Removal of o-Nitrophenol via Adsorption by Porous Carbon Derived from Magnesium Oxide and Waste Polyethylene Terephthalate Prepared by Template Method

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Abstract: In the present paper, the porous carbon material derived from waste PET was fabricated using a one-step recyclable MgO template synthesis approach. The material was subsequently employed as adsorbent for the efficient capture of o-nitrophenol (ONP) from aqueous solutions. With the change of the ratio of MgO template to waste PET, the prepared porous carbon has controllable specific surface area. The sample of WPC-1.5 exhibits a remarkable specific surface area of 885.99 m²/g. Static adsorption experiments demonstrate that this material possesses a substantial adsorption capacity for ONP, achieving a value of 474 mg/g. The WPC-1.5 was characterized by scanning electron microscopy, BET and adsorption kinetic and equilibrium isotherms evaluation.

1. Introduction

In recent years, the rapid advancements in the chemical and pharmaceutical industries have led to the development and production of numerous chemical products. However, their large-scale usage has resulted in excessive utilization and environmental threats due to emissions. Nitrophenol chemicals, crucial intermediates in fine chemicals, play a significant role. Among them, o-nitrophenol (ONP) stands out as a typical example, widely applied in the dye, pesticide and pharmaceutical industries. ONP is listed as a major pollutant by the United States Environmental Protection Agency (USEPA)[1], which is characterized by high toxicity, poor biodegradability, and challenging degradation characteristics.

Polyethylene terephthalate (PET), a commonly utilized material in the food industry, is frequently discarded in household waste, resulting in significant environmental implications. The prevailing disposal techniques, including landfills and incineration, generate secondary pollution and squander resources. Given their high carbon content and negligible inorganic composition, waste PET present themselves as promising precursors for the synthesis of porous carbon materials. Therefore, devising a practicable process for converting waste plastics into porous carbon materials not only enhances the utilization of these plastics but also contributes to wastewater treatment, thereby aligning with the objective of "treating waste as a resource".

In summary, this study endeavors to fabricate porous carbon materials (WPC) derived from waste PET, possessing a high specific surface area and abundant pore structure, employing a one-step recyclable template synthesis technique. The template method focuses on the influence of the amount of template agent on carbon materials. The study also investigates the impact of the adsorption capacity of these materials on the removal of ONP from water. The impact of the preparation method on the structural properties of porous carbon materials was examined using SEM and N₂ adsorption desorption tests. The practical utility was confirmed through static adsorption evaluation. Additionally, we conducted an analysis of adsorption isotherms and kinetics to gain insight into the removal of ONP from industrial wastewater.

2. Experiment

2.1. Material and chemicals

The waste PET was provided by Mingsheng Plastic Industries, Shenzhen, China. Magnesium acetate and acetic acid were purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd. ONP was purchased from Shanghai Aladdin Chemical Co., Ltd., China. Commercial activated carbon (AC) was purchased from Xinsen Cabon Industry., Fujian, China.

2.2. Preparation of porous carbon material

5 g of waste PET and 26.75 g of solid magnesium acetate precursor were fully mixed and crushed. The obtained powder was loaded into the corundum ship, and continuously fed with 25mL/min of high-purity N₂ in a tubular atmosphere furnace. It was directly pyrolyzed at a heating rate of 3 K/min until it reached the activation
temperature of 973 K, and maintained at that temperature for 2 hours. It is to be noted that a higher temperature is required to maximize the pore formation in case of magnesium acetate and temperatures of about 973 K are usually employed. The carbon material was washed with a 30wt% acetic acid aqueous solution, followed by rinsing with deionized water until the filtrate reached neutrality. The resulting carbon material was dried in an oven at 383 K for 12 hours and designated as WPC-1.0, where the number signifies the mass ratio of solid magnesium acetate to waste PET. The template method focuses on the influence of the amount of template agent on carbon materials. The template method focuses on the influence of the amount of template agent on carbon materials. According to the similar processes, different waste PET/solid magnesium acetate were studied: 0.5, 1.5, 2.0. These carbon materials were named WPC-0.5, WPC-1.5, WPC-2.0, respectively. The filtrate obtained after acetic acid washing was subjected to simple evaporation and crystallization to recover magnesium acetate.

2.3. Porous carbon material characterization

The samples' morphological features and structural characteristics were examined through the utilization of field emission scanning electron microscopy. Furthermore, the nitrogen adsorption-desorption isotherms of these samples were accurately determined using an automated physical adsorption analyzer. Before sample testing, all samples were subjected to a vacuum degassing pretreatment at 523 K for 2 hours. The pore structure data of the sample were calculated by NLDFT method.

2.4. Static adsorption capacity test

A standard o-nitrophenol (ONP) solution at a concentration of 500 mg/L was prepared. In a 250 mL conical flask, 0.1 g of porous carbon material was immersed in 100 mL of the prepared ONP solution. The flask was placed in a digital display thermostatic vibrator operating at 298 K and vibrating at 180 rpm for 12 hours, ensuring the adsorption of ONP onto the porous carbons reached equilibrium. Subsequently, the samples were filtered through a 0.45-μm RC membrane and analyzed. The residual ONP concentration was measured at 279 nm using a UV-visible spectrophotometer (UV-3100 PC, Mapada-sh Co., Ltd).

2.5. Adsorption equilibrium isotherms

An o-nitrophenol (ONP) solution with a concentration ranging from 50 to 500 mg/L was prepared. In a 250 mL conical flask, 0.1 g of porous carbon material was placed in a digital display thermostatic vibrator set at 298 K and vibrated at 180 rpm for 12 hours. After filtration through a 0.45-μm RC membrane, the samples were analyzed. The residual ONP concentration was measured at 279 nm using a UV-visible spectrophotometer. The experimental data for adsorption equilibrium were fitted employing two classical adsorption models, namely Langmuir and Freundlich. These models were employed to analyze the equilibrium relationship between the contaminant and adsorbents, expressing the interaction between the contaminant and adsorbents, expressing the interaction between o-nitrophenol and WPC adsorbent. These analyses were conducted at a constant temperature in an aqueous solution.

Langmuir model:

\[ q_e = \frac{q_m b c_e}{(1 + K_c c_e)} \]  

Where \( c_e \) is the equilibrium concentration of the ONP expressed in (mg/L), \( q_m \) is the maximum adsorption capacity (mg/g), and \( K_c \) is the rate constant of adsorption.

Freundlich model:

\[ q_e = K_f c_e^{1/n} \]  

Where \( K_f \) is expressed as (mg/g) × (l/mg) × 1/n, along with \( N \) represent the Freundlich adsorption constants, which are associated with adsorption capacity and adsorption intensity, respectively.

2.6. Adsorption kinetics

A solution of o-nitrophenol (ONP) was prepared with a concentration of 500 mg/L. In each conical flask (250mL), 0.05 g of porous carbon material was added to 50 mL of the standard ONP solution. The flasks were then placed in a digital display thermostatic vibrator set at 298 K and vibrated at 180 rpm for varying durations. After filtration through a 0.45-μm RC membrane, the samples were analyzed. The residual ONP concentrations at different time intervals were measured at 279 nm using a UV-visible spectrophotometer.

Pseudo-first-order model:

\[ q_t = q_e (1 - e^{-k_1 t}) \]  

Pseudo-second-order model:

\[ q_t = \frac{K_f q_e^2 t}{(1 + K_f q_e t)} \]  

Where \( q_e \) is the adsorption at time \( t \), and \( q_e \) is the pseudo-first-order and pseudo-second-order adsorption capacity at equilibrium. \( k_1 \) is pseudo-first-order rate constant.

3. Results and discussion

3.1. Material characterization

The morphology of carbon materials was observed using SEM for characterization. As depicted in Fig. 1, the addition of a limited quantity of template WPC-0.5 induces the formation of a few pores or cracks on the surface. However, with an increase in the MgO template mass ratio, the pore structure of carbon materials becomes more developed. The decomposition of magnesium acetate leads to the formation of magnesium oxide, carbon dioxide, water, and acetone, explaining the observed phenomenon. After removing magnesium oxide using an
acid solution, the porous architecture of the carbon material is particularly advantageous for a wide range of adsorption applications, due to its excellent adsorption properties.

To assess the physical structural characteristics of porous carbon, an analysis involving nitrogen (N\textsubscript{2}) adsorption-desorption was conducted. The resulting isotherms belong to type IV of the IUPAC classification. When the MgO template mass ratio increases from 0.5 to 1.5, the amount of adsorbed N\textsubscript{2} on the surface of WPC gradually increases. However, at a mass ratio of 2.0, the N\textsubscript{2} adsorption capacity starts to decline. All samples exhibit rapid N\textsubscript{2} adsorption within the low relative pressure range (P/P\textsubscript{0} < 0.1), suggestive of the presence of micropores on the carbon sample surfaces [3]. Furthermore, within the medium relative pressure range (P/P\textsubscript{0} = 0.4-0.9), all samples exhibit distinct adsorption-desorption hysteresis loops in their isotherms, resembling H4 hysteresis loops, indicative of the coexistence of mesopores and micropores [4].

### Table 1 Adsorption Textural characteristics of WPCs.

<table>
<thead>
<tr>
<th>Samples</th>
<th>S\textsubscript{BET} (cm\textsuperscript{3}/g)</th>
<th>V\textsubscript{Total} (cm\textsuperscript{3}/g)</th>
<th>V\textsubscript{Micro} (cm\textsuperscript{3}/g)</th>
<th>V\textsubscript{Meso} (cm\textsuperscript{3}/g)</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WPC</td>
<td>372.08</td>
<td>0.22</td>
<td>0.17</td>
<td>0.05</td>
<td>1.19</td>
</tr>
<tr>
<td>WPC-0.5</td>
<td>555.36</td>
<td>3.75</td>
<td>0.24</td>
<td>3.51</td>
<td>13.53</td>
</tr>
<tr>
<td>WPC-1.0</td>
<td>647.42</td>
<td>3.15</td>
<td>0.28</td>
<td>2.87</td>
<td>9.74</td>
</tr>
<tr>
<td>WPC-1.5</td>
<td>885.99</td>
<td>2.94</td>
<td>0.38</td>
<td>2.56</td>
<td>8.40</td>
</tr>
<tr>
<td>WPC-2.0</td>
<td>693.02</td>
<td>3.09</td>
<td>0.30</td>
<td>2.79</td>
<td>8.93</td>
</tr>
</tbody>
</table>

The physical structure of the WPC-1.5 sample, characterized by its ample micropores, facilitates the swift and unhindered access of ONP molecules in aqueous solution to its adsorption sites, thereby enhancing their adsorption. Additionally, the sample's high specific surface area and appropriate pore volume offer ample room for the effective adsorption of ONP molecules.

### 3.2. The evaluation of adsorption

Evaluate the adsorption performance of various materials by measuring their adsorption capacities under identical conditions. As depicted in Fig 3, the adsorption capacities of four porous carbon samples (WPC-0.5, WPC-1.0,
The adsorption capacity of ONP on porous carbon exhibited a positive correlation with the augmentation of specific surface area, as evident from the characterization results pertaining to surface area and pore structure. Surprisingly, although commercial activated carbon possessed a higher specific surface area than WPC-1.5, activated carbon ONP adsorption capacity was only 345 mg/g. This difference can be attributed to the dominance of micropores in commercial activated carbon, leading to limited adsorption and diffusion capabilities. Consequently, the inner surface of some micropores failed to effectively participate in ONP adsorption. Subsequent adsorption evaluation experiments were conducted exclusively with WPC-1.5 to explore its ONP adsorption behavior and mechanisms.

3.3. Adsorption equilibrium isotherms

In order to explore the adsorption mechanism of ONP on the surface of WPC-1.5, the adsorption equilibrium test of ONP was carried out, and the adsorption equilibrium isotherm data of WPC-1.5 on ONP were shown in Fig 4.

The adsorption process and mechanism under equilibrium conditions were studied by fitting and analyzing the Langmuir and Freundlich models for adsorption isotherms. Fig 4 and Table 2 present the result, demonstrating that the Langmuir isotherm model was more suitable for the ONP adsorption system than the Freundlich isotherm model. The $R^2$ value for the Langmuir model (0.98) exceeded that of the Freundlich model (0.85). Consequently, the ONP adsorption by WPC-1.5 aligned more closely with the Langmuir isotherm model, confirming a monolayer adsorption process. This observation is attributed to WPC-1.5 multistage pore structure and substantial mesoporous composition. Additionally, the Freundlich model $1/n$ values were below 0.5, indicating ONP effective adsorption on porous carbons.

3.4. Adsorption kinetics

The study of adsorption kinetics serves as a crucial indicator in assessing the feasibility of industrial adsorption experiments. To elucidate the adsorption rate of porous carbon towards o-nitrophenol (ONP), an investigation was conducted into the dynamic adsorption behavior of ONP on the surface of WPC-1.5. The findings of this exploration are depicted in Fig 5. Furthermore, the kinetics of o-nitrophenol adsorption were investigated utilizing both pseudo-first-order and pseudo-second-order kinetic models. The pertinent kinetic parameters are presented in Table 3.
4. Conclusions

In this study, a porous carbon material derived from waste PET was synthesized using a one-step template method. The resulting material, denoted as WPC-1.5, exhibited an enriched porous structure and a high specific surface area of 885.99 m$^2$/g. The adsorption behavior of ONP on WPC-1.5 resembled single molecular layer adsorption, demonstrating rapid static adsorption with a capacity of 474 mg/g.

Moreover, the utilization of the "treating waste as a resource" strategy presents a promising avenue for the resource utilization of waste PET and the treatment of nitrophenol contaminated wastewater.

References


