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Porous carbon prepared from lotus leaves as potential adsorbent for efficient removal of rhodamine B

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Abstract

Lotus leaf porous carbon (LLPC) prepared from waste lotus leaves has a large specific surface area (2440 m$^2$ g$^{-1}$), and is used for the adsorption of rhodamine B (RhB) from wastewater in this study. The effects of different parameters such as LLPC dose, initial pH of wastewater, adsorption time, initial RhB concentration, and temperature on adsorption have been systematically explored. Notably, 100% removal efficiency of RhB (60 ppm) is obtained at a low LLPC concentration of 0.125 g l$^{-1}$. The adsorption equilibrium with a maximum theoretical adsorption capacity of 718.9 mg g$^{-1}$ at 313 K is described by the Langmuir isotherm. The results for removal efficiency as a function of time are consistent with the pseudo second-order kinetic model and the adsorption process is dominated by chemisorption. Thermodynamic studies confirm that RhB absorption by LLPC is spontaneous at 313 K. The experiments conducted to determine the adsorption mechanism show that intraparticle diffusion is not the only rate-limiting step during adsorption, and the boundary effect becomes more dominant with an increase in adsorption time. The excellent RhB adsorption performance of LLPC and adsorption mechanism afford novel insights into this process for the application of biomass materials in wastewater treatment.

1. Introduction

Industrial effluents from industries such as paper, printing/dyeing, and chemical industries include high discharge, toxic substances, and high content of noxious organic pollutants. The effluents containing organic synthetic dyes can affect light penetration cause carcinogenic and mutagenic changes (Shannon et al 2008). Among the synthetic dyes, rhodamine B (RhB, figure 1) has been widely used in silk, cotton, fiber, soap, wood, and other industries owing to its low price. The wastewater containing RhB shows high toxicity and potential carcinogenicity. To remove organic pollutants from these effluents, numerous treatment techniques have been applied, including Fenton or Fenton-like advanced oxidation, ion exchange membranes, photocatalytic degradation, coagulation, biological treatment, and adsorption (Miguel et al. 2006, Won et al. 2006, Ahmad et al. 2010, Li et al. 2015a, Cai et al. 2016, Mousavi et al. 2018, Sang et al. 2020). Among these, adsorption is a promising treatment method for refractory pollutants because of its good biological compatibility, requirement of simple equipment, convenient operation, and high efficiency and economics (Crini 2006).

Although various materials such as clay and modified clay (Li et al. 2018), graphene-based nanocomposites (Zhu et al. 2014, Li et al. 2017), organosilica nanoparticles (Chen et al. 2017), orderly porous carbon (Peng et al. 2014, Chen et al. 2016), carbon nanotubes (Machado et al. 2016), metallogels (Karan and Bhattacharjee 2016), metal–organic frameworks (Li et al. 2015b, Zhao et al. 2015, Jia et al. 2016), and cellulose materials (Annadurai et al. 2002) have been used for the adsorption of organic pollutants and heavy metal ions, their adsorption capacities, adsorption rates, selectivities, or complex preparation processes restricted their wide application. Activated carbon is the most effective and widely used adsorbent because of its porous structure, high specific surface area, high adsorption capacity, and several functional groups, which allow the safe and fast removal of dyes without any preliminary treatment (Liu et al. 2019). Nevertheless, high cost limits its industrial application.
Therefore, preparation of activated carbon from agricultural waste can afford a good adsorption material with a relatively low cost, providing benefits associated with the recycling of agricultural waste, which has become an important area of research in recent years. For example, Distillers’ grain (Wang et al 2018), chitosan (Marrakchi et al 2017), mango peels (Jawad et al 2017), fruit hulls (Islam et al 2017), ephedra strobilacea saw dust (Agarwal et al 2016), coal tar residues (Gao et al 2016), tetracycline (Acosta et al 2016), coconut leaves (Jawad, et al 2016), nut shells (Ragupathy et al 2015), almond gum (Bouaziz et al 2015), peach gum (Zhou et al 2014), and pine fruit shell (Calvete et al 2010) have been used to prepare effective adsorbents to remove dyes from simulated wastewater. However, there is scope for performance improvement in terms of the adsorption capacity and adsorption rate of reported biomass adsorbent materials; economical, accessible, effective, and environmentally friendly adsorbents are still required.

Lotus, a perennial aquatic herb, is a common farm product and ornamental plant. As a byproduct, a large amount of lotus leaves is often discarded directly, which is a cheap, abundant, renewable, and eco-friendly resource. The leaves are rich in plant fibers, proteins, and include components with various functional groups. Therefore, these are ideal raw materials for bioadsorbents. Herein, a new, low-cost, lotus leaf porous carbon (LLPC) is prepared using lotus leaves as the raw material via KOH activation and is characterized using various techniques. The performance of LLPC is investigated by varying different parameters in the experiments (LLPC dose, adsorption time, optimal pH, initial pollutant concentration, and temperature), using RhB as the simulated adsorbate. The adsorption isotherms, kinetics, thermodynamic properties, and absorption mechanism for RhB adsorption on LLPC are also investigated.

2. Experimental

2.1. Materials
The lotus leaves were collected from Zaozhuang, China. H$_2$SO$_4$, KOH, and HCl were purchased from Sinopharm Chemical Reagent Beijing Co. Ltd (Beijing, China). RhB was synthesized in the Tianjin Guangfu Fine Chemical Research Institute. All chemicals were of analytical reagent grade.

2.2. Preparation
The lotus leaves were grinded into powder, rinsed repeatedly with water, and then immersed in H$_2$SO$_4$ solution to remove the impurities and soluble metals. The samples were then collected, dried, and transferred into a tubular furnace (GSL−1400X, Kejing, Hefei, China), and calcined for 2 h at 400 °C under N$_2$ atmosphere to obtain a brown and black powder, which was named as LLPC precursor.

Thereafter, the LLPC precursor (1.0 g) was mixed with KOH solution (90 ml, 1 M), stirred, dried, and further heated at 800 °C under N$_2$ atmosphere for 2 h, affording another black powder. LLPC was finally obtained after washing this black powder with an appropriate amount of HCl solution and water several times, and subsequent drying.

2.3. Characterization
The phases of the prepared materials were determined using a Bruker D8 advanced x-ray diffractometer (Bruker Corporation, Billerica, Massachusetts, USA) equipped with graphite-monochromatized Cu Kα radiation ($\lambda = 1.5418$ Å). The morphology of LLPC was characterized using field-emission scanning electron microscopy.
An automatic specific surface and porosity analyzer (ASAP 2020HD88, Micromeritics, Norcross, Georgia, USA) was employed to determine the specific surface area according to the N\textsubscript{2} adsorption isotherms at 77 K. Fourier transform infrared (FTIR) spectroscopy was performed using a Nicolet Nexus 470 FTIR spectrometer (Thermo Fisher Scientific, Waltham, Massachusetts, USA) with \textit{KBr} pellets.

2.4. Adsorption experiments

The adsorption experiments were conducted using the prepared LLPC and simulated wastewater solution containing RhB in a thermostatic shaker (HNY-100B, Honour, Tianjin, China) at 200 rpm and 313 K. In these experiments, different adsorbent dosages were added into 80 ml of simulated wastewater containing RhB with concentrations of 60–120 ppm. At fixed intervals, a specific amount of solution was extracted, filtered, and tested using the UV-2401 spectrophotometer (Shimadzu Corporation, Kyoto, Japan) at 553 nm. The removal efficiency of RhB adsorbed on LLPC was calculated using formula (1):

\[ \text{Removal efficiency} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100, \]

where \( C_0 \) ppm is the original concentration of RhB in simulated wastewater and \( C_t \) ppm is the remaining RhB concentration in simulated wastewater at fixed time intervals.

The adsorption capacity \([q (\text{mg g}^{-1})]\) was calculated using formula (2):

\[ q = \frac{(C_0 - C_t)V}{W}, \]

where \( V \) (L) is the volume of the simulated wastewater and \( W \) (g) is the mass of LLPC. When the adsorption reaches the equilibrium, \( C_t \) is named \( C_e \) and \( q \) as \( q_e \).

3. Results and discussion

3.1. Characterization of LLPC

First, the degree of carbonization of LLPC was determined by x-ray diffraction (XRD) and FTIR spectroscopy. As observed in figure 2(a), the XRD patterns of LLPC show a wide peak at \( 2\theta = 26^\circ \) and a weak diffraction peak at \( 2\theta = 44^\circ \), indicating the presence of amorphous carbon structure, which is consistent with the literature reports (Castro \textit{et al} 2009).

The FTIR spectra of LLPC, LLPC precursor, and the raw material shown in figure 2(b) are similar. The intensities of the broad bands at 3130–3200 cm\(^{-1}\) and 1690 cm\(^{-1}\) indicate the existence of a high concentration of oxygen-containing functional groups in the carbon material. An intense and sharp peak at 1394 cm\(^{-1}\) corresponds to the stretching vibration of carboxyl C–O. However, the strong and sharp absorption peaks at 1032 and 1092 cm\(^{-1}\) in the raw material are replaced by a weak absorption peak at 1050 cm\(^{-1}\), which can be attributed to the stretching vibration of C–O of the ester group in the precursor and LLPC. In addition, the peak at approximately 880 cm\(^{-1}\) also disappears when the raw material is converted into the precursor and LLPC. In the data of the raw material, the peaks at 1032 cm\(^{-1}\) and 1092 cm\(^{-1}\) are attributed to the stretching vibration of C–O in alcohols and carboxylic acids, while that at 880 cm\(^{-1}\) corresponds to the out-of-plane bending vibration of –OH. This implies that there are numerous –C = O and –OH groups on the surface of the lotus leaf raw material, and these groups can be the potential active sites that interact with the dyes. Moreover, these functional groups are dehydrated and condensed during the preparation of LLPC, affording enhanced performance of the porous carbon.

The porous structure was also examined using an automatic specific surface and porosity analyzer (figures 2(c)–(d)). The specific surface area (according to the N\textsubscript{2} adsorption isotherms at 77 K) of LLPC is 2440 m\(^2\) g\(^{-1}\), while those of the lotus leaf raw material and precursor are only 2.131 and 2.084 m\(^2\) g\(^{-1}\). The sizes of the pores of LLPC are all \(<4 \text{ nm}, \) most of which are in the range of 1.5–2.5 nm, with an average pore diameter of 1.84 nm. This not only shows that the prepared LLPC has a highly porous structure and large surface area, but also indicates that KOH is an effective activation agent in creating micropores and mesoporous pores on the lotus leaves. Considering that the molecular length and width of RhB (1.8 nm and 0.7 nm, respectively) match the pore size of porous carbon, it is reasonable to predict that the mesopores and micropores combined with the large specific surface area of LLPC are favorable for the adsorption of RhB. The SEM image of the prepared LLPC is shown in figure 3 and the expected crimp morphology is observed. In addition, many pores (several micrometers in diameter) are observed in LLPC, which is beneficial for fast RhB adsorption.
3.2. Equilibrium studies

The adsorption properties of LLPC were studied by removing RhB from the simulation wastewater. The effects of LLPC dosage, RhB concentration, reaction temperature, and initial solution acidity on the adsorption rate are systematically investigated.

The adsorption properties of raw lotus leaf powder, carbon precursor, and LLPC in 60 ppm RhB solution are shown in figure 4(a). The removal efficiency of RhB by LLPC is significantly higher than those of the other materials, and it shows a better adsorption performance. Compared to the raw lotus leaf powder and carbon precursor, LLPC has higher porosity and larger surface area, which results in more active sites for the adsorption of dyes. Therefore, with high amount of LLPC (125–375 mg l⁻¹), the removal efficiency increases, owing to the large surface area and more active sites on the LLPC surface. Based on the results shown in figure 4(a), the LLPC dosage of 125 mg l⁻¹ was selected for subsequent experiments.

The RhB removal efficiency of LLPC as a function of reaction time at RhB concentrations of 60–120 ppm is shown in figure 4(b). Owing to the numerous available active sites on the LLPC surface in the starting 30 min of adsorption, the removal rates of 79.97%, 77.175%, 74.316%, and 70.035% are observed as the concentration of RhB is increased from 60 ppm to 75, 90, and 120 ppm, respectively. As the adsorption interaction continues, there are fewer and fewer active sites on the adsorbent surface. So, the RhB molecules present progressively a difficult to adsorb to LLPC sites. Thereby, the adsorption efficiency rate decreases. The adsorption equilibrium could be achieved from 150 min. With an increase in the initial concentration (60 ppm to 75, 90, and 120 ppm), the high driving force that transfers the RhB molecules from the aqueous phase to the adsorption sites increases the equilibrium adsorption amount, qₑ, of LLPC from 441.9 to 537.3, 652.3, 707.3 mg g⁻¹, respectively.

As shown in figure 4(c), the removal efficiency of RhB by LLPC decreases as the original concentration of RhB increases, and long time is required to reach the equilibrium. This may be caused by the collision of RhB molecules at high concentration, which can reduce the adsorption rate of the adsorbent. Moreover, the RhB molecules tend to self-aggregate and form associations in solutions with high initial concentrations (Dare´-Doyen et al 2003), which can also explain this phenomenon.

Figure 4(c) shows the effect of reaction temperature on LLPC adsorption performance employing 120 ppm of RhB at 283, 293, 303, and 313 K. The RhB removal efficiency increases with an increase in temperature, indicating that the RhB adsorption on LLPC is an endothermic process.

The effects of the initial pH on RhB (120 ppm) adsorption on LLPC at 313 K are shown in figure 5(a). The lowest RhB absorption capacity of LLPC is observed at pH 2. The RhB removal efficiency increases rapidly when the initial solution pH is changed from 2 to 4, whereas almost no difference is observed when pH is varied in the range of 4 to 7.
range of 6–12. To further explain this result, the effect of the initial pH of simulated wastewater on the electrical property of LLPC was investigated. The pH_{zpc} value (the pH of LLPC when its net surface charge is zero) of LLPC is 6.5. Therefore, when the pH of wastewater solution is <6.5, the surface of LLPC is positive charged, and it is negatively charged when the pH is >6.5. RhB molecules exist in the form of monomer cations under acidic conditions, i.e., pH < 4.0, and as amphoteric ions at pH > 4.0 (Deshpande and Kumar (2002)). As a result, it is beneficial to remove RhB from aqueous solutions using LLPC (via adsorption) when the pH is >4.0 because of the electrostatic force, which is in accordance with the experimental results.

As there is a high concentration of inorganic ions in industrial wastewater, the effect of salt concentration on the RhB removal efficiency of LLPC was determined. Figure 5(c) shows that the RhB removal efficiency of LLPC...
decreases slightly when the concentration of NaCl solution is gradually increased. This may be owing to the competition between Na\(^+\) and RhB to be absorbed on LLPC through electrostatic interactions. However, the RhB removal efficiency with a high NaCl concentration (0.2 mol l\(^{-1}\), 2395 times of 60 ppm RhB) can be 85.2% of that with no NaCl, indicating the promising applications of LLPC in the treatment of industrial wastewater with high salt content.

Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherm models (Bansal et al. 2009) were investigated to determine the adsorption capacity of LLPC and understand the LLPC–RhB interactions. The results are shown in figure 6 and corresponding parameters are listed in table 1. The experimental data better match the Langmuir model, with higher correlation coefficient \(R^2\) value than those obtained with other models, indicating a homogeneous monolayer coverage of RhB molecules on the LLPC surface. The \(q_m\) (718.9 mg g\(^{-1}\)) obtained by Langmuir model is also consistent with the experimental value (707.3 mg g\(^{-1}\)).

In the Langmuir model, \(R_L\) (Bouaziz et al. 2015), which is the equilibrium adsorption parameter whose magnitude reflects the feasibility of the adsorption process is defined using formula (3):

\[
R_L = \frac{1}{1 + K_C C_0}
\]  

Figure 5. The effects of initial pH(a), Zero point charge(pH\text{ZPC}) of porous carbon (b) and the effect of ionic strength (NaCl) (c) on adsorption of RhB (\(C_0 = 60\) ppm, \(C_{LLPC} = 125\) mg l\(^{-1}\), \(T = 313\) K).

Figure 6. Adsorption isotherms of RhB onto LLPC at different temperatures. Langmuir (a); Freundlich (b); Dubinin–Radushkevich (c) and Tempkin (d).
between 0 and 1, indicating favorable adsorption of RhB onto LLPC. Furthermore, the higher the concentration of RhB, the lower is the value of $R_L$, indicating that a high concentration is conducive to adsorption. In the Freundlich model, $n$ is an empirical parameter to evaluate the adsorption favorability, which exceeds unity, indicating the extent of favorable adsorption. In the RhB–LLPC system, $n$ is 7.92, which further suggests a favorable adsorption between RhB and LLPC. In addition, a high $A$ value ($731.1 \text{ L g}^{-1}$) in the data obtained using the Temkin isotherm model also implies a high spontaneity of the adsorption process, showing that LLPC has good RhB adsorption capacity. To further clarify the adsorption process, the average free energy $E$ (kJ mol$^{-1}$) of adsorption per molecule when RhB in the solution is transferred from infinity to the LLPC solid surface was calculated using equation (4). The $E_D$ value (33.70 kJ mol$^{-1}$), which is significantly greater than 16 kJ mol$^{-1}$, shows that the adsorption is a chemical adsorption process (Demiral et al 2008).

$$E_D = \frac{1}{\sqrt{2K_D}}$$  

The RhB adsorption capacity of LLPC is compared with those of various reported adsorbents in table 2. Of all listed materials, LLPC shows the highest maximum adsorption capacity for RhB, owing to the large surface area and abundant pores on the surface. Therefore, the discarded lotus leaves, a renewable resource, can be employed to manufacture an efficient organic adsorbent with competitive adsorption performance and low cost.

### Table 1. Isotherms parameters for RhB adsorption on LLPC.

| Parameter | Value | $R^2$ |
|-----------|-------|-------|
| $q_m$ (mg g$^{-1}$) | 718.9 | 0.9986 |
| $K_L$ | 1.131 | |
| $K_F$ | 466.4 | 0.9216 |
| $n$ | 7.923 | |
| $A$ (Lg$^{-1}$) | 731.1 | |

$q_m$ (mg g$^{-1}$) is theoretical saturation adsorption capacity, $K$ is the equilibrium binding constant and $b$ (L mol$^{-1}$) is the constant related to the heat of adsorption.

### Table 2. Comparison of the adsorption capabilities on various adsorbents for RhB.

| Sample | Surface area m$^2$ g$^{-1}$ | Capacity mg g$^{-1}$ | References |
|--------|-----------------------------|----------------------|-------------|
| Wood biomass AC | 1161.29 | 76.66 | Danish et al (2018) |
| Modified carbon xerogels | 172 | 132.00 | Ptaszkowska-Koniarz et al (2018) |
| CX/MWCNTs | 192–643 | 154–256 | Shouman and Fathy (2018) |
| Amorphous metal-organic cage | 454 | | Gao et al (2019) |
| Walnut shells | 474.38 | 409.33 | Shah et al (2013) |
| PDDA/PPE resins | 848.4 | 578.2 | Jiang and Huang (2016) |
| Nanoporous polydihyminbenzene | 759.6 | 164.51 | Jia and Liu (2017) |
| Mesoporous silica nanoparticles | 584.98 | 23.26 | Qin et al (2017) |
| Bioconjugated graphene oxide hydrogel | 12.86 | 62 | Soleiman et al (2018) |
| Lignocellulosic waste | 430.695 | 33.315 | Lacerda et al (2015) |
| Hybrid ion-exchanger | 76.4 | | Saruchi and Vaneet (2019) |
| Beta | 410.20 | 27.97 | Cheng et al (2017) |
| GB-3 | 249.62 | 64.47 | |
| Gelatin/activated carbon | 34.73 | 256.41 | Hayeeye et al (2017) |
| Cu/MA | 98 | 38.22 | Ptaszkowska-Koniarz et al (2017) |
| Organoclay | 27.9 | 399.4 | Anirudhan and Ramachandran (2015) |
| NiO nanoparticles | 176.56 | 45.27 | Motahari et al (2015) |
| LLPC | 2440 | 701.4 | This work |

AC: activated carbons; PC: porous carbon.
Experimental data were fitted using pseudo first-order, pseudo second-order, and Elovich mass transfer models (Firdaous et al 2017, Danish et al 2018) to further understand the adsorption mechanisms. As shown in figure 7 and table 3, the correlation coefficients of the linear plots obtained by employing the pseudo second-order model are very high (> 0.99), and the calculated $q_e$ value is also in agreement with the experimental $q_e$ value, suggesting that the sorption system follows the pseudo second-order model. This also implies that the RhB absorption rate of LLPC depends on the effectiveness of its surface adsorption sites, and the adsorption occurs via the chemisorption mechanism. This conclusion is consistent with the adsorption isotherm analysis. Notably, as shown in table 3, the value of velocity constant $k_2$ depends on the original concentration of RhB. With an increase in the RhB concentration, $k_2$ decreases because of the high competitive adsorption of RhB molecules on the LLPC adsorption sites at high RhB concentrations. This indicates that RhB is more easily adsorbed on LLPC at low concentrations. Additionally, the high $R^2$ values (0.9272–0.9901) shown in table 3 reveal that the adsorption process follows the Elovich model, which further confirms that the rate limiting step of adsorption is a chemical process.

Thermodynamic parameters ($\Delta \bar{H}$, $\Delta \bar{S}$, and $\Delta \bar{G}$) for RhB adsorption on LLPC were evaluated at 283, 293, 303, and 313 K using van’t Hoff equation (5), Gibbs–Helmholtz formula (6), and equation (7). The parameters are listed in table 4.

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

$$\Delta \bar{G} = \Delta H - T\Delta \bar{S}$$

$$K = \frac{C_{ae}}{C_e}$$

(5)

(6)

(7)

Here, $K$ is the thermodynamic equilibrium constant, $C_e$ is the concentration of RhB in solution, and $C_{ae}$ is the concentration of RhB on LLPC at adsorption equilibrium (Islam et al 2017).

The value of $\Delta H = 40.49 \text{kJ mol}^{-1} > 0$ confirms that the RhB adsorption on LLPC is an endothermic process within the temperature range selected in this study, which is in line with the results reported in section 3.2. The positive value of $\Delta \bar{S}$ (0.1366 kJ mol$^{-1}$) during the adsorption process indicates that the confusion of the system increases, and LLPC has a strong affinity for RhB. The $\Delta \bar{G}$ values of 1.845, 0.4789, and 2.252 kJ mol$^{-1}$ at 283, 293, 303, and 313 K, respectively, confirm that the adsorption of RhB onto LLPC is spontaneous and becomes more favorable at high temperatures.

According to the prior literature reports, the adsorption of adsorbate (RhB) on adsorbent (LLPC) involves four consecutive steps (Danish et al 2018): (1) external diffusion: transport of RhB molecules from bulk solution to the LLPC exterior surface; (2) film diffusion: RhB molecules pass through the liquid film to reach the LLPC
Table 3. Kinetic parameters for RhB adsorption on LLPC at different initial dye concentrations and temperatures.

| T (K) | C₀ (ppm) | qₑ,exp (mg g⁻¹) | Pseudo-first-order model | Pseudo-second-order model | Elovich model |
|-------|----------|------------------|--------------------------|----------------------------|---------------|
|       |          |                  | ln(qₑ,exp - qₑ) = ln qₑ,k₁t          |  1/k₂ = qₑ/qₑ,2 + 1           | qₑ = 1/k₂ ln t + 1/β ln (αβ) |
|       |          |                  | qₑ,exp (mg g⁻¹) | k₁ | R² | P | qₑ,2 (mg g⁻¹) | k₂ (10⁻⁴) | R² | P | α (10⁵) | β (10⁻⁴) | R² | P |
| 313   | 60       | 441.9            | 291.3                  | 0.033 | 0.9753 | 1.42 × 10⁻⁷ | 456.6 | 3.368 | 0.9991 | 0 | 1.436 | 39.94 | 0.9825 | 8.55 × 10⁻¹³ |
| 75    | 537.3    | 331.6            | 331.6                  | 0.025 | 0.9621 | 2.27 × 10⁻⁹ | 555.6 | 2.402 | 0.9983 | 0 | 1.237 | 49.39 | 0.9766 | 7.52 × 10⁻¹⁴ |
| 90    | 652.3    | 416.3            | 416.3                  | 0.024 | 0.9846 | 1.84 × 10⁻¹² | 675.7 | 1.668 | 0.9984 | 0 | 0.9740 | 14.63 | 0.9919 | 0 |
| 120   | 701.4    | 580.8            | 580.8                  | 0.023 | 0.8244 | 7.20 × 10⁻⁷ | 740.7 | 0.8441 | 0.9935 | 0 | 0.9308 | 12.71 | 0.9901 | 1.11 × 10⁻¹⁰ |

qₑ is the adsorbed amount of RhB on the prepared materials at a specific time, qₑ is the value at equilibrium, and qₑ,exp and qₑ,cal are the experimental and calculated values. k₁ or k₂ is the rate constant of pseudo first-order (min⁻¹) or pseudo second-order (g mg⁻¹ min⁻¹) reaction, β (mg g⁻¹ min⁻¹) is the desorption constant, and α (mg g⁻¹ min⁻¹) is the adsorption constant.
particle surfaces; (3) pore diffusion: RhB molecules diffuse in the LLPC particle pores; (4) reaction: RhB molecules adsorb on the LLPC surface through molecular interactions. The rate controlling step can be any of these steps or a combination of these.

To further understand the adsorption mechanism of RhB on LLPC, the intraparticle diffusion model (Firdaous et al 2017, Islam et al 2017) was applied, and the detailed results are shown in figure 8 and table 5.

\[
q_t = k_{id} t^{1/2} + C_i
\]

In the above formula, \(k_{id} (\text{mg g}^{-1} \text{min}^{-1/2})\) and \(C_i (\text{mg g}^{-1})\) are the intraparticle diffusion rate constant and reflection of boundary layer thickness (film diffusion), respectively. If the plot of \(q_t\) as a function of \(t^{1/2}\) is linear, it indicates intraparticle diffusion. Only when the line passes through the origin, will the rate controlling step be intraparticle diffusion.

Table 4. Thermodynamic parameters for the adsorption of RhB on LLPC.

| T (K) | \(\Delta G^\Theta (\text{kJ mol}^{-1})\) | \(\Delta H^\Theta (\text{kJ mol}^{-1})\) | \(\Delta S^\Theta (\text{kJ mol}^{-1})\) |
|-------|----------------------------------|----------------------------------|----------------------------------|
| 283   | 1.845                            | 40.49                            | 0.1366                           |
| 293   | 0.4789                           |                                   |                                  |
| 303   | –0.8867                          |                                   |                                  |
| 313   | –2.252                           |                                   |                                  |

Table 5. Intraparticle diffusion model and Boyd’s model parameters for RhB adsorption on LLPC.

| \(C_0\) (ppm) | Period | Time (min) | \(q_t/ q_e\) (100%) | \(k_{id} (\text{mg g}^{-1} \text{min}^{-1/2})\) | \(C_i (\text{mg g}^{-1})\) | \(R^2\) |
|-------------|--------|------------|---------------------|----------------------------------|-------------------|-------|
| 60          | 1      | 0–5        | 51.32               | 95.02                            | 26.14             | 0.9906 |
|             | 2      | 5–30       | 79.97               | 43.50                            | 137.67            | 0.9902 |
|             | 3      | 30–120     | 100                 | 10.50                            | 356.80            | 0.9698 |
As shown in figure 8, the plot of $q_t$ as a function of $t^{1/2}$ shows three linear segments, implying that the adsorption process can be divided into three stages. The first stage completes rapidly within approximately 5 min at the start of the absorption, which may result from the intense electrostatic interactions between the LLPC external surface and RhB. The second step (5–30 min) corresponds to the diffusion of RhB molecules through the pores in LLPC. In the third stage after 30 min, the concentration of RhB gradually decreases and the amount of LLPC active sites also decreases, which results in a sharp decrease in the adsorption rate. Gradually, the absorption equilibrium is attained. However, all three linear segments do not pass through the origin, indicating that intraparticle diffusion is not the only rate limiting step during adsorption. Moreover, $k_{1,d}$ and $C_i$ show the trends, $k_{1,d} > k_{2,d} > k_{3,d}$ and $C_3 > C_2 > C_1$, during adsorption, indicating that the driving force becomes weak, whereas the boundary effect becomes dominant during adsorption.

4. Conclusion

In summary, LLPC, prepared from biomass lotus leaves, has numerous pores, large specific surface area (2440 m$^2$ g$^{-1}$), and is negative charged in a wide pH range including weakly acidic to alkaline ($pH > 6.5$). It is found to be an efficient and eco-friendly adsorbent for RhB removal, and has a high adsorption capacity (707.3 mg g$^{-1}$). The adsorption equilibrium and kinetic studies show that the system tends to follow the pseudo second-order and Elovich models, which confirm that adsorption is a chemisorption process. Thermodynamic investigations reveal that the RhB adsorption on LLPC is spontaneous at 313 K. Furthermore, mechanistic studies indicate that RhB adsorption on LLPC can be divided into three stages, and intraparticle diffusion is not the only rate limiting step. The excellent adsorption performance of LLPC indicates that it can be used as a promising adsorbent for removing RhB from the effluents.

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