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Removal of dibutyl phthalate (DBP) from aqueous solution by adsorption using vanillin-modified chitosan beads (CTSV)

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ABSTRACT

To remove dibutyl phthalate from aqueous solution with vanillin-modified chitosan beads (CTSV), the environmental materials (chitosan and vanillin) were prepared by the green chemistry modification technology of microwave radiation. Compared with unmodified chitosan powders and beads, this new material CTSV was characterized with satisfied adsorption capacity by scanning electron microscope and Fourier translation transform-infrared analyses. Dynamics investigation and isothermal research were conducted to clarify the adsorption process of the CTSV. Results suggested that the adsorption process could be well described by Freundlich model. Meanwhile, dynamics investigation showed that the adsorption equilibrium could be reached after an hour and the correlative coefficient of pseudo-second-order kinetic model was 0.9333.

Keywords: Dibutyl phthalate; Vanillin; Chitosan; Microwave radiation; Adsorption kinetics

1. Introduction

Phthalic acid esters (PAEs) are important industrial chemicals, which are widely used as solvents, emollients, humectants, and antifoaming agents in cosmetics and many other necessities [1]. Not only those people exposed to phthalates for occupational requirements, the potential for others is also high as chemicals widely used in all walks [2]. PAEs have become prevalent environmental pollutants for their large quantities production, due to their toxicity and endocrine-disrupting activity. The widespread use of PAEs has raised concerns regarding human welfare and environmental safety [3]. Some phthalates have even been suspected carcinogens with their effect on male reproductive system [4–7]. Furthermore, many studies

reported that PAEs would bring acute/chronic toxicity to aquatic organisms, animals, and even to humans [8–10]. Generally, the toxicity increases with the length of alkyl chains extended. At present, there are six phthalates selected as priority-controlled organic pollutants by EPA. In China, three PAEs have been listed as the priority controlled pollutants, which are dimethyl phthalate (DMP), dibutyl phthalate (DBP), and di-(2-ethylhexyl)-phthalate (DEHP). PAEs can exist in the environment for a long time due to their refractory nature. Both photolysis and chemical hydrolysis of PAEs commonly occurred at slow rate, and the major mechanism for PAEs' dissimilation process is considered to be microbial degradation. Nevertheless, PAEs have been detected in soil, natural water, and groundwater.

DBP is the most frequently identified PAEs in diverse environmental samples including groundwater,

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river water, drinking water, ocean water, soil humates, lake sediments, and marine sediments [11]. DBP is often used as a plasticizer and especially personal care products such as solvents for perfumes and fixatives for hair spray [12]. According to "Environmental Quality Standards for Surface Water in China" (GB3838-2002), the upper limit concentration of DBP is 0.003 mg/L, which would be appended later [13].

Chitosan (CTS) is a kind of polysaccharide prepared by the de-N-acetylation of chitin, which is widely spread among marine and terrestrial invertebrates and in lower forms of plant kingdom [14]. Also, vanillin (4-hydroxy-3-methoxy benzaldehyde) is one of the most important aromatic compounds used in foods, beverages, perfumes, and pharmaceuticals [15]. Both CTS and vanillin are regarded as safety materials [16-18] and easily obtained [19]. It has been reported that CTS studied in removing dyes [20], heavy metals [21-23], organic compounds [24,25], and humic acid [26]. What is more, aldehyde groups in vanillin and the amino groups in CTS may undergo Schiff base reaction to form network structure, which will take sides with the stabilization [18]. Despite their wide usage, present studies have not combined two materials for the removal of PAEs.

In this paper, the CTS flakes were transferred into CTS beads and then they were modified by vanillin. We hope to remove DBP from aqueous phase by this new combined material. We compared the method of making such modified material. The CTS products modified by microwave radiation were further investigated on adsorption properties.

2. Materials and methods

2.1. Materials

DBP was purchased from LingFeng Chemical Reagent Co., Ltd. (Shanghai, China). Vanillin was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Acetic acid was purchased from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). All of them were of analytical grade. The CTS powders with a deacetylation degree of 80% were provided by Nantong Xingcheng Biological Industrial Limited Co. in China. Other chemicals were of analytical grade and purchased from Chinese chemical companies. The water used was deionized water.

To avoid contamination, plastic equipment was not used in any sampling or experimental process and all glass vessels used were soaked in chromic acid solution for at least 10 h, washed with deionized water for three times.

2.2. Preparation of CTS adsorbents

In this study, there were 4 kinds of CTS adsorbents. They were CTS powders, CTS beads, CTSV-W, and CTSV. CTS powders were the raw materials bought from the business. The CTS beads were made from CTS powders through vacuum instillation. The CTSV-W was the CTS beads modified by vanillin through water heating. And the vanillin-modified CTS beads by microwave radiation were named CTSV. The distinctions between CTSV-W and CTSV were the modification ways. One was water heating, but the other was microwave radiation. The CTS adsorbents are prepared as follows:

CTS powders were dissolved in 2% (v/v) acetic acid [10,17,27] to give a final concentration of 2% (w/v). Stirring the solution until it becomes homogeneous took about 2 h. Instead of being left overnight [10], putting the beaker into ultrasonic generator for 10 min to give off the gas whose constituent was unknown. Then, the solution was dropped to a mixed solution consisted of 2% (w/w) sodium hydroxide and 10% (v/v) ethanol [28]. The spherical uniform beads were formed soon with a relatively uniform diameter size of ~4 mm. The reaction solution was mildly stirred for 4 h and let standing for 12 h at room temperature. The CTS beads were washed by deionized water until pH 7 in order to remove residual sodium hydroxide [10] and kept in water at room temperature for later use.

Vanillin-modified CTS beads with water heating (CTSV-W) were prepared. It was to add a certain amount of CTS beads (without surface water) into a three-necked flask with a 2:3 vanillin solution (the mass ratio of vanillin and CTS was the same as that under microwave radiation) of ethanol/water. The suspension was stirred at 100 rpm under 60°C to ensure the reaction reached equilibrium. After 6 h, the CTSV-W beads were transferred and washed with ethanol for several times. The CTSV-W beads were dried in a vacuum oven at 60°C for 24 h and kept in a desiccator for further analysis.

CTS beads (without surface water) were added to a 2:3 vanillin solution (the mass ratio of vanillin and CTS contained in beads was 3:1) of ethanol/water. The mixture in the glass beaker was kept for 10 min under microwave radiation (400 w, 60 °C, 400 rpm). The CTS beads were transferred from white to yellow soon. After that, the beads were washed with ethanol for several times, dried in a vacuum oven at 60 °C for 24 h, and kept in a desiccator for further analysis. The material we got was named as CTSV.

Either modification method is based on the Schiff base reaction, which is illustrated in Fig. 1. Pure water



Fig. 1. Schiff base reaction of CTS and vanillin.

must be firstly allowed in this reaction, which would help aldehyde group hydrolyze. The second step would be the amino group reacting with hydrolyzed vanillin after which the vanillin has successfully modified CTS beads.

2.3. Characterization and analyses

The surface morphology and internal structure of the CTS beads were observed by a scanning electron microscope (SEM) (Quanta 200, USA). The CTS beads were analyzed by a Fourier transform-infrared (FT-IR) spectrophotometer (Nicolet 380, USA).

DBP was analyzed by Ultimate 3000 High Performance Liquid Chromatography (HPLC) (Dionex, USA). The HPLC column was Eclipse XBD-C18 USP L1 (4.6 mm × 250 mm, i.d., 5 μ m). The column temperature was 35 °C. Mobil phase (CH₃OH:H₂O) was 9:1, flow speed was 1.0 mL/min [29], and injection volume was 20 μ L [10]. DBP was detected by the UV detector at a wavelength of 225 nm. The retention time was (5.708 ± 0.05) min.

All plastic instruments were strictly prohibited. For every six samples, a method blank, a matrix spike, and a sample duplicate were processed together with water samples. The average recoveries in matrix spikes for DBP ranged from 84% to 97%. The relative standard deviation was below 9.2%. Limits of detection were $0.4-0.7 \,\mu g/L$. Results in this study were blank and recovery corrected.

2.4. Kinetic adsorption and adsorption isotherm tests

Batch experiments for the adsorption of DBP on CTSV beads were performed in 250 mL Erlenmeyer flasks with 100 mL aqueous solution containing 50 mg/L DBP and 0.05 g of CTSV beads. The solution containing CTSV beads were shaken at a constant speed of 150 rpm in an incubator shaker for 24 h to

ensure the equilibrium adsorption. Preliminary kinetic experiments indicated that 10 h was sufficient to reach adsorption equilibrium onto CTS beads and CTSV beads. The amount of DBP trapped by the adsorbent particles was calculated based on mass balance before and after the test. The amount of adsorbed DBP was calculated as:

$$Q = \frac{(C_{\rm o} - C)V}{m} \tag{1}$$

where Q is the amount of adsorbed DBP on a unit mass of the beads (mg/g); C_o and C are the concentrations of DBP in the initial solution and in the aqueous phase after treatment for a certain period of time, respectively (mg/L); V is the volume of the aqueous phase (mL); and m is the mass of the beads used (g).

The adsorption isotherm experiments were carried out with a series of known concentration DBP in the way as stated above. For the kinetics experiments, an increase in the initial DBP concentration leads to an increase in the adsorption capacity of DBP on CTSV beads. The adsorption capacity for 4 h with initial DBP concentration at 100 mg/L is 97.3%. This indicates that the initial DBP concentration plays an important role in the adsorption capacity of DBP on the CTSV beads. Thus, 500 mL DBP solution with initial concentration of 100 mg/L was transferred into a 1,000 mL flask, into which 0.500 g of a given adsorbent particle was added subsequently. 0.5 mL solution at different time intervals was sampled from the flasks to determine DBP concentration.

2.5. Desorption and regeneration study

The desorption studies played important roles in economic success of materials. 99.5% CH₃OH was tried to regenerate the CTSV. The CTSV beads were slightly compacted in a glass column without gaps

and the height was 50 mm. The bottom of the column was linked with a peristaltic pump by flexible pipes. One-hundred milliliter CH_3OH was put into the column. When the peristaltic pump was started at a very slow rate, the desorption began. The regeneration finished until DBP was hardly detected.

3. Results and discussion

3.1. Morphology of CTS beads

The CTS beads before and after modification were in a spherical form of 0.5-1.0 mm in diameter. The entire spherical form and surface morphology of CTS beads modified before and after were visualized by SEM as depicted in Fig. 2. Fig. 2(a) showed that the CTS beads were almost in spherical form, but they were not perfect balls as a result of preparation for unmodified CTS in the laboratory instead of those like commercial resins, which can be bought from the market. Fig. 2(b) showed the rough surface of CTS beads at magnification of 300 and 1,200, respectively. Both of them showed that the CTS beads had an uneven surface. It was more clearly to be seen from Fig. 2(b) with a higher magnification. Fig. 2(b) and (c) showed a relatively rough surface of CTSV beads, which was at a magnification of 300 and 1,200 as well. It seemed that the CTSV beads' surface had been blanketed with something, but we could still observe many rises and falls. Relatively, the surface of CTSV beads was more smoothing than that of CTS beads. Most CTS beads had microspores being observed from low magnification, which formed as a result of gas escaping during the preparation of CTS, for it was very difficult to remove all the bubbles before dropping. Looking it from another way, it could add the surface area of these beads and create opportunities for inner adsorption both of which would promote the adsorption amount.

3.2. Fourier transform-infrared spectroscopy

Fig. 3(c) shows the FT-IR spectrum of CTS beads. The presence of -OH and N–H was confirmed due to stretching vibration at 3,421 cm⁻¹ in which the -OH stretching vibration was overlapped by N–H stretching. The absorption of C–H stretching of methyl or methylene groups of CTS was at 2,879 cm⁻¹, and the peak at 1,655 cm⁻¹ corresponded to the C=O in amido cyanogen. The peak at 1,319 and 1,382 cm⁻¹ referred to stretching vibration adsorption of C–N in amido cyanogen. The stretching vibrations of C–O in alcoholic hydroxyl groups were found at 1,154 and 1,079 cm⁻¹.

Fig. 3(b) showed the FT-IR spectrum of CTS beads modified by vanillin. It was obvious that the peaks at 1,640 and 1,603 cm⁻¹ were separately corresponding to characteristic stretching vibration of C=N and bending vibration of N-H, which could be attributed to the Schiff base reaction between aldehyde group of vanillin and amino group of CTS. Compared with Fig. 3(b) and (c) reserved the stretching vibration adsorption of -OH/N-H and C-H in methyl groups at 3,423 and $2,872 \text{ cm}^{-1}$, respectively. The peaks at 1,517, 1,465, and $1,432 \text{ cm}^{-1}$ were attributed to the benzene ring. The peaks at 1,375 and 1,157 cm⁻¹ were separately corresponding to stretching vibration adsorption of C-N in amine and C-O in alcoholic hydroxyl groups. The peaks at 1,201 and 1,286 cm⁻¹ corresponding to stretching vibration of -OH/N-H were also found. Totally, the above analysis and evidence led us to the conclusion that CTS was modified by vanillin successfully through Schiff base reaction and hydrogen bond interaction.

3.3. Adsorption capacity of DBP onto CTS, CTSV, and CTSV-W

The comparison of adsorption capacity of DBP onto CTS beads before and after modification is shown in Fig. 4. Compared with CTS powders, CTS beads had a lower adsorption capacity, as CTS taken in powder form had a higher specific surface area, which was highly correlated with adsorption behavior. In order to prevent adsorption materials from losing and to strengthen their mechanical properties, it was absolutely essential to change from the powders to spheres in spite of a relatively lower adsorption capacity. The study aimed at obtaining strong materials with big adsorption capacity of DBP. It was apparent that the adsorption capacity of vanillin-modified chitosan beads through either water heating (CTSV-W) or microwave radiation (CTSV) was higher than that unmodified ones. What drew more attention was CTS beads modified by vanillin through microwave radiation could adsorb much more DBP than that modified by vanillin through water heating. And it is fully illustrated by the jumped curve in Fig. 4.

Compared with traditional heating methods, microwave radiation could efficiently achieve the goal as it could speed up the reaction rate by orders of magnitude [30–32]. Like the complicated mechanism about microwave radiation [33], no final conclusion has yet been reached on the mechanism of microwave radiation for rapid organic synthesis. On one hand, microwave radiation could stimulate heterogeneous chemical reactions and increase the chemical reaction rate. On the other hand, taking account of the high



Fig. 2. SEM images of CTS and CTSV beads: (a) spherical form; (b) rough surface of CTS at different magnification; and (c) surface of CTSV at different magnifications.

speed vibration of microwave, the crystal structures of CTS beads changed, which might be beneficial to adsorption.

3.4. Adsorption isotherms

Adsorption isotherm data of DBP from the aqueous solution onto CTSV beads were derived at 298 and 308 K separately. As shown in Fig. 5, DBP

concentrations were changed in the range from 10 to 150 mg/L at different temperatures. The adsorption amount increased with increasing DBP concentration.

The isotherm data were treated according to Langmuir and Freundlich isotherm models. The Langmuir equation was given in Eq. (2):

$$\frac{1}{Q_e} = \frac{1}{B_L Q_m} \frac{1}{C_e} + \frac{1}{Q_m} \tag{2}$$



Fig. 3. Infrared spectra of the vanillin (a), CTSV (b), and CTS (c).



Fig. 4. Comparison of adsorption capacity of DBP onto the CTS adsorbents at 298 K.

where Q_m is the maximum amount of DBP adsorbed; C_e is the DBP concentration in equilibrium (mg/L); Q_e is the amount of DBP adsorbed in equilibrium (mg/g); and B_L is the binding constant to be determined.

The Freundlich equation is generally described as Eq. (3), and its linearized form is given in Eq. (4):

$$Q = KC^{1/n} \tag{3}$$

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{4}$$

where Q_e is the amount of DBP adsorbed at equilibrium time (mg/g); C_e is the equilibrium concentration of DBP in solution (mg/L); and K_F (mg/g) (L/mg)^{1/n}

and n are isotherm constants that indicate capacity and intensity of the adsorption, respectively.

The parameters of Langmuir and Freundlich equations were depicted in separate figures. Fig. 5(a) shows the DBP adsorption isotherm could be well fitted by both Langmuir and Freundlich models at 298 K, and the correlation coefficients were high, to 0.9952 and 0.9945 separately. As a result, at 298 K, the adsorption of DBP onto CTSV was a combination of Langmuir monolayer adsorption and Freundlich multilayer adsorption. But which kind of adsorption of DBP onto CTSV should belong to? Some articles claimed that a number of monolayer adsorption data could not only fit Langmuir model but also Freundlich model because of some hypotheses in the derivation, and it had been verified in many experiments [33]. So the adsorption of DBP onto CTSV might still be the monolayer adsorption. The amount of DBP adsorbed in equilibrium concentration increased with growing initial DBP concentration and tended to remain steady in high concentration.

Fig. 5(b) illustrated the adsorption of DBP onto CTSV at 308 K. The basic trend was the same with that at 298 K. The data was fitted by Langmuir model and Freundlich model as above. Compared with the adsorption at 298 K, the amount of DBP adsorbed is much higher at 308 K. This indicated that higher temperature had advantages to adsorption of DBP onto CTSV. On the contrary, the correlative coefficients of Langmuir and Freundlich model were low, to 0.8798 and 0.8740, respectively. Overall, the adsorption of DBP onto CTSV could be basically fitted by the two



Fig. 5. Adsorption isotherms for DBP onto CTSV at 298 K (a) and 308 K (b).

models. What should be highlighted was that the two models fitted keep consistency with each other either at 298 or 308 K.

3.5. Adsorption kinetics

Aiming at adsorption for DBP onto CTSV, the pseudo-first-order kinetic model and pseudo-second-order model were fitted by dynamic experimental data at 298 K, and they were displayed in Figs. 6 and 7.

The curve in Fig. 6 showed Q_t (DBP uptake at different time) rapidly increased with time. And about an hour later, the system reached equilibrium. We kept monitoring for nearly four hours, but actually it took only about a quarter to achieve the adsorption balance.

The pseudo-first-order kinetic model of Lagergren is given as follows:

$$Log (Q_e - Q_t) = log Q_e - \frac{K_1}{2.303}$$
(5)



Fig. 6. Adsorption kinetic for DBP onto CTSV at 298 K.

where Q_e and Q_t (mg/g) are the amounts of DBP adsorbed at equilibrium and at time (min), respectively. K_1 (L/min) is the rate constant of pseudo-first-order adsorption. The pseudo-second-order kinetic model of McKay is depicted as:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{1}{Q_e} t$$
(6)

where Q_e and Q_t (mg/g) have the same definitions as in Eq. (6) and K_2 (L/min) is the pseudo-second-order rate constant at the equilibrium ((g/mg)/min).

As shown in Fig. 7, it was apparent that the correlative coefficient (0.9333) of pseudo-second-order kinetic model was much higher than that (0.6412) of pseudo-first-order kinetic model. So the adsorption kinetic for DBP onto CTSV could be well presented by the pseudo-second-order kinetic model.

3.6. Regeneration and recycling of the spent CTSV

Disposal or regeneration of spent adsorbent is an important economic factor in assessing the feasibility of an adsorption system. In the present study, CTSV offers considerable potential on the field of DBP removal from aqueous solution. Other factors affect the overall economics of adsorption such as regeneration and recycling of the spent adsorbent CTSV. Actually, an adsorbent could be regenerated and reused so that it can be put into cyclic use in a cost-effective manner. Regeneration of CTSV was achieved by 99.5% CH₃OH. In determining the reusability of CTSV, three successive cycles of adsorption studies were carried out. This study revealed that 99.5% CH₃OH was to be an excellent eluent. Three elution rates of the continuous adsorption and desorption were 97.1, 96.9, and 96.5%, respectively, while the CTSV regenerated still satisfied adsorption. Some detailed applications of CTS were listed in Table 1.



Fig. 7. The fitting of adsorption kinetic models for DBP onto CTSV at 298 K.

1				
Contaminates	Types of CTS beads	Experimental conditions (shake speed/equilibrium time/temperature/pH)	Adsorption capacity (mg/g)	References
PAEs PAEs	Vanillin-modified CTS beads CTS beads	150 rpm/24 h/25–35 °C/7.0 200 rpm/12 h/25 °C/7.0	DBP (59.22) DBP (0.022)	This study [10]
PAEs	CTS beads cross-linked by 2-0-formylmethyl-a-cyclodextrin and	100 rpm/12 h/25°C/7.0	DMP (0.009) DEHP (0.01) DBP (3.16) DEP (2.82)	[20]
	N,N-diméthylformamide.		DMP (2.76) DHpP (3.21) DEHP (3.09)	
Ammonium	NaA zeolite/CTS hybrid beads CTS beads graffed by amonium	180 rpm/288–308 K 120 rnm /150 min /25–45°C /5 0	5.84–25.22 100	[21] [22]
	persulfate			Ĩ
As(V) and As(III)	${ m Fe}_3{ m O4}$ ·Zr(OH) ₄ -impregnated CTS beads	140 rpm/24 h/ ambient temperature/ 7.0 ± 0.2	As(V) 35.7 As(III) 35.3	[23]
indium(III)	CTS coated bentonite (CCB) beads	50 rpm/300 min/298 K/2–6	17.89 500	[24]
(b(II) Vitrate and phosphate	Dithiocarbamate modified C1S beads Ouaternary ammonium chloride	24 h/30 C/6 120 rpm/3 h/room temperature/4-5	500 Nitrate (20.3)	[26]
	functionalized CTS beads (QCB)		Phosphate (17.2)	Ĩ
Phenol, 2-chlorophenol (2-CP) 4-chlorophenol (4-CP)	CS-SA-CD made from CTS and salicylaldehyde	120 rpm/3 h/293 K	Phenol (21.65) 2-CP (26.72)	[27]
2,4-dichlorophenol (DCP) 2,4,6-trichlorophenol (TCP)	and modified by β-cyclodextrin,		4-CP (35.72) DCP (70.36) TCP (78.91)	
Remazol black B(RB) Erythrosine B	CTS hydrogel/SiO ₂ by the	120 rpm/room temperature (25°C)	RB (124 ± 8)	[28]
(EB Neutral red (NK) Gentian violet (GV)	sol-gel method		EB (87 ± 5) NR (347 ± 14)	
			GV (256±46)	

Table 1 Comparison of the adsorption characteristics of CTSV with different CTS sorbents

4. Conclusion

In this study, vanillin-modified CTS beads for removing DBP from aqueous solution were prepared and characterized. Both morphology and inner chemical structures of beads were presented through SEM and FT-IR analysis, respectively. Two heating modification methods were compared; the results strongly demonstrated that the microwave modification had obvious advantage over traditional water heating method. The microwave modification technology is rightly in accordance with the concept of green chemistry. Although the difference between Langmuir model and Freundlich model was small, the adsorption process could be better described by the Freundlich model at either temperature. The kinetic study indicated that the adsorption equilibrium for DBP onto CTSV could be reached in one hour. And the pseudosecond-order kinetic model could be well fitted, which demonstrated the adsorption rate determined by comprehensive action of DBP and CTSV. Overall, CTS beads modified by vanillin through microwave radiation could be considered as a potential adsorbent.

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