Article

Removal of Various Pollutants from Wastewaters Using an Efficient and Degradable Hypercrosslinked Polymer

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Abstract: Adsorption is an effective strategy for the removal of pollutants from the wastewater. Herein, a 2-hydroxyterephthalic acid (HTC) modified hypercrosslinked polymer (HTC-HCP) is successfully synthesized via Friedel-Crafts reactions, and used as an adsorbent for the different types of pollutants including organic contaminants and heavy metal ions from wastewater. Excellent adsorption capacities are observed for amines (aniline, *p*-methylaniline (*p*-MA), *p*-chloroaniline (*p*-CA), and *p*-aminobenzoic acid (*p*-ABA)), phenols (phenol, *p*-chlorophenol (4-CP) Bisphenol A (BPA), 1-Naphthol (1-NP)), dyes (rhodamine B (RhB) and methyl orange (MO)), and metal ions (Pb^{2+}, Hg^{2+}, and Cd^{2+}). The resulting polymers exhibited excellent adsorption performance towards these pollutants. Especially, the removal rate of aniline is above 95% in the concentration of 2.5 mg/L in 40 min at 25 °C. The interaction mechanism has been investigated, and confirmed by FTIR and the theoretical calculation results. It is due to surface complexation and chemisorption between adsorbent and adsorbate. The polymer exhibits good performance such as high adsorption capacity, high separation efficiency, biodegradable properties, and easy regeneration, suggesting that its potential technological applications for the removal of organic compounds and heavy metal ions from actual industrial effluent.

Keywords: Hypercrosslinked polymer; *p*-hydroxy-phthalic acid; pollutants; adsorption; biodegradation

1. Introduction

Water pollution caused by toxic organic chemicals and heavy metal ions has aroused global attention because of their adverse influence to human health and the environment [1, 2]. For the sustainable development of water environment, it has become a very urgent concern to develop new efficient methods to remove the compounds from wastewater [3, 4]. Many methods have been developed for the removal of organic pollutants and heavy metal ions including chemical precipitation, photocatalytic degradation, biodegradation, membrane filtration, and adsorption [5-10]. Among these methods, adsorption is an effective, efficient, and economic method for the removal of pollutants from wastewaters due to its low cost, easy operation, and practical application in large scale [11]. In recent years, polymeric sorbents have been widely studied as adsorbents because of their obvious advantages including good mechanical strength, easy modified properties, and feasible regeneration [12, 13]. In comparison, hypercrosslinked polymers (HCPs) are more efficient for adsorption of pollutants due to their high specific surface areas, favorable pore structures, and excellent adsorption performance [14-17]. Generally, HCPs can be prepared from linear polystyrene or low cross-linked polystyrene by Friedel-Crafts reaction under the help of catalyst [18]. However, in review of the previous refs, the as-synthesized HCPs show relatively low performance toward the pollutants [14-16]. Therefore, it is necessary to introduce some special groups on the polymers by chemical modification to improve their

adsorption selectivity towards these pollutants from wastewater. Adsorbents containing amino, amide, hydroxyl, and carbonyl groups have been applied for the removal of organic pollutants and heavy metal ions from wastewater [16, 19-21].

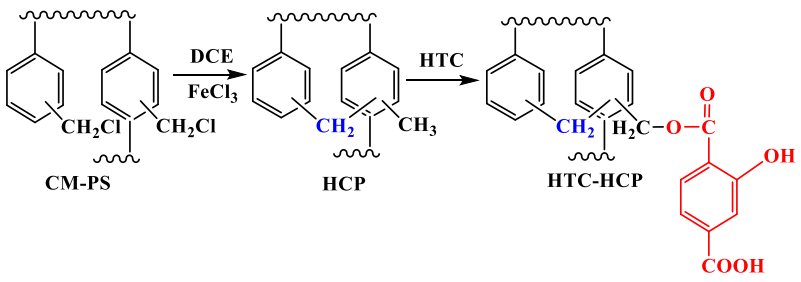
2-hydroxyterephthalic acid (HTC), has been used extensively in medicine and functional materials [22]. HTC contains the -OH and -COOH groups, which are used to improve adsorption selectivity of the polymers. It is grafted onto the surface of HCPs to form surface complexation, acid-base complex, and hydrogen bonding in the limited micro domains, which greatly enhance the adsorption performance towards pollutants. However, for the waste synthetic polymers such as polyethylene, polystyrene, and polypropylene, environmental pollution has been a serious problem due to their nonbiodegradability. Therefore, studying biodegradable materials including a fully or partially biodegradable film or resin has been the focus of much research over the past two decades. However, little literature was published in the previously reported refs about HTC-HCP on how to enhance sorption of different types of pollutants including toxic organic chemicals and heavy metal ions from aqueous solution and their biodegradability so far.

The objective of this work is to synthesize a polar monomer HTC modified HCP (HTC-HCP) for the removal of organic pollutants and heavy metal ions from wastewater. Its surface chemistry and structure are characterized by using Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), Thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), and N_2 adsorption-desorption measurements. The resulting HTC-HCP can remove various organic pollutants, such as dyes, amines and phenols, and metal ions like Pb^{2+}, Hg^{2+}, and Cd^{2+} from aqueous solutions. Biodegradation experiment is also tested. Finally, a possible adsorption mechanism is proposed based on the experimental and computational results. It provides an industrialized application as a reference for the removal of aniline components and heavy metal ions from industrial wastewater.

2. Materials and Methods

2.1. Synthesis of HTC-HCP

As described in Scheme 1, HTC-HCP was synthesized according to previous works with minor modification [23, 24]. 10 g of chloromethylated poly(styrene-co-divinylbenzene) (CM-PS) beads was first dispersed in 50 mL of 1,2-dichloroethane (DCE) to swell overnight. About 2 g of anhydrous $FeCl_3$ as catalyst was added to the system and stirred until the catalyst was completely dissolved. Then, the reaction mixture was heated to 115 °C within 1.5 h and kept the same temperature for 12 h. After the reaction was finished, the product was filtered and washed alternately with 1% aqueous hydrochloric acid and 95% (v/v) ethanol until pH of the washings was neutral, and finally dried under vacuum at 80 °C for 12 h to acquire HCP. After that, 2.5 g of the above as-prepared HCP was mixed with 60 mL of N,N-dimethylformamide (DMF) containing 1.0 g of HTC, and the reaction mixture was maintained at 115 °C for 12 h with N_2 protection. The reaction mixture was separated by filtration, washed with deionized water until neutral pH, and the corresponding HTC-HCP was further purified by Soxhlet extraction with ethanol for 24 h and dried in vacuum to obtain the final product.



Scheme1. The synthesis procedure of HTC-HCP

2.2. characterization

The chlorine content in the polymers was calculated according to the Volhard method[25]. FTIR spectra of the polymers were recorded on a Fourier transform infrared spectrometer (Perkin-Elmer 2000, USA) using KBr as background over the range of 4000–400 cm^{-1} under ambient conditions. TGA of HTC-HCP was performed on a Netzsch STA-449C thermal analysis system (Netzsch,

Germany). For TG measurements, the weight loss of dried samples was monitored under N_2 atmosphere from room temperature to 850 °C at a rate of 10 °C/min.. The BET surface area and pore distribution of the polymers were analyzed by nitrogen adsorption-desorption isotherm at 77 K in a Micromeritics ASAP 2020 accelerated surface area and porosimetry analyzer (Micromeritics, Norcross, GA, USA). XPS (Thermo, ESCALAB 250XI, USA) was used to determine the electron binding energy of the surface to achieve the qualitative analysis of the elements. To detect surface properties of the hydrophobic polymers in aqueous phase, their contact angles were recorded with a contact angle measuring system (OCA20, Dataphysics, Germany).

2.3. Adsorption experiments

Adsorption was carried out with dyes (RB and MO), amines (aniline, *p*-MA, *p*-CA, and *p*-ABA), or phenols (phenol, 4-CP, BPA, 1-NP) at a desired temperature and an agitation speed of 200 r/min until the equilibrium. 0.1 g of HTC-HCP was mixed 100 mL of solution containing initial concentration 100 mg/L of organic compounds in a 250 mL a conical flask. The reaction mixture was shaken at 25 °C. During the adsorption, 0.5 mL of the solution was sampled at regular intervals, and transferred to a 10 mL volumetric flask and diluted with water to the volume. After that, the samples were determined by UV-Vis spectroscopy until adsorption equilibrium was reached.

Adsorption of metal ions was performed in a 100 mL Pb^{2+}, Hg^{2+}, and Cd^{2+} aqueous solution (concentration 100 mg/L) at 25 °C with 0.1 g HTC-HCP. 0.5 mL of supernatant was taken at intervals. The supernatant samples of Pb^{2+} and Cd^{2+} was diluted to 5 mL and analyzed by atomic absorption spectrometry (AAS), and the supernatant samples of Hg^{2+} were diluted for 50 times, and analyzed by ICP-AES.

The adsorption amount of the organic pollutants and heavy metal ions at a contact time t was expressed as:

$$q_t = (C_o - C_t)V_0 / W \quad (1)$$

where q_t is the adsorption amount at contact time t (mg/g resin); C_t is the concentration of each compound in solution at t (mg/L). All the experiments were performed in triplicate. The average values were reported and all standard errors were smaller than 5%.

For equilibrium adsorption, 0.1 g of HTC-HCP was mixed 100 mL of solution containing initial concentration 2-1000 mg/L of aniline in a 250 mL a conical flask. The reaction mixture was shaken at a desired temperature (25, 30, and 35 °C) and an agitation speed of 200 r/min until the equilibrium in 24 h. The original solution pH of aniline used in the equilibrium adsorption was adjusted with 0.1 mol/L hydrochloric acid or 0.1 mol/L sodium hydroxide. The concentration of the aniline was measured by UV-Visible spectrometer. Based on the working curve, the adsorbed amount of aniline at the equilibrium was calculated as *Eq* (1).

2.4. Biodegradation experiments

A certain amount of CM-PS and HTC-HCP are dried to constant weight in a vacuum oven at 70 °C for 24 h. A certain amount of dried CM-PS (w_1) and HTC-HCP (w_2) was mixed with some soil containing a stain, which was identified as *Stenotrophomonas sp*., respectively. The degradation of adsorbents were studied by shaking flask culture at 30 °C. After shaking culture with the initial concentration of HTC in the solution being about 15 mg/L, the samples were withdrawn at 2 d intervals until the weight was constant . Therefore, CM-PS (w_1') and HTC-HCP (w_2') were obtained, and the degraded radio (%) could be calculated as follows:

$$CM\text{-}PS(\%) = ((w_1 - w_1^{'}) / w_1) \times 100\% \quad (2)$$

$$HTC\text{-}HCP(\%) = ((w_2 - w_2^{'}) / w_2) \times 100\% \quad (3)$$

*2.5.**Computational chemistry calculations***

Quantum calculations are usually used to examine the formation of chemical bonds between the adsorbate and adsorbent at the molecular level, which can yield some information on the structure and energy. The intermolecular interaction was modeled by calculating the hydrogen bond distances and complexation energies between aniline and HTC-HCP. In the present work, a

basic assumption was proposed that the binding sites in the polymer are HTC of HTC-HCP connected with aniline. The feasibility of the simulation with the similar structures has been reported in the literature [26]. In addition, the high convergence option was considered as the energy minimization of each model in aqueous media.

Binding energy (*BE*) could be expressed as

$$BE = E_{complex} - E_{guest} - E_{host} \quad (4)$$

$E_{complex}$ is the total energies of the inclusion complex of aniline with HTC. E_{guest} is the sum of total energy of aniline. E_{host} is the total energy of HTC. The more negative the binding energy is, the more thermodynamically favorable the inclusion complex is.

3. Results and Discussion

3.1. Characterization of HTC-HCP

Fig.**1** shows the FTIR spectra of the CM-PS, HCP, HTC, and HTC-HCP in the wavenumber range of 4000-400 cm^{-1}. For CM-PS, the bands due to the C-Cl stretching vibration of the $–CH_2Cl$ groups are observed at 1265 cm^{-1} and 670 cm^{-1}[27] (Fig.**1**a). After the Friedel-Craft reaction, the peak at 1265 cm^{-1} is significantly weakened in HCP (Fig.**1**b). As seen in Fig.**1**c, the characteristic band at 3250 cm^{-1} is due to –OH stretching vibration, and the strong adsorption peak at 1706 cm^{-1} is ascribed to the carbonyl groups of HTC [22]. After the reaction of HTC with HCP, the peaks at 1265 and 670 cm^{-1} almost disappear and the peak at 1706 cm^{-1} is also present for HTC-HCP (Fig.**1**d). In addition, a strong peak due to the –OH stretching of HTC also appears at 3400 cm^{-1}. Table 1 shows that chlorine content for HCP (7.61%) is lower than that of CM-PS (18.32%). The residual chlorine content for HTC-HCP decreases from 12.61% to 0.21% after the reaction, revealing the reduction of $–CH_2Cl$ groups as it reacts with the neighboring aromatic rings of HTC and transformed to the rigid methylene cross-linking bridges [28]. These results indicate that HTC was successfully introduced into HCP.

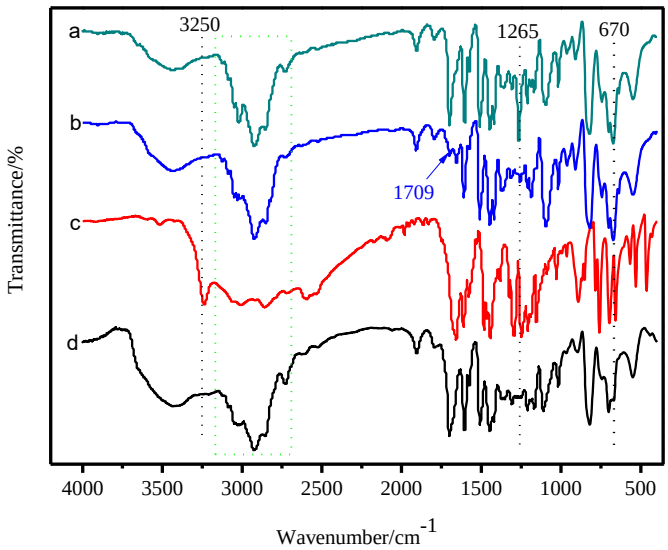


Fig. 1. FTIR spectra of CM-PS (a), HCP (b), HTC (c), and HTC-HCP(d).

The surface chemical compositions and their changes of HCP and HTC-HCP are analyzed by XPS [29]. As shown in Fig.**2**a, the respective XPS wide scan of HCP and HTC-HCP shows that the O_{1s} peak of HTC-HCP is at 532.7 eV, while the Cl_{2p} peak almost disappears completely for HTC-HCP, suggesting $–CH_2Cl$ groups are involved in the reaction with HTC. As shown in Fig.**2**b, HTC-HCP has three different chemically shifted components [30, 31]: sp^2 C=C (284.7 eV), sp^3 C-C (285.0 eV), and O=C-O (286.7 eV). This phenomenon could be attributed to the fact that HTC possesses high ratio of C=C, C-C, and O=C-O in their structure, implying the presence of HTC on the surface of HCP.

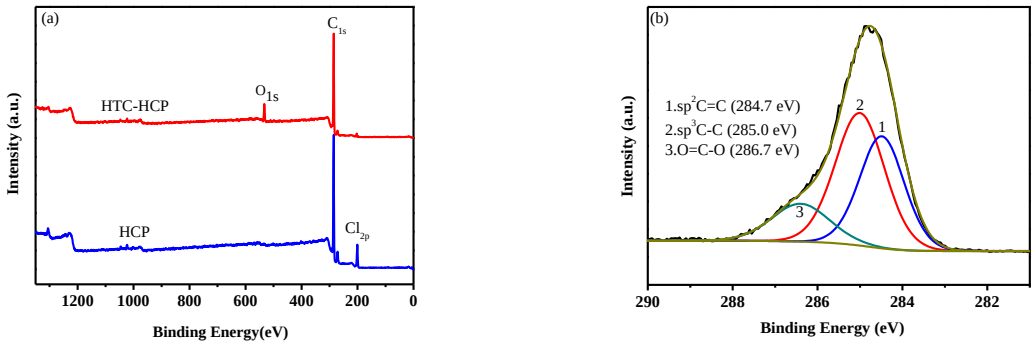


Fig. 2. XPS wide scan of (a) HCP and HTC-HCP; (b) C1s XPS spectra of HTC-HCP.

TGA shows that the thermal decomposition temperature of HTC-HCP is up to 180 °C under nitrogen atmosphere, the 13% mass loss in the range 180-450 °C is due to heat decomposition of HTC, and HTC-HCP retains about 28% mass at the temperature above 800 °C (**Figure S1**), implying the high thermal stability because of the highly crosslinked network of the polymer [32, 33]. Such a high thermal stability could be beneficial for the regeneration of adsorbent in practical applications. To analyze the polarity, the elemental analysis and the contact angle were carried out to analyze the polymers. As shown in Table 1, the O content of HTC-HCP is 4.98%, but its contact angle is 124°, which is lower than that observed for HCP (142°). This difference may be caused by the addition of HTC onto the surface of HCP, which improve hydrophilicity. These results indicate that the uploaded –COOH and –OH groups of HTC onto HCP is beneficial for the adsorption of organic contaminants.

Table1. Characterization of HTC-HCP

Materials	Surface area(m^2/g)		Pore volume (cm^3/g)	Average pore size (nm)	Chlorine content (%)	O content (%)	Contact angle (deg)
	S_{BET}	S_{micro}					
CM-PS	40.25	3.53	0.07012	0.77	18.32	0	138
HCP	320.85	164.68	1.2363	75.32	12.61	0	142
HTC-HCP	167.98	80.34	0.3019	13.34	0.21	4.98	124

Fig. 3 shows N_2 adsorption–desorption isotherms and pore-size distribution of HTC-HCP and structural properties of pore surfaces for all the materials at 77 K. As Table 1 shown, CM-PS has low BET surface area (40.25 m^2/g) and pore volume (0.07012 cm^3/g). While the BET surface area (320.85 m^2/g) and pore volume (1.2363 cm^3/g) of HCP significantly increase after the Friedel-Crafts reaction, demonstrating that the reaction can greatly improve the pore structure of the polymers. However, when HTC is uploaded on the surface of HCP, the BET surface area and pore volume decrease to 167.98 $^2/g$ and 0.3019 cm^3/g, respectively, implying blockage of some pores with the added functional groups [34] (**Fig. 3**a). Based on the IUPAC classification [35], the N_2 adsorption of HTC-HCP belongs to type II. It significantly increases at the relative pressure ($P/P° = 0$ to 0.05), and steadily rises at the pressure of $0.1<P/P°<0.9$ and rapidly climbs in the range of $P/P°>0.9$ (**Fig. 3**b), implying that some micropores and mesopores ranging 10-50 nm mostly exist in HTC-HCP [36, 37].

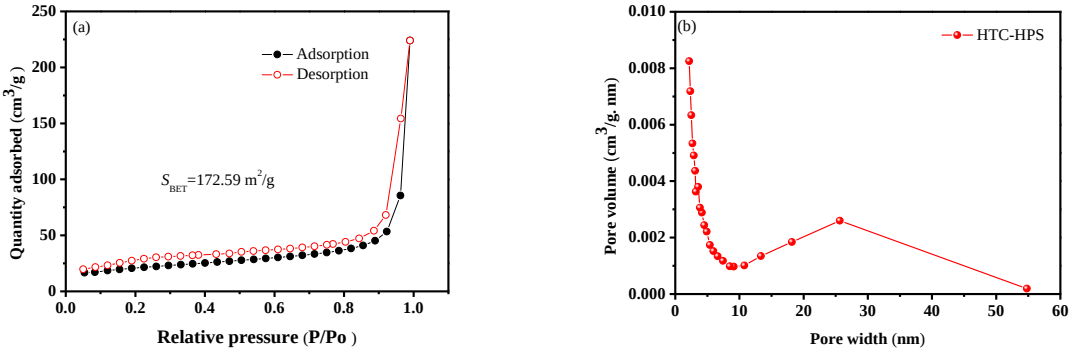


Fig. 3. (a) Adsorption–desorption isotherms of N_2 at 77 K and (b) pore-size distribution of HTC-HCP.

3.2. Adsorption performance of HTC-HCP

HTC-HCP has adsorption ability for a wide variety of organic compounds such as amines, phenols, and dyes from aqueous solutions, and the adsorption curves of amines, phenols, and dyes are shown in **Fig. 4**.

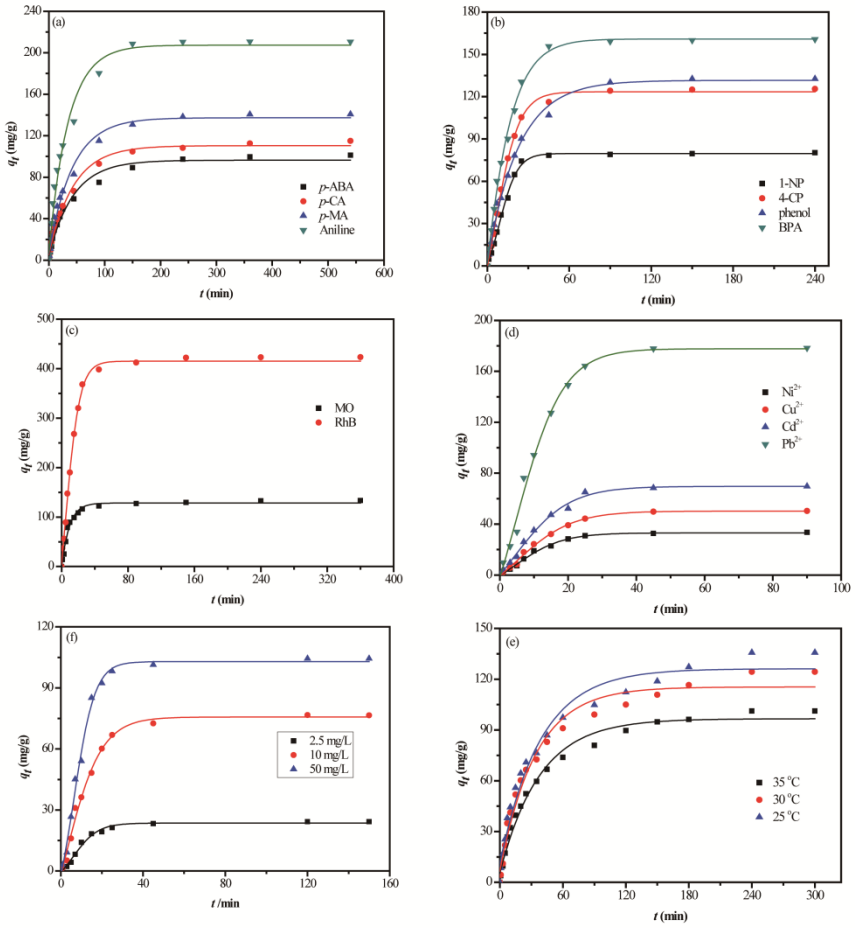


Fig. 4. Adsorption curves of HTC-HCP for (a) amines, phenols (b), dyes (c), and (d) metal ions (Ni^{2+}, Cu^{2+}, Cd^{2+}, and Pb^{2+}) at 25 °C (0.1 g, pH = 7, 100 mL of 100 mg/L solution, and 200 rpm). e) Effect of temperature on the adsorption capacity of aniline from aqueous solution (0.1 g, pH = 7, 100 mL, 80 mg/L, and 200 rpm). f) Adsorption capacity for aniline with various concentration (2.5, 10, and 70 mg/L) at 30 °C (0. 01 g HTC-HCP, pH = 7, and 200 rpm).

Fig. 4a displays that the adsorption capacity of amines (aniline, *p*-MA, *p*-CA, and *p*-ABA) increases quickly in the first 100 min, and then gradually gets to equilibrium. Adsorption equilibrium is reached about in 250 min for aniline, *p*-MA, *p*-CA, and *p*-ABA. Further increase of contact time has a negligible effect on the equilibrium adsorption capacity of the amines. The maximum adsorption capacity for *p*-ABA, *p*-CA, *p*-MA, and aniline is 101.12, 115.98, 140.75, and 210.59 mg/g, respectively. The polymer also adsorbs other organic contaminants such as dyes and phenol compounds from wastewater. The maximum adsorption capacity for 1-NP, 4-CP, phenol, and BPA is 80.24, 125.52, 132.64, and 160.73 mg/g, respectively, in 120 min. The adsorption equilibrium for RhB and MO is observed in 160 and 240 min, respectively, and their adsorption capacity is 133.46 and 423.22 mg/g, respectively, which is higher than some the previously reported adsorbents [38-41]. The results implied that HTC-HCP has good potential applications for the removal of various organic contaminants from wastewater.

HTC-HCP can also capture various metal ions fast and effectively from aqueous solution (**Fig. 4**d). The adsorption capacity of Ni^{2+}, Cu^{2+}, Cd^{2+}, and Pb^{2+} is 33.46, 50.33, 69.69, and 178.27 mg/g after 30, 45, 45,and 80 min, respectively, at 25 °C. The adsorption capacity of HTC-HCP is higher than some commonly used adsorbents such as chitosan, activated carbon and newly developed adsorbents (Table S1). It suggests that HTC-HCP is a promising sorbent in the removal of metal ions.

To understand the adsorption, aniline is applied as the model adsorbate, and adsorption experiment is performed in detail. The removal efficiency of HTC-HCP for aniline is studied at 25, 30, and 35 °C, respectively (**Fig. 4**e). The adsorption capacity increases rapidly in 100 min and then gradually reaches equilibrium for 101.21, 124.37, and 135.75 mg/g about in 240 min, respectively. Further increase of contact time has no significant effect on the adsorption equilibrium. Higher temperature decreases adsorption equilibrium time because of the faster molecular motion, but results in a lower absorption capacity due to the exothermic process during the absorption process of aniline. Effect of initial aniline concentration on the adsorption capacity of HTC-HCP is also investigated at different concentrations, which are 2.5, 10, and 50 mg/L, respectively, at 25 °C. The corresponding adsorption capacity is 24.22, 89.52, and 160.23 mg/g, respectively. When the adsorption is performed with 2.5 mg/L at 25 °C, the removal rate of aniline is above 95% in 40 min. The results indicate HTC-HCP may be used in the wastewater treatment with very low concentration of aniline. In order to elucidate the adsorption mechanism, the adsorption data of aniline are analysed with the pseudo-firstorder and pseudo-second-order kinetic models in supplementary information, and the results are displayer in **Fig. 5. Table 2** shows that the correlation coefficient for the pseudo-second-order kinetic model ($R^2 > 0.99$) is higher than that of the pseudo-first-order kinetic model ($R^2 < 0.99$), indicating that the adsorption process fitted by the pseudo-second-order kinetic model is more reasonable. Furthermore, the theoretical calculated values ($q_{e,cal}$) obtained from the pseudo second-order model are in good agreement with the experimental values ($q_{e,exp}$), implying the model better describe the adsorption behavior of aniline onto HTC-HCP. The results show that the chemical adsorption may be involved in the adsorption process [42, 43].

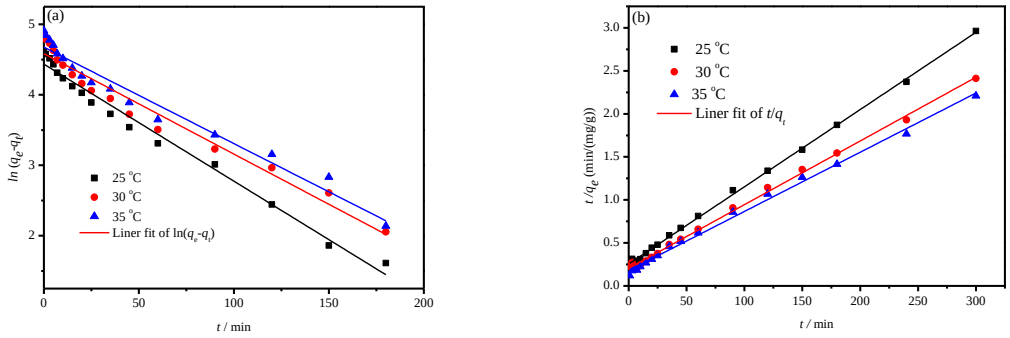


Fig. 5. Linear regressions of kinetics plots (a) pseudo-first-order model, and (b) pseudo-second-order model.

Table 2. Adsorption kinetics parameters for aniline on HTC-HCP.

Model	Parameter	Temperature/°C		
		25	30	35
	$q_{e,exp}$ (mg/g)	135.75	124.37	101.21
	k_1 (min^{-1})	0.01369	0.01425	0.01660
pseudo-first-order	$q_{e,cal}$ (mg/g)	107.35	97.87	84.33
	R^2	0.984	0.962	0.964
	k_2 (g/mg/min)	0.006880	0.007402	0.008981
pseudo-second-order	$q_{e,cal}$ (mg/g)	145.34	135.09	111.35
	R^2	0.998	0.997	0.996

Aniline is further used to evaluate the equilibrium adsorption of HTC-HCP. **Fig.6** displays the adsorption isotherms of aniline at 25, 30, and 35 °C, respectively. Adsorption amount of aniline increases with the increasing the initial concentration until the maximum adsorption is reached. For the compound, adsorption amount decrease with the rising temperature, implying the adsorption is an exothermic process and higher temperature is unfavorable for the adsorption. Langmuir, Freundlich, and D-R models are used to analyze the equilibrium adsorption data of aniline on the HTC-HCP and are given in supplementary information [37, 44]. **Table 3** shows that the Freundlich model has a better fit to the experimental data than the Langmuir model because of higher R^2, suggesting that the adsorption of aniline onto HTC-HCP should be a multilayer process [28]. From **Table 3**, K_f values calculated from the Freundlich model increase with the increasing temperature, but n values decrease with the rising temperatures for the compound onto the HTC-HCP and are greater than 1 at all the temperature studied, implying that aniline are favorably adsorbed by HTC-HCP [45].

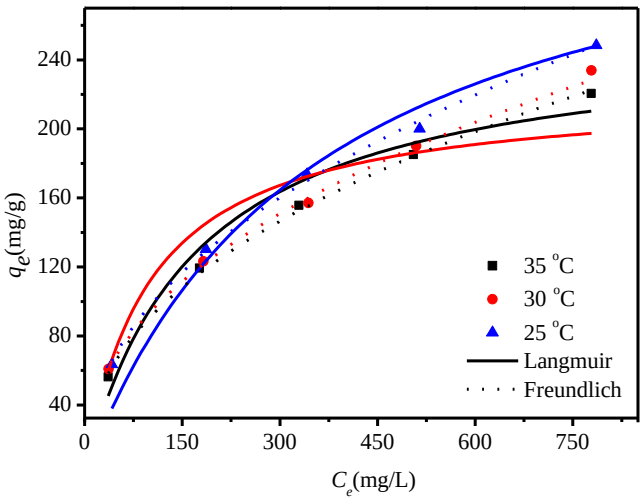


Fig. 6. Adsorption isotherms and fitted data of aniline on the HTC-HCP at 25, 30, and 35 °C, respectively. Each point represents the average of three replicates (± standard deviation, 5%). Adsorption conditions: HTC-HCP (0.1 g), Vo (100 mL), pH = 7, 200 r/min, 720 min.

277
278 **Table 3**. The correlated parameters for the adsorption of aniline via HTC-HCP according to
279 Langmuir, Freundlich, and D-R models

Model	Temperature (°C)	Parameter	
Langmuir Model	25	K_L (L/mg)	5.89×10^{-3}
		q_m (mg/g)	361.18
		R^2	0.986
	30	K_L (L/mg)	1.01×10^{-2}
		q_m(mg/g)	302.58
		R^2	0.988
	35	K_L (L/mg)	2.79×10^{-3}
		q_m(mg/g)	256.17
		R^2	0.963
Freundlich Model	25	K_f (L/mg)	9.10
		$1/n$	0.24
		R^2	0.994
	30	K_f (L/mg)	10.67
		$1/n$	0.32
		R^2	0.993
	35	K_f (L/mg)	11.99
		$1/n$	0.40
		R^2	0.997
D-R Model	25	β	2.98×10^{-4}
		q_m (mg/g)	128.68
		E_a (kJ/mol)	42.05
		R^2	0.673
	30	β	2.80×10^{-4}
		q_m(mg/g)	114.89
		E_a (kJ/mol)	28.87
		R^2	0.498
	35	β	2.70×10^{-4}
		q_m(mg/g)	107.48
		E_a (kJ/mol)	24.98
		R^2	0.836

280
281 **Table S2** shows that the negative $\Delta H°$ demonstrates the exothermic nature of the adsorption
282 process for aniline on HTC-HCP, which is supported by the decrease of aniline adsorption with the

increase in temperature. The negative $\Delta G°$ implies that the adsorption process is spontaneous, indicating a higher preference of aniline onto the HTC-HCP at lower temperature. Besides, the positive ΔS values reveal that the adsorption process is an entropy increase process.

3.3. Biodegradation test and reuse experiments

As shown in **Fig. 7**, biodegradation experiments displayed that CM-PS was almost non-degradable, but HTC-HCP gained a certain degree of biodegradability (about 12.4 wt%), implying that it can effectively reduce the damage to the environment. In addition, HTC-HCP was used repeatedly for five adsorption-desorption cycles (**Figure S2**) to test its stability and reusability, the equilibrium capacity remained unchanged, confirming that HTC-HCP could be efficiently recovered and it exhibited a good regeneration property.

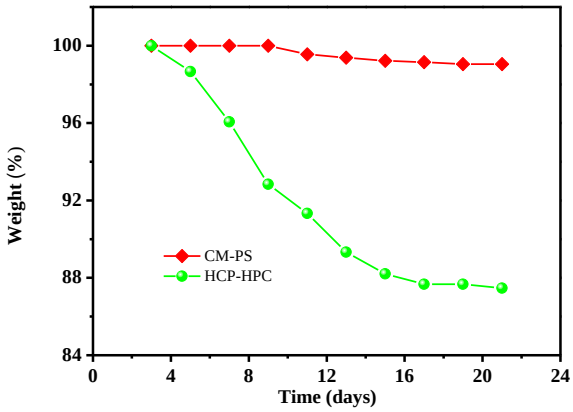


Fig. 7. Weight lost of CM-PS and HTC-HCP after biodegration.

3.4. Adsorption mechanism

To demonstrate the adsorption mechanism, FTIR spectra of HTC-HCP and HTC-HCP after adsorption of aniline was investigated (**Fig. 8**). In the FTIR spectra of **Fig. 8**, the IR band in the 3300-3500 cm^{-1} region is due to the -OH stretching mode. After adsorption, the band is slightly weakened in intensity and is red-shifted by 5-15 cm^{-1}, implying the presence of strong affinities between HTC-HCP and aniline compounds. The result shows that the weak interactions of the –OH or –COOH functional groups of the HTC-HCP with aniline compounds formed during the adsorption process.

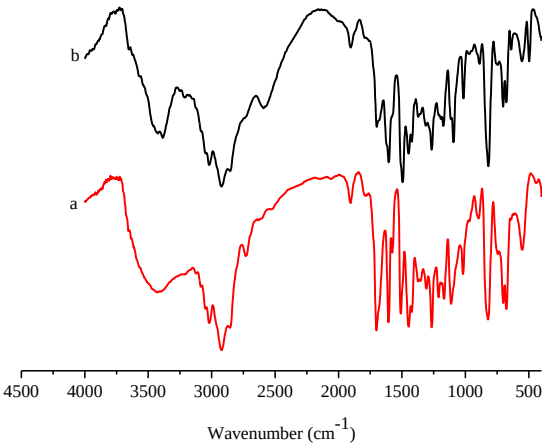
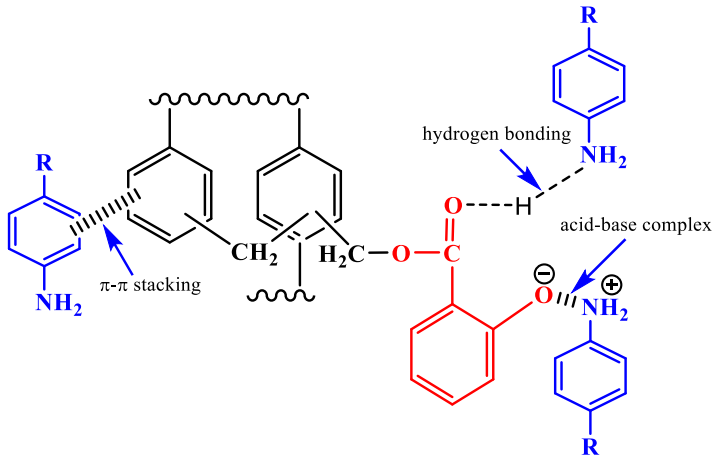


Fig.8. FTIR spectra of (a) HTC-HCP; (b) after aniline adsorption.

When HCP is grafted onto the surface of HCP, the two functional groups of HCP such as carboxyl group and hydroxyl group on the surface of HTC-HCP are maintained, which could form acid-base interaction and hydrogen bonding interaction between HTC molecule and HTC-HCP. However, the hydrogen bonding interaction between HTC and the aniline compound is regarded as a dominant attractive force. In order to evaluate the weak interaction, the binding energies of HTC and aniline have been calculated using the local density approximation (LDA) in the Perden-Wang (PWC) form at the DND basis set level (Supporting Information), which was used in previous report [46, 47]. As shown in Figure S4 and Table S5, the results demonstrate that HTC form stable complex with aniline. The complex can significantly increase the adsorption amount of aniline. In the process of the compound adsorbed by HTC-HCP in aqueous solution, the NH_2 group of the adsorbate and the –CO– and –OH groups of the adsorbent can form N-H...O and O-H...O hydrogen bonding interactions. In addition, the π-π conjugation and acid-base complex also can play an important role in the adsorption process of aniline, according to previous reports [46, 48]. As shown in Scheme 2, it was clear that the significant improvement of adsorption of aniline by HTC-HCP was driven by the synergistic effects of weak interactions such as π–π stacking, hydrogen bonding, and acid-base complex.



Scheme2. Schematic mechanism of the adsorption of aniline compounds with HTC-HCP.

4. Conclusion

A HTC-modified hyper-crosslinked polymer (HTC-HCP) is successfully synthesized, and used to assess the capacities for removal of organic contaminants and heavy metal ions from wastewater. The introduction of HTC onto the surface of HCP significantly enhances the adsorption of the pollutants, and the synergistic effects of weak interactions play an important role. The equilibrium adsorption amounts are 101.12, 115.98, 140.75, and 210.59 mg/g for *p*-ABA, *p*-CA, *p*-MA, and aniline, respectively, which are more than most adsorbents in the literature. The adsorption kinetic data of four aniline are well fitted with the pseudo-second-order kinetic model. The adsorption isotherms of aniline can be fitted better to the Freundlich model. Adsorption mechanism indicates that formation of chemical bonding via π-π stacking, acid-base interaction, and hydrogen bonding plays a crucial role in the enhanced adsorption of aniline. Moreover, biodegradation experiments show that HTC-HCP is an environmentally friendly adsorbent. In short, the present adsorption material exhibits great potential for the application in water treatment.

Supplementary Materials: The following are available online at *http://www.mdpi.com/*

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