



Preparation and characterization of biomimetic adsorbent from poly-3-hydroxybutyrate

Xiaoxuan Zhang^{1,2}, Chaohai Wei^{1,*}, Qincong He¹, Yuan Ren¹

1. College of Environmental Science and Engineering, South China University of Technology, Guangzhou 510006, China. E-mail: zhxx1976@163.com

2. College of Chemistry and Material Science, Anhui Normal University, Wuhu 241000, China

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Abstract

Biomimetic adsorbent named as PHBBMA was prepared from lipophilic poly-3-hydroxybutyrate (PHB) by a modified double emulsion solvent evaporation method. PHBBMA, characterized by using scanning electron microscope and nitrogen adsorption/desorption measurements, is porous spherical particles. The characterization with the thermal gravimetric analysis and differential scanning calorimetry, ¹H nuclear magnetic resonance and Fourier transform infrared spectroscopy showed that PHBBMA preparation was a physical process without chemical reaction. The adsorption of PHBBMA for *o*-nitrochlorobenzene (*o*-NCB) was fitted better by Langmuir model than by Freundlich model, while the pseudo second-order model fitting was better than the pseudo first-order model fitting. The maximal adsorption capacity of PHBBMA for *o*-NCB was 57.83 mg/g at 30°C, although its specific surface area (S_{BET}) was only 8.45 m²/g. PHBBMA is a safe and environmental friendly adsorbent with high adsorption capacity because its component is innocuous and biodegradable PHB produced reusing wastes and contaminants, no byproduct can produced, and its ester and hydrocarbyl groups have strong affinity with organochlorine compounds. The further work will focus on the modification and improvement of PHBBMA in order to increase its S_{BET} and adsorption capacity.

Key words: poly-3-hydroxybutyrate; solvent evaporation technique; biomimetic adsorbent; adsorption

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Introduction

The pollutions of organochlorine compounds (OCICs) are of great concern owing to toxicity, refractory and extensive distribution (Khan et al., 2008). OCICs are mainly from industrial and agricultural discharges, chlorine disinfection byproducts (DBPs) and incineration of wastes (Xu, 2007; Zhang et al., 2002, 2009; Yang et al., 2005; Richardson et al., 2007; Taylor and Lenoir, 2001). OCICs can be degraded with biodegradation and advanced oxidation methods (Adrian and Görsch, 2002; Adebusoie et al., 2007; Lifka et al., 2003), but it is kinetically limited because of extremely low levels (Adebusoie et al., 2007; Gao et al., 2008). OCICs are liable to bioaccumulation in organisms containing abundant lipid, such as zooplankton, fish, seal and waterbird (Fisk et al., 2001; Muir et al., 2003; Zhou et al., 2007; Sakellarides et al., 2006). This is because OCICs with hydrophobic and lipophilic had strong interaction with lipid. Therefore, poly-3-hydroxybutyrate (PHB) will have an accumulation capacity for OCICs, since it has the same functional groups of the lipid which have lipophilic and hydrophobic nature. According to this idea, PHB was used to prepare porous biomimetic adsorbent, which had three advantages. First, the biomimetic

adsorbent have excellent adsorption capacity owing to its porosity and lipophilic nature. Second, adsorbent is environmental friendly because that PHB is biodegradable and innocuous. Third, wastes can be reutilized since PHB is produced by many microorganisms through degrading wastes and contaminants under unbalanced growth conditions (Braunegg et al., 1998; Khardenavis et al., 2007).

The monomer polymerization is a commonly used preparation method for organic polymer adsorbent, but it always includes a series of complex process under strict reaction conditions (Abrams and Millar, 1997; Jayakumar et al., 2006; Ghosh et al., 2007), and the toxic pore forming agents and long preparation period are inevitable. O'Donnell and McGinity (1997) used solvent evaporation technique to encapsulate drugs. The drug aqueous solution was intra-water phase in the double emulsion solvent evaporation (DESE) technique (water-in-oil-in-water, $W_1/O/W_2$). Considering the simple process and low cost, we modified the method to prepare adsorbent. That is to say, the proper intra-water phase was selected and pore forming agent was added to intra-water phase or/and oil phase to get more pores according to the need.

In this study, a biomimetic adsorbent was prepared with PHB by modified DESE method, which was named as PHBBMA. PHBBMA was characterized with various

* Corresponding author. E-mail: cechwei@scut.edu.cn

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techniques, and applied to treat *o*-nitrochlorobenzene (*o*-NCB) wastewater.

1 Materials and methods

1.1 Chemicals

PHB with melting temperature (T_m) 172°C and analytical standard *o*-NCB were purchased from Sigma-Aldrich Co. (USA). Polyvinyl alcohol (PVA) and chloroform were purchased from Guangdong Guanghua Chemical Factory Co. (China).

1.2 PHBBMA preparation

Deionized water was used as a pore forming agent. The preparation process is shown in Fig. 1. After preliminary experiments, the preparation conditions were selected as: deionized water (W_1) of 12 mL, 3% (W/W) PHB chloroform solution (oil phase) of 30 mL, 3% (W/W) PVA aqueous solution (W_2) of 200 mL. The stirring rate and time, respectively, for primary emulsion were 10,000 r/min and 2 min, for double emulsion were 800 r/min and 4 min, and for evaporation were 500 r/min and 36 hr.

The preparation processes are as follows. First, deionized water was dropped into oil phase under evenly stirring to get the primary emulsion (W_1/O). Second, the primary emulsion was injected into PVA solution and emulsified to form the double emulsion ($W_1/O/W_2$). Third, the double emulsion was diluted with proper deionized water, and stirred to evaporate the chloroform and solidify PHBBMA. Last, PHBBMA particles were filtered, washed with deionized water and freeze-dried.

1.3 Characterization methods

The shape and surface morphology of PHBBMA were investigated by JSM-6300F scanning electron microscope (SEM) from JEOL Ltd. (Japan). Samples were dried

overnight and sputter coated with gold prior to imaging.

The specific surface area and pore distribution of PHBBMA were measured by ASAP 2010M from Mirometitics (Norcross, USA) with the BET (Brunauer-Emmett-Teller) and BJH (Barrett-Joyner-Halenda) methods through N_2 adsorption at 77 K (Kindoh et al., 2006).

The thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out on STA449C (Netzsch, Germany) at a heating rate of 10 K/min from 30 to 700°C.

PHB and PHBBMA were dissolved in deuterated chloroform, and 1H nuclear magnetic resonance (1H NMR) spectra were recorded at 400 MHz in an AVANCE digital spectrophotometer (Bruker, Germany).

The surface groups of PHB and PHBBMA were analyzed by Fourier transform infrared spectroscopy (FT-IR). PHB and PHBBMA (5 mg each) were mixed with 100 mg of FT-IR grade KBr and pelletized. The FT-IR spectra were recorded at 4000–400 cm^{-1} in Nicolet 6700 spectrometer (Thermo, USA).

1.4 Adsorption experiments

o-NCB was selected to test the adsorption efficiency of PHBBMA. For each isotherm experiment, 100 mL of *o*-NCB aqueous solution containing 100 mg of PHBBMA in a 150-mL conical flask was sealed with a stopper, and agitated at 200 r/min in an air bath, where temperature was controlled at 30°C. Seven different concentrations of *o*-NCB between 0.98 and 97.55 mg/L (6.19×10^{-3} –0.62 mmol/L) were used. The equilibrium time was 36 hr, which determined by preliminary study. After attaining equilibrium, the aqueous phase was separated to determine the final concentration of *o*-NCB. The adsorbed amount was calculated from the difference between the initial and final concentrations.

The initial concentration of *o*-NCB used in kinetics experiments was 9.76 mg/L (61.9 μ mol/L). A series of 150-mL conical flasks with stopper filled with 100 mL of *o*-NCB solution and 100 mg of PHBBMA were agitated at 200 r/min and 30°C. At given time intervals, the solutions were separated to measure the concentration of *o*-NCB.

The concentration of adsorbate on PHBBMA, q (mg/g), was calculated by Eq. (1):

$$q = (c_0 - c)V/m \quad (1)$$

where, c_0 (mg/L) and c (mg/L) are concentrations of adsorbate in the solution at time 0 and t (hr), respectively. V (L) is the solution volume, and m (g) is the dose of adsorbent.

1.5 Analysis method of *o*-NCB

The concentrations of *o*-NCB were determined by LC-20A high performance liquid chromatography (HPLC) from Shimadzu (Japan) with external standard method. Samples were separated using an Agilent HC-C18 column (4.6 \times 250 mm) (Santa Clara, USA) at 40°C and detected by UV detector at 254 nm. The mobile phase was methanol/water (70/30, V/V) at a flow rate of 1.000 mL/min, and sample injection volume was 10 μ L for 18

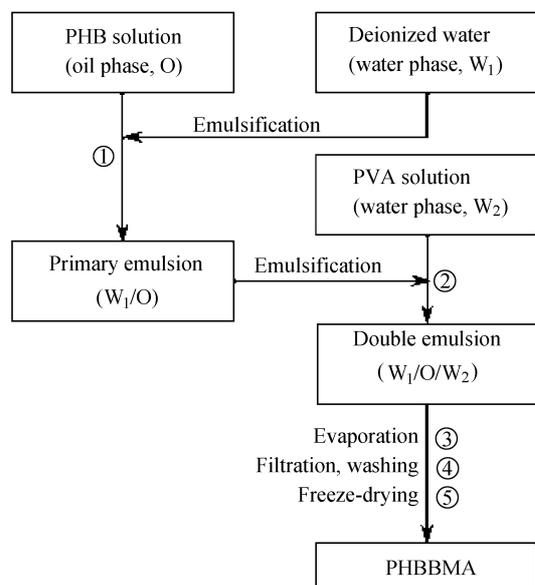


Fig. 1 Diagram of PHBBMA preparation. ①, ②, ③, ④, and ⑤ express the operation order.

min of the retention time. Samples were filtered through a 0.45 μm syringe filter prior to injection into HPLC column. The calibration curves were established by injecting six standard solutions, ranging from 0.52 to 104.3 mg/L (3.31×10^{-3} to 0.66 mmol/L) with R of 0.9999. The minimum detection limit (MDL) was the compound concentration at a signal-to-noise ratio of 3, and the MDL value of *o*-NCB was 0.06 mg/L.

2 Results and discussion

2.1 Morphological and textural characteristics of PHBBMA

PHB can not be used as adsorbent directly, because it is fine powder and can not be dispersed in water and separated from water. However, PHBBMA prepared from PHB is porous spherical particles with big surface area and has a good dispersibility and separation performance, therefore, can be used as a suitable adsorbent.

SEM images (Fig. 2) show that PHBBMA adsorbent represented small spherical particles with rough surface and micropores, and the diameter for most particles was 100–200 μm . As shown in Fig. 2a, few particles were collapsed because that the thin PHB walls broke up under the pressure when the big cavities were produced by big water particles (W_1).

Nitrogen adsorption/desorption isotherms and pore size distributions of PHBBMA are shown in Fig. 3. The specific surface area (S_{BET}) is 8.45 m^2/g , total pore volume (V_{cp}) 0.0105 cm^3/g , and average pore diameter of PHBBMA 4.9 nm. Figure 3 shows that PHBBMA has a wide pore distribution with diameter from 1.9 to 89.7 nm, and the main pores are meso- and macro-pores according to the IUPAC definition (IUPAC, 1982).

PHBBMA particle size and pore diameter are affected by the concentrations of oil phase and extra-water phase (W_2), the volume ratio of W_1 and oil phase, the volume ratio of oil phase and W_2 , and the stirring speed. Under these preparation conditions, PHBBMA has a small S_{BET} . Therefore, its optimization and improvement are the further work because S_{BET} was an important parameter for adsorbent.

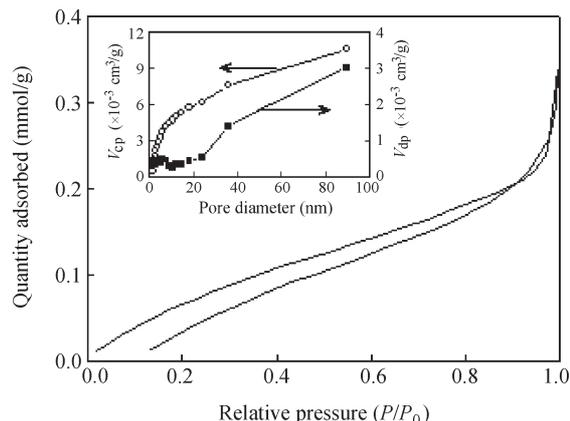


Fig. 3 Nitrogen adsorption/desorption isotherms for PHBBMA. Insert is pore size distributions of PHBBMA, where, V_{cp} is cumulative and V_{dp} is differential pore volume.

2.2 TG and DSC measurements

The TG-DSC curves of PHB and PHBBMA are shown in Fig. 4. Both PHB and PHBBMA show the same change trend. That is to say, a big weight loss step and two endothermic peaks were present in TG-DSC curves. At 177.4°C, PHB had an endothermic peak without weight loss, which indicated that the temperature was the melting temperature (T_m). This is confirmed by provider (about 172°C, Section 1.1). As shown in Fig. 4, T_m of PHBBMA was 177.0°C, which is in accordance with that of PHB. The weight loss of PHB between 240 and 308°C was around 97% due to the decomposition, while that of PHBBMA reached approximately 98% between 255 and 312°C. The onset decomposition temperature of PHBBMA was higher than that of PHB (15°C), because the preparation of PHBBMA was a recrystallization process of PHB which would produce bigger crystals. The end decomposition temperature had no significant difference (only 4°C) for PHBBMA and PHB, describing that they had the same components. The experimental results indicated that the preparation process is a physical recrystallization process without chemical reaction, and no byproduct was produced. That is to say, PHBBMA is innocuous owing to safe material and no byproduct. PHBBMA have excellent adsorption capacity because it holds ester and hydrocarbyl groups, which play important roles for adsorption owing to their strong affinity with OCICs.

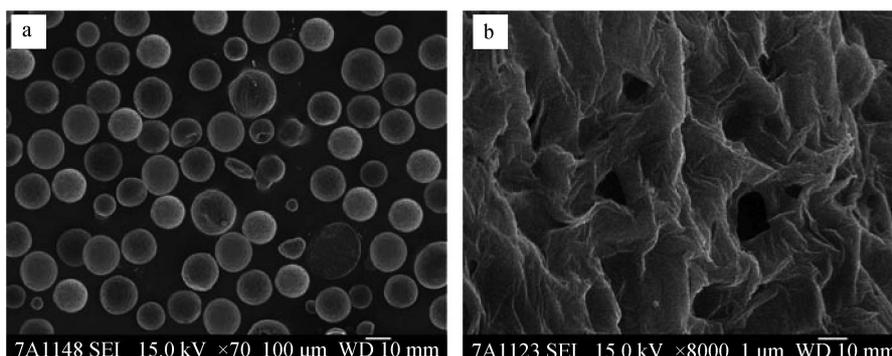


Fig. 2 Scanning electron micrographs (SEM) of PHBBMA. (a) whole particles $\times 70$, and (b) surface of particle $\times 8000$.

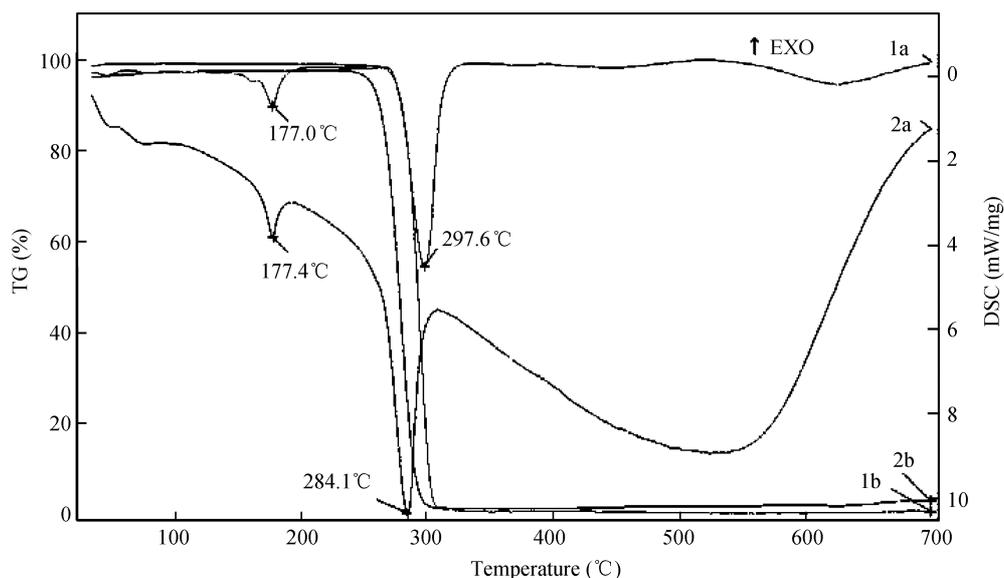


Fig. 4 TG-DSC curves of PHB and PHBBMA. 1a: PHBBMA-DSC; 1b: PHBBMA-TG; 2a: PHB-DSC; 2b: PHB-TG.

2.3 ^1H NMR spectra

^1H NMR spectra of PHB and PHBBMA are shown in Fig. 5. The chemical shifts (δ) were combined with PHB structure to confirm the groups. Chemical shifts of 1.268, 2.430–2.620 and 5.232 ppm were produced by methyl, methylene and methylidyne, respectively. The result is in accordance with the reference of Long et al. (2004). The residual proton signal of deuterated chloroform was present at the chemical shifts of 7.260 ppm. Figure 5 shows that ^1H NMR spectra of PHBBMA is accordant with that of PHB, indicating that there was no chemical reaction and the group including hydrogen had no change. The same conclusion was also obtained from TG-DSC analysis.

2.4 FT-IR spectra

FT-IR spectra are used to analyze the surface groups of PHB and PHBBMA. As shown in Fig. 6, the FT-IR spectrum of PHBBMA was in accordance with that of PHB. It indicated that they had same surface groups, and the preparation of PHBBMA was a physical process. The obvious absorption bands were ascribed to $\text{C}=\text{O}$ (1724 cm^{-1} stretch), methyl (2871 and 2981 cm^{-1} stretch),

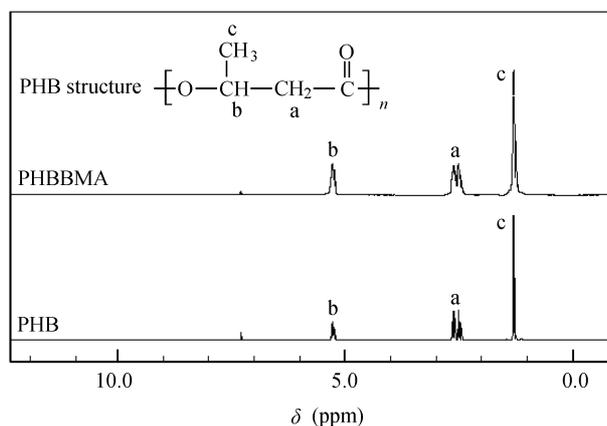


Fig. 5 ^1H NMR spectra of PHB and PHBBMA.

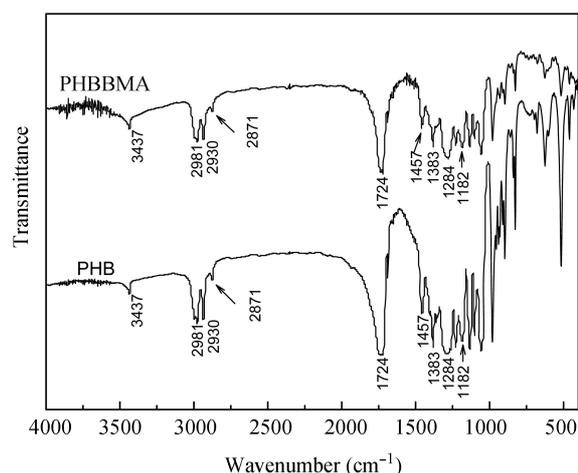


Fig. 6 FT-IR spectra for PHBBMA and PHB.

methylene (2930 cm^{-1} stretch), methyl (1383 cm^{-1} bending), methylene (1457 cm^{-1} bending), $\text{C}-\text{O}-\text{C}$ (1182 cm^{-1} stretch), methylidyne (1284 cm^{-1} stretch), $-\text{OH}$ (3437 cm^{-1} bending). The FT-IR spectra also proved that the preparation is a physical process, and PHBBMA has all characters of PHB.

The characterization with TG-DSC, ^1H NMR and FT-IR all show that the preparation of PHBBMA is a physical process without chemical reaction, and PHBBMA, an aggregate of PHB, kept the advantage of PHB for adsorption. PHBBMA is an environmental friendly adsorbent because that it is innocuous, biodegradable, and without byproduct. PHBBMA can have a good adsorption capacity because the ester and hydrocarbonyl groups have strong affinity with OCICs like the lipid.

2.5 Characters of adsorption

The adsorption isotherms are shown in Fig. 7 and parameters are presented in Table 1. The experimental data were analyzed using Langmuir and Freundlich models

Table 1 Adsorption isotherm parameters for *o*-NCB on PHBBMA

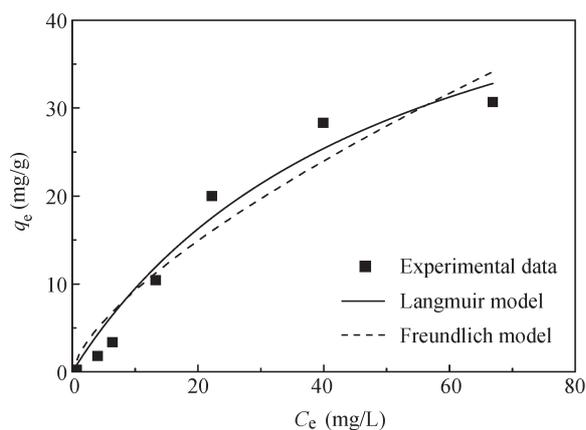
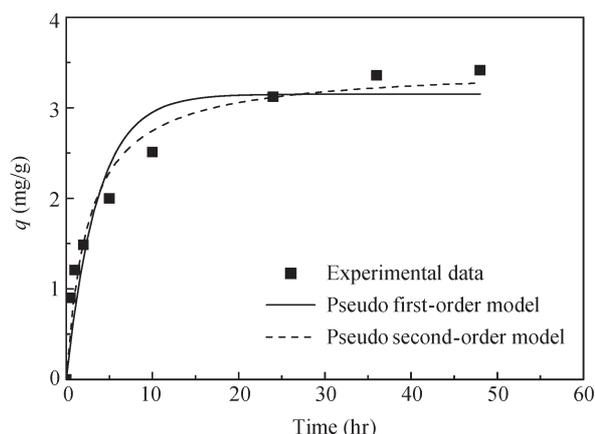
Model	Langmuir			Freundlich		
	q_m (mg/g)	b_L ($\times 10^2$ L/mg)	R^2	K_F ($\text{mg}^{(1-\frac{1}{n})} \cdot \text{L}^{\frac{1}{n}}/\text{g}$)	$\frac{1}{n}$	R^2
	57.83 (13.10)	1.96 (0.79)	0.967	1.91 (0.84)	0.69 (0.11)	0.938

Data in parenthesis are errors of the fitting values of the parameters.

Table 2 Kinetic parameters for *o*-NCB on PHBBMA

Model	Pseudo first-order			Pseudo second-order		
	q_e (mg/g)	k_1 (hr^{-1})	R^2	q_e (mg/g)	k_2 ($\text{g}/(\text{mg}\cdot\text{hr})$)	R^2
	3.15 (0.19)	0.276 (0.066)	0.922	3.45 (0.16)	0.114 (0.026)	0.970

Data in parenthesis are errors of the fitting values of the parameters.

**Fig. 7** Adsorption isotherms of *o*-NCB on PHBBMA at 30°C.**Fig. 8** Kinetics for *o*-NCB on PHBBMA. Initial concentration: 9.76 mg/L; PHBBMA: 100 mg; solution volume: 100 mL; temperature: 30°C.

with the non-linear fitting method by the software Origin 7.5. Langmuir isotherm can be represented as Eq. (2) (Langmuir, 1918; Kindoh, 2006; Pavan et al., 2008):

$$q_e = \frac{q_m b_L c_e}{1 + b_L c_e} \quad (2)$$

where, q_e (mg/g) and c_e (mg/L) are concentrations of adsorbate on PHBBMA and in the solution at equilibrium, respectively. q_m (mg/g) and b_L (L/mg) are constants related to adsorption capacity and energy of adsorption, respectively. The Langmuir equation is used for homogeneous surfaces. The Freundlich isotherm is given as Eq. (3) (Freundlich, 1906; Kindoh et al., 2006; Pavan et al., 2008):

$$q_e = K_F c_e^{\frac{1}{n}} \quad (3)$$

where, K_F ($\text{mg}^{(1-\frac{1}{n})} \cdot \text{L}^{\frac{1}{n}}/\text{g}$) and n are constants. The Freundlich isotherm originally was an empirical equation, but has been later interpreted in theory. K_F and n are indicators of adsorption capacity and intensity, respectively.

According to obtained R^2 (Table 1), Langmuir equation fitted experimental data better than Freundlich equation. The maximal adsorption capacity of PHBBMA was (57.83 ± 13.10) mg/g, and was 6.84 mg per unit surface area because S_{BET} was 8.45 m^2/g .

The kinetics is shown in Fig. 8, and the data fitted with the pseudo first- and second-order models employing the non-linear fitting method using the software Origin 7.5. The parameters are presented in Table 2. The pseudo first-order model is expressed as Eq. (4) (Lagergren, 1898;

Pavan et al., 2008):

$$q = q_e(1 - \exp(-k_1 t)) \quad (4)$$

where, k_1 (hr^{-1}) is the rate constant of the first-order sorption. The pseudo second-order model is in the form of Eq. (5) (Ho and McKay, 1999):

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

where, k_2 ($\text{g}/(\text{mg}\cdot\text{hr})$) is the rate constant of the second-order sorption.

Figure 8 and Table 2 show that the pseudo second-order model could fit the experimental data better than the pseudo first-order model. The equilibrium adsorption capacity was (3.45 ± 0.16) mg/g according to the pseudo second-order model, when the initial concentration was 9.76 mg/L, and the dosage of PHBBMA was 1 g/L at 30°C.

3 Conclusions

PHBBMA prepared with PHB by a modified DESE technique, is a new environment friendly biomimetic adsorbent. At the preparation conditions, its S_{BET} is only 8.45 m^2/g and pore distribution is wide with diameter from 1.9 to 89.7 nm.

The characterization determined using TG-DSC, ^1H NMR and FT-IR spectra show that PHBBMA preparation is a physical process without chemical reaction and any

byproduct. PHBBMA kept ester and hydrocarbyl groups which have strong affinity with OCICs. The experimental results indicate that PHBBMA is environmental friendly adsorbent because its component is innocuous and biodegradable PHB, no byproduct can be produced, and PHB can be produced from reusing wastes and contaminants.

The adsorption experimental results show that Langmuir equation fit the experimental data better than Freundlich, and the pseudo second-order model fit data better than the pseudo first-order model. PHBBMA has a good adsorption capacity because that its ester and hydrocarbyl groups had strong affinity with OCICs. The maximal adsorption capacity for *o*-NCB is about 57.83 mg/g at 30°C, although its S_{BET} is only 8.45 m²/g. The modification and improvement will be the further work for PHBBMA to improve its S_{BET} and control its pore diameter.

Acknowledgments

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