Strategies for recovering inhibition caused by phenolic compounds in a short-cut nitrogen removal reactor treating coal gasification wastewater

Qian Zhao, Hongjun Han, Fang Fang, Haifeng Zhuang, Dexin Wang and Kun Li

ABSTRACT

Different strategies, including extension of hydraulic retention time (HRT), dilution, and addition of powdered activated carbon (PAC) and super-powdered activated carbon (S-PAC), were investigated for the quick recovery of nitrifying bacteria activity from the inhibition of coal gasification wastewater (CGW). A laboratory-scale short-cut biological nitrogen removal (SBNR) reactor treating CGW, achieving high levels (90%) of nitrogen removal, was used. After a shock of phenolic compounds (around 250 mg/L) and a failed performance, the results of the batch recovery tests indicated that the PAC and S-PAC addition were the best recovery strategies. In the SBNR reactor, the addition of 1 g/L PAC and S-PAC shortened the recovery time from the natural recovery of 32 days to 13 days and 10 days, respectively. Fluorescence in situ hybridization (FISH) assay and the adsorption isotherms revealed that activated carbons absorbed phenolic compounds, reducing the toxicity and allowing for the quick recovery of SBNRs treating CGW. S-PAC showed greater adsorption capacity for phenol than PAC.

Key words | coal gasification wastewater, phenol, powdered activated carbon, recovering inhibition, short-cut nitrogen removal, super-powdered activated carbon

INTRODUCTION

In China, the recycling and disposal of coal gasification wastewater (CGW) has become a bottleneck for the development of the coal gasification industry. It contains high concentrations of phenolic compounds, ammonia, cyanide, and other toxic pollutants (Zhu et al. 2009). For a typical case, the content of phenolic compounds and ammonium in the raw wastewater was as high as 5,000 mg/L and 2,500 mg/L, respectively, at a coal gasification plant located in the north of China (Yang et al. 2006). In this context, new technologies, such as the short-cut biological nitrogen removal (SBNR) process, provide a cost-effective way to treat highly contaminated effluent (Hwang et al. 2006; Yang et al. 2007; Cui et al. 2011). It reduces the organic matter (40%) and oxygen (25%) required for ammonia removal in comparison to more conventional technologies (Park et al. 2010a). It is an excellent alternative to be applied after pretreatment and anaerobic processes. However, poor stability in the preceding processes would cause a sudden increase in concentration of toxic and refractory compounds as well as their derivatives in the effluent. These typical nitrification inhibitors, such as polynuclear aromatic hydrocarbons and nitrogen heterocyclic compounds, especially phenolic compounds, probably result in insufficient nitrification (Amor et al. 2005; Li et al. 2011). This unsatisfactory feed into the nitrogen removal process results in a completely failed performance. Thus, it is very important to find an appropriate way for the quick recovery of the failed SBNR reactor treating CGW.

Toxicological or inhibitory influence of the compounds in CGW on lithoautotrophic nitrifying micro-organisms (Dyreborg & Arvin 1995; Ben-Youssef et al. 2009) can adversely affect the efficiency of biological treatment systems to
different levels, ranging from mild suboptimal reactor performances (‘inhibited steady-state’) to severe inhibition affecting the nitrogen discharges. In the worst case, the inhibition might last for several months with continuous failure of recovery and serious economic losses to the gasification plants. Numerous studies have focused on the prevention of various process imbalances, particularly via development of different process control strategies and via automation and enhancement of process monitoring. For an SBNR system, process control is essential to ensure successful reactor operation under different influent conditions. The main control option would consider the influent total inorganic carbon (TIC) control, base/bicarbonate dosing and adjustment of dissolved oxygen (DO), sludge retention time (SRT) and temperature in the reactor (Ge et al. 2012; Zanetti et al. 2012; Gonzalez-Martinez et al. 2013). Park et al. (2013) exploited the concept of the minimum/maximum substrate concentrations for identifying proper start-up conditions and achieving stable and low effluent total ammonium nitrogen (TAN) concentrations in suspended-growth short-cut biological nitrogen removal. Calculations indicated that maximum TAN concentration, above which ammonium-oxidizing bacteria (AOB) are washed out, was around 450 mgTAN/L at the given operating conditions of 2 mg/L of DO and pH 8, while nitrite-oxidizing bacteria (NOB) should be washed out at around 40 mgTAN/L. Park et al. (2013b) noted that a pH near 8 is optimal for SBNR, since alkaline systems could sustain lower total ammonium than the acidic systems. Chung et al. (2007) successfully operated an SBNR system after 5–10 months of the start-up period to establish good SBNR with high TAN concentration. Kosari et al. (2014) believes that the operation of SBR under higher DO in combination with slow feeding resulted in significantly reduced hydraulic retention time (HRT) without nitrate accumulation. Although there have been many reports about optimization of the operating strategy for selecting AOB, suppressing NOB, and rapidly obtaining quick start-up optimal performance, few researches have been carried out to discuss recovery strategies for the SBNR process following CGW or phenol inhibition, and studies have seldom been reported on the effect of super-powdered activated carbon (S-PAC) on nitrogen removal processes treating CGW.

In our previous study, the SBNR reactor was operated with an anaerobic process and powdered activated carbon technology (PACT) in advance (Zhao et al. 2013, 2014). The SBNR showed a low nitrogen conversion rate with or without poor performance of PACT in advance. The reactor needed a period of 30 days or longer to resume the sludge activity. The aim of this work was to evaluate the recovery strategies including the extension of HRT, dilution, SRT, and the addition of powdered activated carbon (PAC) and S-PAC, on the quick recovery of an SBNR reactor impacted by phenolic compounds using batch tests. The most appropriate recovery methods for PAC and S-PAC addition were investigated in an SBNR reactor shocked by 250 mg/L of phenolic compounds.

MATERIAL AND METHODS

Experimental setup

The SBNR reactor prepared for the reactor experiment was constructed of cubic plexiglass. The reactor dimensions were: 50 cm long, 15 cm wide and 15 cm high, with a total working volume of 5.7 L. A spacing baffle was placed in the SBNR, which was separated into two parts: an aerobic compartment and an anoxic compartment, with a volume ratio of 2:1. The horizontal flow sedimentation tank II after PACT had a total working volume of 0.5 L. The SBNR was maintained at 32 ± 1°C by an electrothermal thread warming system.

Characteristics of sludge and wastewater

Seed sludge SBNR was originally obtained from the contact oxidation tank treating Lurgi CGW at the China Coal Longhua Harbin Coal Chemical Industry Co., Ltd and the reactor was operated for more than 8 months before the batch test. The sludge was gray-black with a good settlement property. The volatile suspended solids/suspended solids (VSS/SS) ratio of the seed sludge was about 0.7.

The raw wastewater employed in the current study was synthesized according to the effluent composition of the contact oxidation reactor in the same site. The concentration of chemical oxygen demand (COD), NH_{3}-N, total phenols (TP), and volatile phenols in the real wastewater were 1,050 mg/L, 153 mg/L, 50 mg/L and 5 mg/L, respectively.
The SBNR reactor was fed with the synthetic wastewater, which consisted of crude phenol obtained from the same company, phenol, NH₄Cl of analysis grade, and the following macro-nutrients: 50 mg/L MgSO₄·7H₂O, 20 mg/L K₂HPO₄, 20 mg/L CaCl₂·2H₂O, 15 mg/L FeSO₄·7H₂O, 10 mg/L KH₂PO₄, 15 mM/L NaHCO₃. The main characteristics of the influent are shown in Table 1.

The sludge used for the batch test was obtained from an SBNR reactor, which had been kept operating continuously for 21 months. The steady-state operating conditions and performance of the continuous reactor have been described previously (Zhao et al. 2013).

**Batch tests**

The recovery strategies, including the extension of HRT, dilution, PAC addition and S-PAC addition aeration, were investigated using five quadrate aeration containers (1.0 L working volume). The mixed liquor suspended solids (MLSS) was controlled at approximately 3,000 mg/L. Feeding was applied once a day in the batch experiments. All the bottles were fed with CGW with a normal phenolic concentration of around 0.05 g/L, NH₃-N of 0.15 g/L and an HRT of 48 h. This was carried out to achieve a stable performance before the shock load, with the TP of around 0.25 g/L. The control reactor (R0) was not inhibited and was fed daily with normal loading during the entire experimental period. No feeding was applied to the other four containers after phenolic loading for HRT. The recovery strategies were applied to the other four containers after the impact of the phenolic compounds. The detailed recovery strategies are described as follows: (1) extension of HRT (R1): reduction of 75% in the feeding daily, corresponding to an HRT of 8 days; (2) dilution (R2): replacement of 80% of the feeding daily with tap water corresponding to the TP and NH₃-N concentrations of around 10 and 50 mg/L; (3) addition of 1 g/L PAC (R3): addition of 1 g/L PAC; (4) addition of S-PAC (R4): addition of 1 g/L S-PAC. For all the experiments, the recovery strategies tested were applied at 2 HRT periods (4 days except Ra) after the impact of phenolic compounds, and then the bottles were operated at the normal load.

To study the inhibition effects of toxicants on the bacterial activity, the substrate utilization rate (SUR) of ammonia before and after the inhibition was used, using the sludge and biomass from the SBNR reactor. An SUR test was carried out in the sealed vials with a working volume of 100 mL. SUR values were expressed as mg ammonia/(gVSS·d). The vials were prepared with 0.4 g VSS/L. All batch tests were performed in triplicate and were incubated at room temperature and 120 rpm.

**Reactor experiment**

The SBNR was operated in the mode of a continuously stirred tank reactor (CSTR), and achieved steady performance with TP and NH₃-N concentrations of around 50 and 150 mg/L at an HRT of 24 h and SRT of 15 days. Inhibition was induced at day 16 of the experimental period by increasing the TP concentration to 250 mg/L and then the corresponding concentrations were reduced to the initial concentration of around 50 mg/L on day 18. The reactor was allowed to recover fully from the impact effect of the phenolic compounds, and the recovery time was defined as the time between the initiation of recovery action and the time when the ammonia removal efficiency exceeded the mean value of the reactor during days 1–15. Then, the reactor was continuously operated at a pseudo-steady-state for 10 days. On day 58, the phenolic loading rate of around 250 mg/L was shocked in the SBNR reactor for 2 days, and the normal phenolic loading was resumed on day 62. The PAC at 1 g/L was added for 2 days on day 62 and 63 and then the reactor performance was gradually recovered without the addition of PAC. After the reactor performance achieved a pseudo-steady-state that was maintained for 10 days, the reactor was subsequently exposed to a second inhibition with the same TP pulse. S-PAC at the same amount as PAC was added and then the reactor performance was gradually recovered without S-PAC.

### Table 1 | Main characteristics of the SBNR influent

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Normal value</th>
<th>Value of impulse</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg/L)</td>
<td>147.4–160.8</td>
<td>1,010.9</td>
</tr>
<tr>
<td>NH₃-N (mg/L)</td>
<td>128.4–159.3</td>
<td>–</td>
</tr>
<tr>
<td>TP (mg/L)</td>
<td>4.8–5.3</td>
<td>269.3</td>
</tr>
<tr>
<td>Volatile phenols (mg/L)</td>
<td>1.2–3.3</td>
<td>88.0</td>
</tr>
<tr>
<td>Bicarbonate alkalinity (mmol/L)</td>
<td>10–15</td>
<td>–</td>
</tr>
<tr>
<td>pH</td>
<td>7.2–7.3</td>
<td>–</td>
</tr>
</tbody>
</table>

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Microbial analyses

Sludge samples were fixed and analyzed using fluorescence in situ hybridization (FISH) to determine the bacterial composition, especially AOB and NOB composition. It can be revealed that the proportion of AOB and NOB accounted for the total eubacterial population. Oligonucleotide probes used in this study were NSO190 with fluorescence tag FITC (for ammonia oxidizing β-Proteobacteria) and Ntspa662 (for Nitrospira) with fluorescence tag TRITC (Zhao et al. 2013). In the hybridization buffer, formamide concentrations for NSO190 and Ntspa662 were 55% and 35%, respectively. FISH images were collected using an OLYMPUSBX52 fluorescence microscope. FISH quantification was performed according to Crocetti et al. (2002), where the relative abundance of each group was determined as a mean percentage of all bacteria.

The negative effect of toxic compounds on the activity of nitrifying bacteria was investigated by raising the pollutant concentration in the influent. The SUR of the ammonia was tested using the seed sludge obtained from the UASB reactors. Specific methanogenic activity (SMA) was determined in batch assays with acetate as the substrate. SUR and SMA tests were carried out in 140 mL sealed vials with a working volume of 100 mL. The substrates of phenol and sodium acetate were controlled at a concentration of 500 mg/L and 2,500 mg/L, respectively.

SUR and SMA values were expressed as mg phenol/(gVSS d) and mg COD-CH$_4$/(gVSS d), respectively. The vials were prepared with 3–5 g VSS/L. All batch tests were performed in triplicate and were incubated at 37 °C and 120 rpm.

Activated carbons

Commercially available wood-based PAC (Guanbaolin Chemical Industries Co., Qingdao, China) was prepared as a slurry in ultrapure water and pulverized to super-fine particles with a wet bead mill (Espread Industries Co., Shanghai, China). In this paper, we refer to this pulverized activated carbon as S-PAC and the as-received PAC as PAC. The median diameter of the as-received PAC was 6 mm, and about 70% by volume of the PAC particles were larger than 5 mm. Micro-grinding yielded a median diameter of 0.9 mm; the effective diameter was 0.3 mm, and 65% by volume of the S-PAC particles were smaller than 1 mm. The characteristics of PAC and S-PAC are shown in Table 2. The S-PAC and PAC were stored as slurries in ultrapure water at 4 °C and used after dilution and placement under vacuum, and no decant or other cleanups were conducted for the S-PAC and the PAC before use.

Adsorption studies for PAC and S-PAC

The adsorption study was performed in 500 mL flasks with stoppers to prevent volatilization, and the content was agitated at 160 rpm and 25 °C in a thermostatic shaker (THA-82, Guoli Co. Ltd, Jiangsu). The time required for reaching an equilibrium phenol concentration was the equilibrium time for adsorption. The equilibrium time was determined for estimating the shaking time required for adsorption isotherm tests. For this purpose, phenol values in 500 mL stoppered flasks with different activated carbon concentrations were analyzed with respect to time until reaching equilibrium concentrations.

For determination of the adsorption isotherms, different weights of PAC or S-PAC (100 mg/L–10 g/L) were mixed with different concentrations of phenol (20–200 mg/L). These 200 mL mixtures were agitated until reaching equilibrium, i.e. the point when the concentrations of the bulk solution reached a constant value. Initial and final equilibrium concentrations in the adsorption flasks were measured and used for the construction of adsorption isotherms. The data were the average results of triplicate experiments.

<table>
<thead>
<tr>
<th>Items</th>
<th>Characteristics of PAC and S-PAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation method</td>
<td>Thermal</td>
</tr>
<tr>
<td>Surface area (m$^2$/g)</td>
<td>1,257.99</td>
</tr>
<tr>
<td>Methylene blue adsorption (g/100 g)</td>
<td>25.00</td>
</tr>
<tr>
<td>Total pore volume (cm$^3$/g)</td>
<td>0.19</td>
</tr>
<tr>
<td>Micro (Φ &lt; 2 nm)</td>
<td>0.12</td>
</tr>
<tr>
<td>Meso (Φ 1.7–30 nm)</td>
<td>0.07</td>
</tr>
<tr>
<td>Macro (Φ &gt; 30 nm)</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Analytical methods

COD, SS, VSS, MLSS, TP, ammonia NH$_3$-N and NO$_2$-N were measured according to *Standard Methods* (APHA 1998). The COD, TP, NH$_3$-N, NO$_2$-N, TN in the SBNR were analyzed once daily. The NO$_3$-N was analyzed once every 2 days. DO and pH values were determined daily with a pH meter (pHS-5C, Leici, China) and a DO meter (HACH 30d). The AOB activity was evaluated with the NH$_3$-N to NO$_2$-N conversion rate in this study, considering the AOB growth as a result of these additions is believed to be insignificant relative to the size of their populations.

In the adsorption studies, phenol concentrations were quantified by high performance liquid chromatography (HPLC) (Agilent 1100) after sample filtering with 0.45 μm millipore filters. HPLC analyses were performed on a reverse phase C-18 column with methanol:water (60:40) mobile phase at a constant flow rate of 0.5 mL/min, and detected using UV at 285 nm, at room temperature.

RESULTS AND DISCUSSION

Recovery from phenol inhibition in the batch tests

The ammonia conversion rate decreased from 90% to approximately 40% after the shock of phenolic compounds. According to previous reports (Dyreborg & Arvin 1995), the pseudo-critical phenol concentrations introducing nitrification inhibition for the pure culture and batch activated sludge system were 3.7 mg/L and 200 mg/L, respectively. In this study, after a TP (250 mg/L) impulse, the system could be self-recovered with normal feed in a period of more than 35 days (data not shown). The SUR decreased from 105.7 to 41.6 mgNH$_3$-N/(gVSS·d), indicating the strong toxicity and inhibition on AOB. With different recovery strategies, the profile of the nitrogen conversion and removal rate in the batch tests is shown in Figure 1. It was clear that the strategy of extending the HRT (R1) was the strategy that resulted in the slowest recovery time, in which serious inhibition was observed even 30 days after the impact of phenolic compounds, compared to 18 or 12 days for dilution and addition of activated carbons, respectively (Figure 1). Although the concentration of both phenol and ammonia in the feed was reduced immediately after the dilution action, the ammonia conversion rate did not recover the control value for up to 16–18 days. This was consistent with Tomlinson et al. (1966) and Keener & Arp (1994), who observed 75–90% inhibition when the phenol concentration was 4.7–5.6 mg/L. In contrast, the addition of activated carbons was fastest in resuming the ammonia-to-nitrification conversion rate to around 90% in 12 days. With S-PAC, the process recovered more rapidly in the initial 4 days, with effluent TP concentration decreasing to approximately 3.4 mg/L compared to 6.2 and 21.3 mg/L for the control test (R0) and the method of PAC addition (R3), respectively. The SURs for R1–R4 on day 12 were 50.3 mgNH$_3$-N/(gVSS·d), 41.3 mgNH$_3$-N/(gVSS·d), 35.4 mgNH$_3$-N/(gVSS·d), and 27.6 mgNH$_3$-N/(gVSS·d), respectively. According to previous reports, activated carbon was characterized by a high level of microporosity and various active sites, and therefore showed high adsorption capacities for aromatic compounds (Bradley 2011). It is noteworthy that nitrification recovery reached the same level in the methods of PAC and S-PAC addition eventually. Considering almost no PAC or S-PAC was wasted in the batch test, the organic compounds loading onto the surface of the activated carbons might induce an accumulation of refractory inhibitors in R3 and R4 and would disturb the original metabolic environment in the reactor, leading to the inhibition of nitrification and denitrification. This fact was consistent with Figure 1 which revealed that the nitrification rate in R3 and R4 was eventually stable at approximately 86–88%. This was slightly lower than the control level. Obviously, the four strategies...
above could quickly reduce the residual phenolic compounds after the impact loaded, which was necessary but not sufficient for the recovery of the SBNR. Thus, the main problem in tackling phenolic inhibition in short-cut nitrogen removal of CGW was how to carry out the reduction of phenolic compounds as much as possible and recover the sludge activity as soon as possible. Based on the results obtained in the batch tests, the methods of PAC and S-PAC addition were selected to further investigate the recovery efficiency and mechanism in the SBNR reactor.

**Recovery from phenol inhibition in the SBNR reactor**

When studying the impact of TP inhibition on biomass activities, the most important questions to be answered from a practical point of view are: (i) Can the process fully recover when the inhibition period ceases? (ii) How quickly can a full recovery occur?

The output of the laboratory-scale SBNR reactor experiment is illustrated in Figure 2. Before the addition of PAC, a stable process was observed. On day 16, the TP shock load resulted in an immediate inhibition in the activity of AOB, which was indicated by the sharp decrease in the ammonia conversion rate. Only 42.7% of ammonia was oxidized into nitrite; the corresponding NH$_3$-N concentration in the effluent was high, up to 87.2 mg/L. Besides, a remarkable decrease of 50% in denitrifying efficiency in the anoxic zone was also observed, which illustrates that the ammonia inhibition was an overall inhibition of the process and not only an inhibition of AOB. According to Wett & Rauch (2003), CO$_2$ was generated from the oxidation of organic matter and dissolved in aqueous solution to form H$_2$CO$_3$. H$_2$CO$_3$ partly dissociates into HCO$_3^-$, releasing a proton that acidifies the media. Such an acidification reduces the buffering capacity of the wastewater to balance protons produced during the oxidation of total NH$_3$, which will eventually reduce the amount of ammonia converted to total nitrite. So the decrease in the nitrification performance could be partly attributed to the increase in organic matter. Then the self-recovery process started with 5 days of ‘lag time’, and the normal operation of the reactor was resumed in 32 days.

After the second TP shock loading, the lag time was less noticeable and the recovery time was 12 days, which was shortened by about 20 days compared to the natural recovery process. The PAC loaded with phenolic compounds during the shock load was decreasing because the SRT was controlled by wasting a certain amount of the mixed liquor. Therefore, it was reasonable to obtain a slightly shorter recovery period compared to the batch test with PAC. By the addition of S-PAC, the nitrification rate and denitrification rate quickly improved and reached their initial value within 10 days. Obviously, the S-PAC addition was an effective way to tackle the failed performance of the SBNR reactor after the impact of phenolic compounds.

After inducing the activated carbons as carriers, the micro-organisms in the SBNR gradually began to attach to the carbon’s surface and reside in the gaps and pores of the carbons. Therefore, the nitrifying bacteria were less easy to wash out compared to those in suspension systems. The forming attached biofilm contributed to a higher SRT of the reactor and less sensitivity to the change of environment, such as shock loading and high strength of inhibitory compounds. The adhered system is suitable for nitrification because the nitrifying bacteria grow adhering to the carrier and cannot be washed out easily (Kim et al. 2009). Besides, nitrification recovery is easier in the adhered system than in the suspended system because the nitrifying bacteria are more susceptible in suspended form.
et al. 2008). At the same time, the SBNR reactor in this study was operated in CSTR mode, which is usually recommended to avoid an increase in inhibitory compound concentration in the feed.

**FISH**

The results found in the reactor experiment are supported by the FISH quantification results. Figure 3 revealed the FISH profiles at different stages. Most of these cells reacted with the probes specific for the beta-proteobacterial AOB, belonging to the genus Nitrosomonas. The probes Ntspa662, which are specific for the Nitrosospira spp., showed a comparatively very weak signal. Over the inhibition period, the AOB population targeted by FISH probe NSO190 decreased by some 40%, which correlates well with the 40% decrease in the measured AOB activity. The NOB population targeted by probes Ntspa662 also decreased by

**Figure 3** | FISH results of aggregated AOB in the SBNR biomass before and during inhibition and after recovery (on day 12, 92 and 105, respectively).
23%. It should be noted, however, that the FISH quantification results should be interpreted qualitatively, as they are given as percentages of the size of the total bacteria population (targeted by the EUBmix probe) which is also subject to reduction during inhibition. Also, FISH probes target the ribosome RNA, and consequently the signal intensity is proportional to the quantity of ribosome RNA present in cells rather than the number of cells.

Comparison of PAC and S-PAC

To clarify the effect of activated carbon type on the extent of adsorbability during the recovery of the SBNR reactor, we obtained the adsorption isotherm data of PAC and S-PAC for phenol (shown in Figure 4). The adsorption isotherm data were found to fit the theoretical Freundlich equation and Langmuir expression defined in Equations (1) and (2), respectively (Zhao et al. 2015).

\[ q = K_f C^{1/n} \]  
\[ q = Q_0 b C / (1 + b C) \]

In Equation (1), \( q \) is the adsorption capacity of the activated carbon (mg phenol adsorbed/g activated carbon); \( C \) is the equilibrium phenol concentration (mg/L), and \( K_f \) and \( 1/n \) are the Freundlich constants (Freundlich exponent and slope).

In Equation (2), \( C \) is the measured concentration in solution at equilibrium; \( Q_0 \) is the maximum adsorption capacity; \( q \) is the adsorption capacity of the activated carbon (mg phenol adsorbed/g activated carbon) at concentration \( C \), and \( b \) is the constant related to the energy of adsorption.

To clarify the difference between PAC and S-PAC in their contribution to the SBNR recovery, their pore size distribution and adsorption capacity were assayed. We did not, however, obtain any clear data indicating differences between S-PAC and PAC. Only a slightly larger pore volume or surface area in the mesopores was observed in S-PAC by means of the Dollimore-Hill (DH) method, and the Density Functional Theory (DFT) method showed no significant difference in the micropores. Also, the difference was not so large when compared with the adsorption capacity differences observed for phenolic compounds.

Freundlich and Langmuir adsorption isotherm constants obtained by regression analysis for phenol are shown in Tables 3 and 4, respectively. The \( K_f \) value, an indicator of adsorption capacity, was found to be higher for S-PAC, indicating that phenol was more strongly adsorbed onto the S-PAC. The fine fraction of activated carbon obtained by grinding might have a higher adsorption capacity than other fractions. The differences in adsorption capacities between the PAC and S-PAC were certainly caused by their different surface characteristics. Some researchers found that changes in the adsorption characteristics of activated carbon with particle size may be due to the fact that the inner regions of large particles are less accessible to the activation process during manufacturing than are the inner regions of smaller particles (Randtke & Snoeyink

<table>
<thead>
<tr>
<th>Carbon type</th>
<th>( K_f ) [(mg/g)(L/mg) (^{1/n} )]</th>
<th>( 1/n )</th>
<th>( R^2 )</th>
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<tbody>
<tr>
<td>PAC</td>
<td>3.02</td>
<td>0.667</td>
<td>0.952</td>
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<td>S-PAC</td>
<td>4.53</td>
<td>0.639</td>
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<table>
<thead>
<tr>
<th>Carbon type</th>
<th>( Q_0 ) (mg/g)</th>
<th>( B ) (L/mg)</th>
<th>( R^2 )</th>
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<tr>
<td>PAC</td>
<td>103</td>
<td>0.0160</td>
<td>0.913</td>
</tr>
<tr>
<td>S-PAC</td>
<td>151</td>
<td>0.00544</td>
<td>0.939</td>
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</table>

Figure 4 | Adsorption isotherms of PAC and S-PAC for phenol.


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