adsorption of bisphenol A by highly hydrophobic MCM-41 mesoporous molecular sieves. *Res. Chem. Intermediat* **2016**, *42*, 7169–7183. [\[CrossRef\]](#)
34. Jung, C.; Son, A.; Her, N.; Zoh, K.D.; Cho, J.; Yoon, Y. Removal of endocrine disrupting compounds, pharmaceuticals, and personal care products in water using carbon nanotubes: A review. *J. Ind. Eng. Chem.* **2015**, *27*, 1–11. [\[CrossRef\]](#)
35. Yan, B.; Niu, C.H.; Feng, R. Site energy distribution and X-ray analyses of nickel loaded on heterogeneous adsorbents. *Ind. Eng. Chem. Res.* **2017**, *56*, 8283–8291. [\[CrossRef\]](#)
36. Carter, M.C.; Kilduff, J.E.; Weber, W.J. Site energy distribution analysis of preloaded adsorbents. *Env. Sci. Technol.* **1995**, *29*, 1773–1780. [\[CrossRef\]](#)
37. Yan, B.; Niu, C.H. Modeling and site energy distribution analysis of levofloxacin sorption by biosorbents. *Chem. Eng. J.* **2017**, *307*, 631–642. [\[CrossRef\]](#)
38. Yan, B.; Niu, C.H.; Wang, J. Analyses of Levofloxacin Adsorption on Pretreated Barley Straw with Respect to Temperature: Kinetics, pi-pi Electron-Donor-Acceptor Interaction and Site Energy Distribution. *Env. Sci. Technol.* **2017**, *51*, 8048–8056. [\[CrossRef\]](#)
39. Wan, Y.; Xu, C.; Zhou, Q.; Chen, H.; Xu, Q. Synthesis of Nanoporous Acicular-Mullite Ceramic and Electroless Platinum Coating for Particulate Matter Entrapment and Catalytic Combustion. In *IOP Conference Series: Earth and Environmental Science 2022*; IOP Publishing: Bristol, UK, 2022; p. 012107.
40. Esharghawi, A.; Penot, C.; Nardou, F. Contribution to porous mullite synthesis from clays by adding Al and Mg powders. *J. Eur. Ceram. Soc.* **2009**, *29*, 31–38. [\[CrossRef\]](#)
41. Cerofolini, G.F. Localized adsorption on heterogeneous surfaces. *Thin Solid Film* **1974**, *23*, 129–152. [\[CrossRef\]](#)
42. Jayaprakash, D.; Dhabhai, R.; Niu, C.H.; Dalai, A.K. Selective water removal by sorption from butanol-water vapor mixtures: Analyses of key operating parameters, and site energy distribution. *Energy Fuels* **2017**, *31*, 5193–5202. [\[CrossRef\]](#)