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Poplar leaves reclamation for porous granules and their application in nitrobenzene removal from aqueous solution

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ABSTRACT

Poplars produce quantities of leaves during their growth, which are usually burned or deserted directly. In this study, the deciduous leaves were reclaimed and made into organic granules. During the granulation, the adsorption capacity was not obviously depressed compared with leaf powder, but the granules were more convenient to be separated from the solution after saturation. Being made under relatively low temperature of 378 K, this material maintained the natural structure and ingredients of poplar leaves and supplied quantities of nanolevel structures in the cell wall and other cellular parts. The application of the granules in nitrobenzene removal indicated that this material was efficient in nitrobenzene adsorption from water. The adsorption was spontaneous under normal room temperature and neutral pH, which made it more competent than other adsorbents. The adsorption of nitrobenzene onto the granules complied well with the pseudo-second-order model and Langmuir isotherm model.

Keywords: Poplar leaves; Reclamation; Granulation; Nanolevel; Nitrobenzene; Adsorption

1. Introduction

Nitrobenzene is widely used in the manufacture of organic products, such as aniline, lubricating oils, dyes, drugs, explosives, pesticides, and synthetic rubber [1,2]. Many countries have listed it as a priority pollutant because of its mutagenicity, recalcitrance, and tendency to accumulate in the environment [3]. In recent years, many pollution affairs have been related with nitrobenzene for its high toxicity in water and air [4]. In China, the leakage of about 100 tons of nitrobenzene into Songhua River made many cities along this river suffer from drinking water shortage for several days in 2005 [5]. There are many methods for nitrobenzene removal such as adsorption by activated carbon [6], biological treatment [7,8], and advanced oxidation process. Because of the recalcitrant characteristics of nitrobenzene, many kinds of advanced oxidation processes have been developed such as s O_3/UV processes [9], photocatalytic oxidation [10,11], and electrochemical system [12,13]. Although these advanced oxidation processes are mostly effective in nitrobenzene removal, they are also complex and costly with high energy or resources consumption [14], which hampers their treatment performances and limits further application. In some abrupt pollution, activated carbon adsorption is usually the most effective method for nitrobenzene

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removal. However, the adsorption process with activated carbon is also very expensive. Consequently, there are many explorations on cheaper materials for nitrobenzene removal such as maize and rice stems [15], smectite clays [16], and fly ash [17].

Poplar is one of the deciduous trees widely planted in China, Europe, and North America. In most places of China, poplar is the most popular tree in plantation and man-made forestry. When compared with other forest species, poplars have many characteristics that make them more suitable for plantation culture. These include fast growth with large quantities of wood production, adaptability to different environmental conditions, and suitability for diverse silvicultural systems [18]. The leaves of poplar usually fade in short time in autumn, and are the main byproducts of poplar forestry [19]. The poplar leaves' litter can represent 25–60% equivalent of total yield in poplar forestry [20]. There are several studies for poplar leaves reclamation such as forage [21], natural fertilizer [22], and paper production. However, forage and fertilizer usually need green leaves which are cut off in poplar's growing period. The deciduous leaves are seldom utilized, and are usually burned directly or deserted as litters. In fact, the deciduous leaves mainly contain cellulose, protein, fat, and mineral. When the leaves fall down in autumn, there is not much water content left, and they can be easily disposed or reclaimed.

In this study, the deciduous poplar leaves were reclaimed and made into granular material for organic pollutants removal from water. Firstly the leaves are dried in nature and ground to powder, and then made into spherical granules. The granules are used to adsorb nitrobenzene from the water. The structure and composition of granules were studied. The operating parameters in nitrobenzene adsorption, adsorption kinetics, and isotherm were also investigated to illustrate the adsorption process of nitrobenzene onto the poplar leaf granules. To our knowledge, although there were some studies using natural poplar leaves and other leaves in heavy metals or organic pollutants removal from water, there was no similar study using molded granules from deciduous leaf in such pollutant removal.

2. Material and methods

2.1. Poplar leaf powder and granules preparation

The poplar leaves were collected after withering and falling in the autumn. After being dried in the sun, they were ground and sieved. The powder screened with 40-meshes sifter was then dried at 378 K in a baking furnace. Ninety-five grams of dried powder and five grams of sodium alginate were mixed with 70 ml distilled water, and the mixture was used to produce spherical granules with diameter of 5–8 mm in a granulator. After being dried at 378 K in a baking furnace, the finished granules were finally produced, and were used as adsorbent to remove nitrobenzene from aqueous solution.

2.2. SEM and EDS analyses of the granules

The structure and composition of the granules were vital for their adsorption performance. The surface and intersection structure were analyzed with a scanning electron microscope (SEM) (SEM, Quanta 200, FEI, Holand) to ascertain the external and sectional structures of the granules. During SEM analysis, the granules were also analyzed with energy dispersive X-ray spectrometry (EDS) (EDS, GENESIS, EDAX, USA) to investigate the main compositions [23].

2.3. Adsorption experiments

The poplar leaf granules or powder was dosed into the aqueous solution with certain nitrobenzene concentration. The pH of the solutions was controlled around 7.0 with 1 mol/L solution of HCl or NaOH. The samples were stirred in a temperature-controlled oscillator at a constant speed of 150 rpm. After certain time, the supernatant was withdrawn and filtered through 0.45 μm membrane filter. Residual nitrobenzene concentration was analyzed with the method of spectrophotometry [24]. The effect of operation parameters such as dosage, contact time, and temperature on nitrobenzene removal was investigated. The adsorption kinetics, thermodynamic parameters, and isotherm model were also studied.

The removal percentage of nitrobenzene (η) and adsorption capacity q (mg/g) were calculated using the following equations:

$$\eta\ (\%) = \frac{C_0 - C}{C_0} \times 100 \tag{1}$$

$$q = \frac{(C_0 - C)V}{w} \tag{2}$$

where C_0 is the initial nitrobenzene concentration (mg/L); C is nitrobenzene concentration (mg/L) after adsorption in certain time; V is the volume of the solution (L); and w is the mass of the granules (g).

3. Results and discussion

3.1. SEM characterization

The shape of materials, surface texture, and even particle distribution can be observed and analyzed by SEM [25,26]. Fig. 1 showed the external and sectional SEM pictures of the poplar leaf granules. It can be seen that the surface and intersection of the granules had many drapes and pores. The drapes and pores in the surface were more abundant and even than those in the inner section. Some pores in the surface even penetrated into the inner deep areas. The distribution of the drapes and pores was relatively even compared with many inorganic granules [27]. The soft wood such as poplar has four different levels of structures: (1) macroscopic structure such as vein and growth rings; (2) microscopic structure including cellular structure and the main elements of the cell wall; (3) nanostructure including the fine structure of the cell wall and fibril/matrix structure; and (4) molecular structure [28]. The main structure of the poplar leaf cells might be maintained well to generate micropores and nanolevel structures in the tissue space and the cell walls [29], which probably amplified the specific surface area of the granules and supplied quantities of adsorption positions.

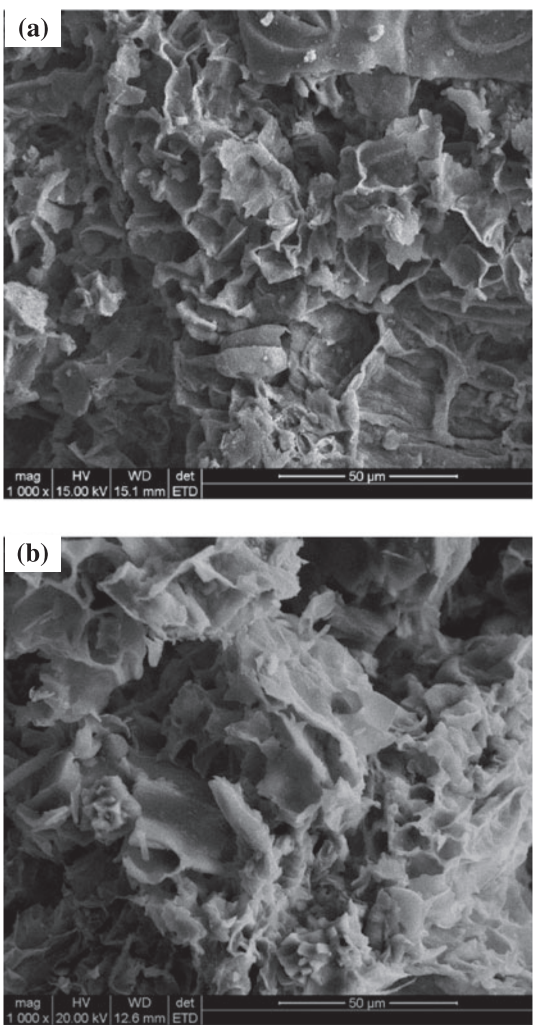

Fig. 1. Typical SEM photographs of the poplar leaf granules: (a) external; (b) sectional.

3.2. Chemical composition

The results of EDS (Fig. 2 and Table 1) indicated the main constituents with weight fraction in the poplar leaf granules as O (54.69%), C (32.44%), Si (4.68%), Ca (3.27%), K (1.39%), and S (1.07%). The atomic composition of C and O accounted for 93.81%, which indicated the poplar leaf granules mainly contained organics. These organic constituents had many organic functional groups, which could adsorb organic pollutants with intermolecular forces and hydrogen bonds. The granules were dried in a baking furnace at 378 K during the fabrication, which did not change the main composition of the original leaf. The granules maintained the cells and microstructures of poplar leaf. This is significant to get high porosity and pore area in the granules with natural structure and nanolevel dimensions.

3.3. Effect of dosage on nitrobenzene adsorption

The effect of poplar leaf granules' dosage on nitrobenzene adsorption was studied with granules' dosage varying in the range of 5–40 g/L (Fig. 3). The solution with nitrobenzene initial concentration of 10 mg/L and pH 7 was adsorbed with the granules with contact time and temperature controlled at 70 min and 293 K, respectively. Fig. 3 indicates the adsorption rate increased while the adsorption capacity decreased gradually with the dosage increase. At 5 g/L dosage, the adsorption rate and capacity were 37.6% and 0.75 mg/g, respectively. When the dosage was increased to 40 g/L, the adsorption rate and capacity, respectively, attained 67.1% and 0.17 mg/g. However, there was no much improvement of the adsorption with dosage increased above 20 g/L, at which the adsorption rate and capacity reached 60.0% and 0.30 mg/g, respectively.

3.4. Effect of contact time and adsorption kinetics

Contact time is usually a vital parameter for pollutants removal in adsorption process [30]. In this

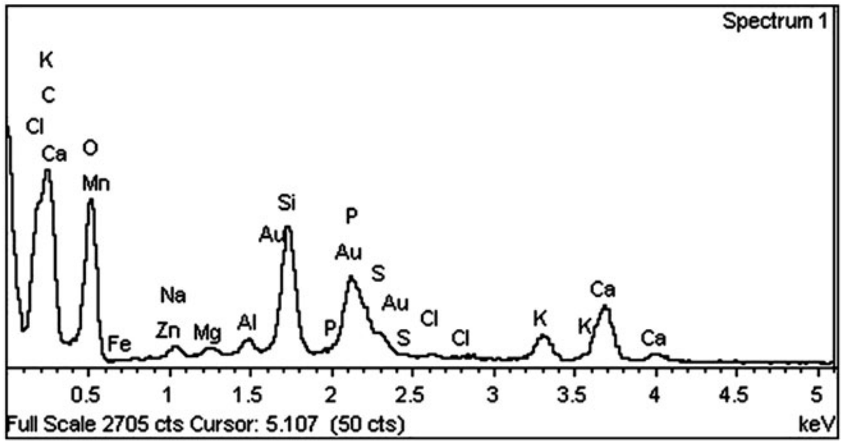

Fig. 2. Spectrum of EDS of the constituents of the granules.

Table 1
Main elements composition of the granules

Main elements	O	C	Si	Ca	K	S
Weight (%)	54.69 ± 0.36	32.44 ± 0.24	4.68 ± 0.29	3.27 ± 0.08	1.39 ± 0.03	1.07 ± 0.01
Atomic (%)	52.41 ± 0.06	41.4 ± 0.16	2.55 ± 0.10	1.25 ± 0.04	0.54 ± 0.01	0.51 ± 0.00

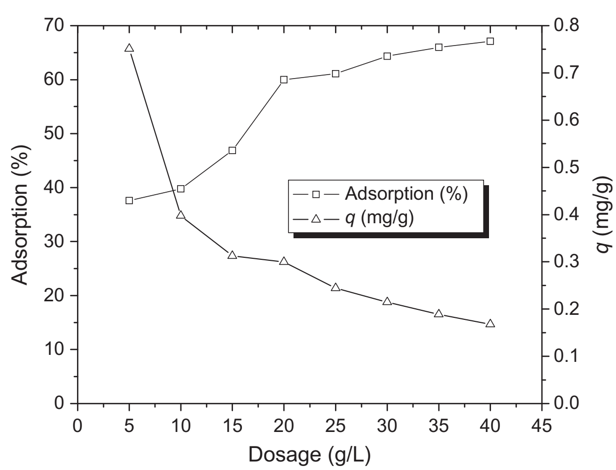

Fig. 3. Effect of dosage on nitrobenzene removal. pH: 7.0; temperature: 293 K; initial concentration: 10 mg/L; and contact time: 70 min.

study, the effect of contact time on nitrobenzene adsorption onto the poplar leaf granules was investigated to ascertain the equilibrium point and adsorption kinetics at pH 7 and 293 K with the granules dosage of 20 g/L and initial nitrobenzene concentration of 10 mg/L. As shown in Fig. 4(a), a gradual rise in nitrobenzene adsorption was seen with contact time extension from 30 to 70 min, and nitrobenzene removal increased from 46.9 to 65.5%. However, after 70 min, the removal decreased obviously. With contact time of 130 min, the removal decreased to 57.3%. Accordingly, the adsorption capacity also reached the highest value of 0.33 mg/g at the contact time of 70 min, which indicated the adsorption reached dynamic equilibrium. In the study of Wang et al. using maize stems and rice stems as adsorbents in nitrobenzene removal, the adsorption equilibration time of nitrobenzene at 298 K was about 72 h [15], which was about 60 times longer than the equilibrium time in this study.

Kinetic performance of a given adsorbent is of great significance for the pilot application. Several adsorption reaction models have been widely developed or employed to describe the kinetic process of adsorption such as the pseudo-first-order kinetic model, pseudo-second-order kinetic model, and an intraparticle diffusion kinetic model [31]. The adsorption of nitrobenzene on nanomaterials usually had the characteristics of both physisorption and chemisorption [32]. Consequently, the pseudo-second-order model might be more suitable for nitrobenzene adsorption on the granules. The pseudo-second-order model can be expressed with Eq. (3).

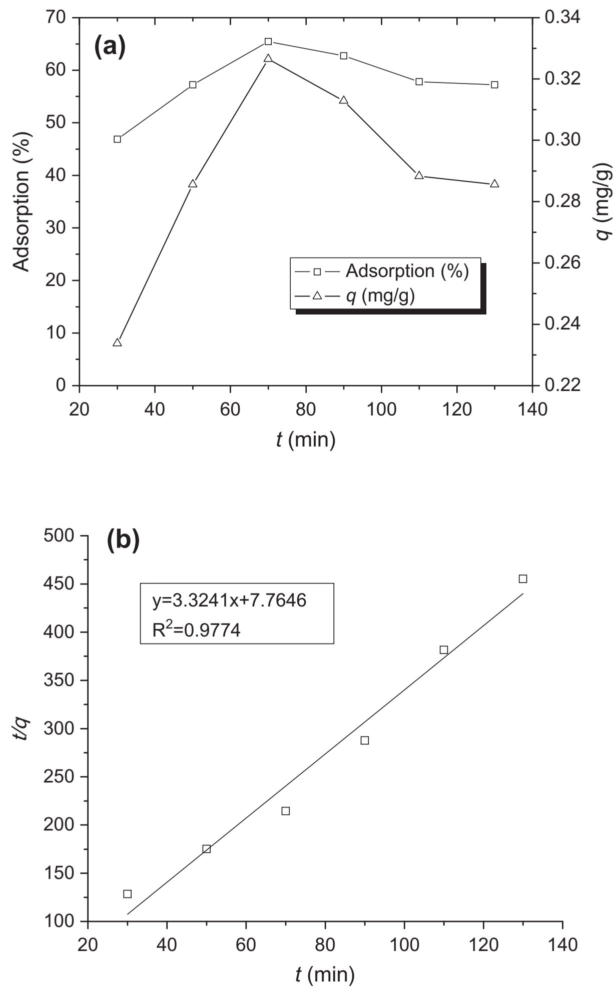

Fig. 4. Effect of contact time on nitrobenzene adsorption: (a) adsorption percentage and capacity variation; (b) pseudo-second-order kinetic model simulation. pH: 7.0; dosage: 20 g/L; temperature: 293 K; and initial concentration: 10 mg/L.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{3}$$

where q_e is the equilibrium adsorption capacity (mg/g); q_t is the amount of nitrobenzene adsorbed at time t (min); and k_2 is the rate constant of pseudo-second-order adsorption (g/(mg min)).

The linear simulation of the pseudo-second-order model with t/q_t against t is shown in Fig. 4(b). The regression coefficient (R^2) reached 0.9774, indicating the adsorption of nitrobenzene onto the granular material followed the pseudo-second-order model.

3.5. Adsorption isotherm

Adsorption isotherm describes the equilibrium between the adsorbent and adsorbate and is significant for characterization of adsorption process. Among the analytical isotherm models, Langmuir (Eq. (4)) and Freundlich (Eq. (5)) isotherms are widely used for modeling the distribution of adsorbates between the liquid phase and the solid phase [33]. In the Langmuir model, a dimensionless separation factor (R_L, Eq. (6)) can be used to describe the difficulty level of the adsorption process. The adsorption is favorable with the R_L value between 0 and 1 and unfavorable with the R_L value over 1 [34]. The adsorption isotherm of nitrobenzene on the granules was studied with dosage of 20 g/L under several temperatures with initial concentration ranging from 3 mg/L to 40 mg/L.

$$\frac{C_e}{q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \tag{4}$$

$$q_e = k_f \, C_e^{\frac{1}{n}} \tag{5}$$

$$R_L = \frac{1}{1 + bC_0} \tag{6}$$

where Q_m is the adsorption capacity (mg/g) and b, k_f, and n are characteristic constants of adsorption, C_0 is the highest nitrobenzene concentration (mg/L). For linearization of the data, the Freundlich equation can be written in logarithmic form:

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \tag{7}$$

Fig. 5(a) and (b) shows the linearization of equilibrium data with Langmuir and Freundlich isotherm models, respectively. With the slope and intercept of the linearization, the main parameters of the two models are given in Tables 2 and 3. The R_L values in Table 2 at different temperatures lie between 0.1 and 0.4, indicating highly favorable adsorption of nitrobenzene on the granules. The data in Fig. 5 and Table 2 show the Langmuir model is more applicable than the Freundlich model for the adsorption of nitrobenzene onto the poplar leaf granules. The R^2 value of the Langmuir model under 293 K and 318 K was above 0.9583, while that of the Freundlich model was below 0.9168. This suggests that the adsorption of nitrobenzene mainly occurred on the homogeneous surface of the poplar leaf granules by monolayer. However, under 328 K, the adsorption isotherm also deviates the Langmuir model because the excessive increase in temperature destroyed the balance of adsorption and desorption of nitrobenzene onto the granules [35].

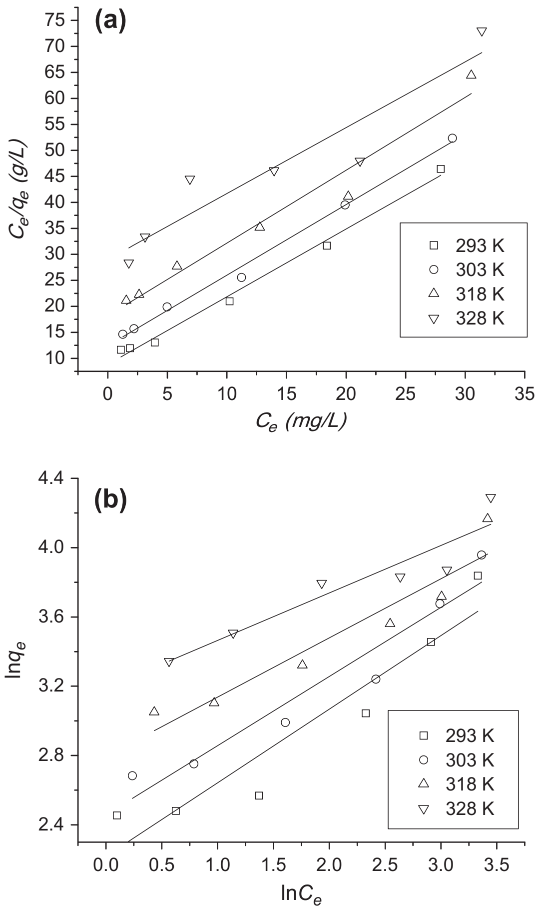

Fig. 5. Adsorption isotherm simulation of nitrobenzene onto the granules under different temperatures: (a) the Langmuir model; (b) the Freundlich model.

3.6. Influence of temperature and thermodynamic parameters

The influence of temperature on nitrobenzene adsorption onto the granules was studied with initial concentration in the range of 3–40 mg/L at different temperatures ranging from 293 to 328 K. As shown in Fig. 6, with temperature rise, the equilibrium concentration increased obviously, while the equilibrium adsorption capacity decreased accordingly. The equilibrium concentration and capacity increased greatly with the initial concentration increase. The adsorption capacity with initial concentration of 3 mg/L was only 0.09 and 0.06 mg/g at 293 and 328 K, respectively, while that with initial concentration of 40 mg/L reached 0.60 and 0.43 mg/g. The decrease of the adsorption with temperature increase indicated the adsorption of nitrobenzene onto the poplar leaf granules was exothermic. At 318 and 328 K, when initial concentration was increased from 30 to 40 mg/L, the equilibrium adsorption capacity obviously decreased. At other circumstances, the equilibrium adsorption capacity usually increased with initial concentration increase.

Table 3
The Freundlich equation parameters at different temperatures

Temperature (K)	k_f	n	R^2	Intercept
293	9.182964	2.352775	0.87924	2.21735
303	11.68341	2.506203	0.91675	2.45817
318	16.37867	2.928258	0.88638	2.79598
328	24.29596	3.648304	0.85752	3.19031

The influence of temperature on nitrobenzene adsorption onto the granules can be analyzed with thermodynamic parameters including free energy change (ΔG°), enthalpy (ΔH°), and entropy (ΔS°). The relation among the three parameters can be expressed with Eq. (8), and ΔG° can be calculated with Eq. (9) [36,37].

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{8}$$

where T is the temperature.

$$\Delta G^\circ = -RT \ln K_a \tag{9}$$

where R is the universal gas constant (8.314 J/(mol K)), and K_a is the equilibrium constant of the adsorption.

Table 2
The Langmuir equation parameters at different temperatures

Temperature (K)	Q_m	b	K_a	R_L	R^2	Intercept
293	0.768285	0.14734	1.3016	0.145062	0.99073	8.83399
303	0.736865	0.10918	1.3571	0.186317	0.99383	12.42997
318	0.713674	0.077176	1.4012	0.244676	0.95833	18.1559
328	0.789141	0.04365	1.2672	0.364164	0.86094	29.03071

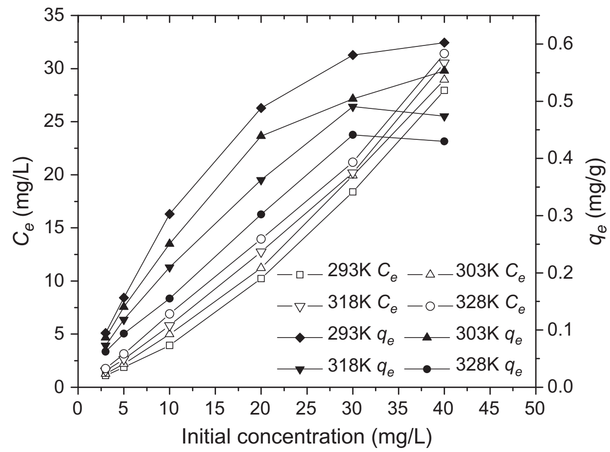

Fig. 6. Equilibrium concentration and adsorption capacity variation of the granules under different temperatures.

Consequently, Eq. (10) can be obtained with the combination of Eqs. 8 and 9. With the data in 3.5, it can be seen that the Langmuir model was more appropriate for the adsorption than the Freundlich model. At 328 K, the desorption process influenced the adsorption isotherm, and the adsorption deviated the Langmuir model. With the K_a value in the Langmuir model shown in Table 2 at temperatures of 293–318 K, the thermodynamic parameters of ΔH° and ΔS° were acquired, then ΔG° was calculated with Eq. (8). The values of ΔG°, ΔH°, and ΔS° for the adsorption of nitrobenzene on the ceramic granules are shown in Table 4.

$$\ln K_a = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{10}$$

The negative value of ΔH° indicated the adsorption of nitrobenzene onto the granules was exothermic, which was also supported by the decrease of the equilibrium adsorption capacity with temperature rise. The negative value of ΔS° suggested the decrease of randomness at liquid/solid interface during nitrobenzene adsorption. The poplar leaves mainly contained organic constituents such as cellulose, protein, and fat, which made nitrobenzene adsorb onto the similar functional groups in the poplar leaves with high stability [38]. The negative free energy changes (ΔG°) indicated the adsorption of nitrobenzene on the granules was spontaneous.

Table 4
Main thermodynamic parameters at different temperatures

T (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
293	−5.15	−9.67	−39.82
303	−5.25		
318	−5.40		
328	−5.50		

3.7. Comparison of nitrobenzene adsorption with poplar leaf powder and granules

According to the data in Figs. 6 and 7, the poplar leaves powder could adsorb more nitrobenzene. At 293 K, with the same adsorbent dosage of 20 g/L and initial nitrobenzene concentration of 10 mg/L, poplar leaf powder and granules, respectively, removed 73.7 and 60.5% of nitrobenzene, and the corresponding adsorption capacities were, respectively, 0.37 and 0.30 mg/g. When the temperature was increased to 318 K, the adsorption capacity of powder decreased to 0.23 mg/g, which was only a little higher than that of the granules. These data indicate that the powder could adsorb the nitrobenzene more completely from the aqueous solution. However, the difference was not so large as powdered activated carbon and granular activated carbon during adsorption. In the study of Tancredi et al. the Langmuir maximum adsorption capacity of powdered activated carbon was about 40% higher than that of granular activated carbon in phenol adsorption [39]. Xu and Liu found powdered activated carbon was 10.3 times more efficient in Pb^{2+} adsorption compared with granular activated carbon [40]. Moreover, the leaf powder was difficult to be separated from the solution after saturation. Consequently, the poplar leaf granules can be more

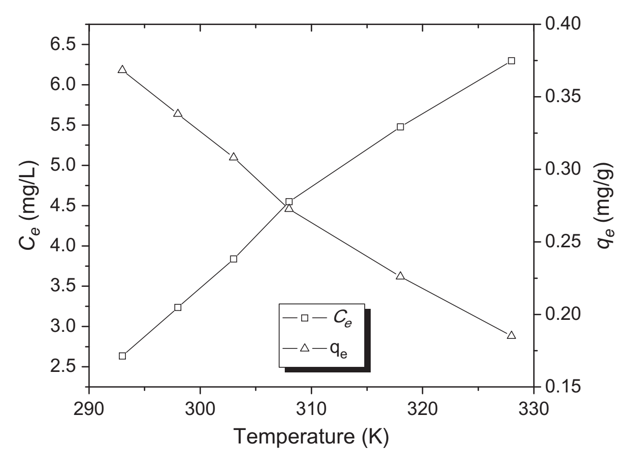

Fig. 7. Equilibrium concentration and adsorption capacity variation of poplar leaf powder under different temperatures.

conveniently used in nitrobenzene removal with satisfying adsorption capacity.

3.8. Overall evaluation and comparison with other adsorbents

The poplar leaf granules are efficient and convenient to be used in nitrobenzene removal from water. After saturation, the granules can be easily separated from the aqueous solution. There are many studies on nitrobenzene removal with powdered activated carbon, fly ash, and smectite clays [41]. However, disperse and powder materials are difficult to be separated from the water after saturation. Consequently, these materials are usually used with extra disposal processes such as coagulation and sedimentation [42]. In this study, when the poplar leaf powder was made into granules, the adsorption capacity was not affected greatly compared with powder. But the granules were more convenient to be separated and regenerated after saturation, and there is no need of other disposal steps. Moreover, the adsorption of nitrobenzene with the poplar leaf granules can be operated under normal temperature and neutral pH quickly. In some studies, the adsorption of nitrobenzene with activated carbon and other materials was optimized in acid condition and low temperature under 283 K [43]. During aromatic compounds adsorption, the main mechanisms by which surface oxygen groups influence the adsorption capacity include water adsorption, dispersive/repulsive interactions, hydrogen-bonding, and electrostatic interactions [44]. In the adsorption of nitrobenzene with the poplar leaf granules, pH had little influence on the adsorption, indicating electrostatic interactions were minor during adsorption. The minute adsorption capacity difference between the powder and granules indicated dispersive/repulsive interactions were also not the main adsorption mechanism for the adsorption of nitrobenzene onto the poplar materials. As shown in the results of EDS, the granules mainly contained C and O, which could constitute carboxylic and carbonyl groups and hydrogen-bond in water [44] between the poplar tissues and nitrobenzene. Consequently, the adsorption of nitrobenzene onto the poplar leaf granules was probably caused by the mechanism of water adsorption and hydrogen-bonding.

4. Conclusions

The poplar leaves were ground into powder and made into spherical granules. The granules maintained the microstructures of the natural poplar leaf tissue, which made these granules enriched with plenty of pores and drapes on the surface and inner space. The cell wall and other cellular structures supplied quantities of nanometer dimensions. The main ingredients in the granules were C and O, which made it more appropriate for organic pollutants adsorption with the mechanism of water adsorption and hydrogen-bonding. The adsorption of nitrobenzene onto the granules complied well with the pseudo-second-order model and Langmuir isotherm.

Acknowledgments

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