



Adsorption and bioregeneration in the treatment of phenol, indole, and mixture with activated carbon

Qian Zhao, Hongjun Han*, Shengyong Jia, Haifeng Zhuang, Baolin Hou, Fang Fang

State Key Laboratory of Urban Water Resource and Environment, School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China, Tel. +86 13354513390; email: 286005112@qq.com (Q. Zhao), Tel. +8613946003379, +86 451 87649777; Fax: +86 451 86283082; email: han13946003379@163.com (H. Han), Tel. +86 18804511681; email: 1102550354@qq.com (S. Jia), Tel. +86 18345140565; email: 286339399@qq.com (H. Zhuang), Tel. +86 15104682842; email: hbl527@163.com (B. Hou), Tel. +86 13766883540; email: fangfang123.com@163.com (F. Fang)

Received 3 December 2013; Accepted 19 May 2014

ABSTRACT

The study aims to: (1) investigate the adsorption of powdered activated carbon (PAC) and granular activated carbon (GAC) for phenol, indole, and their mixtures, respectively, and (2) determine the bioregeneration efficiency and reusability of PAC loaded with phenol, indole, and their mixtures. The results showed that phenol was easier to be adsorbed than indole. The adsorption using PAC was obviously better than GAC. The considerably higher bioregeneration efficiency of the phenol-loaded PAC as compared to that of indole-loaded PAC was probably due to the recalcitrant nature of indole. PAC exhibited much higher adsorption capacity for indole, especially in the presence of low concentration of phenol. Besides, phenol improved the biodegradation of indole and therefore enhanced the reusability of indole-loaded PAC. Therefore, powdered activated carbon technology (PACT) was appropriate for the treatment of similar wastewater. Within the PACT system, PAC preferentially adsorbed the recalcitrant indole while the relatively easily degradable phenol was utilized by the biomass. Besides, phenol enhanced the degradation of indole and the reusability of PAC, which resulted in a stable and efficient performance.

Keywords: Phenol; Indole; Adsorption; Bioregeneration; Powdered activated carbon technology

1. Introduction

The coal gasification wastewater (CGW) contains huge amount of alkanes, phenolic, and heterocyclic compounds, such as phenol, 2-methyl-phenol, quinoline, indole, and 5,5-dimethyl-2,4-imidazolidinedione [1–3]. The arbitrary discharge of CGW would threaten both the environmental safety and public health.

According to the reports, anaerobic reactor has been successfully applied as the first step in the full-scale treatment plant to remove partially COD and phenol [4,5]. But the remaining COD, phenol, heterocyclic compounds, and ammonia nitrogen, which exhibit poor removal efficiency in anaerobic process need to be removed by subsequent aerobic treatment in order to meet the requirement of concerned standard. The biological treatment combined with activated carbon (AC), i.e. granular activated carbon (GAC)-sludge

*Corresponding author.

process or powdered activated carbon technology (PACT), has been successfully applied to CGW treatment, achieving effective removal of phenolic compounds [6,7]. It efficiently improves hydraulic capacity because of either increased removal rates or operation with higher mixed liquor biomass levels. Moreover, in the hybrid system, the mixed culture of biomass can regenerate the active sites on the adsorbent and therefore, adsorption concentration rises more than the equilibrium adsorption [8,9]. The bioregeneration process effectively increases the reusability of the AC and extends the service life of the spent adsorbent. So far there have been many reports describing adsorption, desorption and bioregeneration in the treatment of phenol [9,10], chlorophenols [9,11], and total organic pollutants [12–15] with AC, however, there is still a lack of knowledge in the literature about the adsorption and bioregeneration of the nitrogen heterocyclic compounds with AC till date. The studies on the adsorption isotherm of these compounds and bioregeneration of AC are also limited.

In CGW treatment plant, the influent composition of the PACT system is very complex in composition, which contains phenol, o-cresol, m-cresol, and 3,5-dimethyl-phenol, which are classified as phenols. Except from above, indole, quinoline, and 6-methyl-4-indanol, as refractory nitrogen heterocyclic compounds, normally exist in the wastewater. Phenol and indole account for the largest proportions in these two categories, respectively [6]. So far, little work has been done on the indole adsorption isotherm, PAC adsorption capacity for the phenol–indole mixture and the bioregeneration of loaded PAC. Hence, this study aims to investigate the adsorption of powdered activated carbon (PAC) and GAC for phenol, indole, and their mixtures, respectively. Besides, the bioregeneration efficiencies and reusability of PAC loaded with phenol, indole, and their mixtures were also determined.

2. Materials and methods

2.1. AC characteristics

The GAC and PAC used in this study are the most commonly used commercial carbon types for wastewater treatment in China. The characteristics are shown in Table 1.

2.2. Adsorption studies

The first step in the experimental work was to determine the adsorbabilities of phenol and indole for PAC and GAC in batch adsorption tests. Adsorption study was performed in 500-mL flasks with stoppers

Table 1
Characteristics of GAC and PAC

Items	GAC	PAC
Activation method	Thermal	Thermal
Surface area (m ² /g)	427.87	1237.99
Iodine number (mg/g)	>600.00	>700.00
Methylene blue adsorption (g/100 g)	20.00	25.00
Total pore volume (cm ³ /g)	0.22	0.19
Micro ($\Phi < 2$ nm)	0.15	0.12
Meso ($\Phi 1.7$ –30 nm)	0.06	0.07
Macro ($\Phi > 30$ nm)	0.02	0.00

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/indole 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/indole values in 500-mL stoppered flasks with different AC concentrations were analyzed with respect to time until reaching equilibrium concentrations.

For determination of the adsorption isotherms, different weights of AC (100 mg/L–10 g/L) were contacted with different concentrations of phenol (20–200 mg/L) and indole (100–2,000 mg/L), respectively. These 200-mL mixtures were agitated until reaching equilibrium, i.e. the point when the concentrations 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.

2.3. Bioregeneration studies

After the adsorption saturation, the bioregeneration study was continued with four of the flasks used in the adsorption test. Initial concentrations in these flasks were 100, 200 mg/L for phenol and 100 and 200 mg/L for indole, respectively (named flasks 1–4). Meanwhile, control test was conducted with four flasks named flasks 5–8 with the same concentrations in the liquid bulk as flasks 1–4, respectively, without PAC. The total volume in each flask was about 200 mL. Flasks 1–8 were seeded with 1.6 g sludge as well as a proper amount of necessary mineral salts. Flasks 9–10 were prepared with the abiotic 100 mg/L phenol and 100 mg/L indole, respectively, in order to evaluate the effect of volatilization. Flasks 11–12 were also prepared with 1.6 g sludge and abiotic 100 mg/L

phenol and 100 mg/L indole, respectively, in order to evaluate the effect of biodegradation during reloading. Table 2 gives a summary of the initial conditions of flasks 1–12.

The activated sludge was obtained from the full-scale aerobic process CGW treatment plant in China Coal Longhua Harbin Coal Chemical Industry Co., Ltd. The sludge was added to the flasks 1–10 after being washed and starving for 24 h to remove the residual organic compounds. Then, all the flasks were aerated and the spent air was removed by a hose and passed through a gas-wash bottle which contained water. Air was supplied by a compressor. One-milliliter sample was collected from each flask and the concentrations of phenol or indole were monitored at different time intervals. The biodegradation was also evaluated by determining the variation of TOC.

The re-adsorption test was to evaluate the reusability of bioregenerated PAC. Aeration lasted for 28 h (the average HRT of the full-scale PACT system treating CGW). Then flasks 1–4 were loaded with the same concentrations of phenol (100 and 200 mg/L) or indole (100 and 200 mg/L) as those in the adsorption study. The re-adsorption capacity was calculated after determining the residual phenol or indole in the supernatant. Then, a second and third regeneration tests were conducted with the same procedure. In order to investigate the effect of biodegradation time on PAC reusability, a parallel re-adsorption study was also conducted after biodegradation for 36 h. Before the reloading test, some measures should be taken to “quench” the biological degradation. However, reducing the temperature or dosing some reagents would probably interfere the re-loading of phenol and indole. In the reloading test, no oxygen was provided for the biomass. And the “immediate absorption of the organics” was found to be

negligible in the biodegradation test. Therefore, the biomass activity had little effect on the reloading ability.

2.4. Dual-adsorbate adsorption and bioregeneration of the AC

The study on dual-adsorbate adsorption aimed to investigate on the adsorption capacity of PAC for the mixture of phenol and indole at different initial concentrations and phenol/indole ratios. Initial phenol/indole concentrations were respectively 100 mg L⁻¹/100 mg L⁻¹, 100 mg L⁻¹/200 mg L⁻¹, 100 mg L⁻¹/300 mg L⁻¹, 100 mg L⁻¹/400 mg L⁻¹, 100 mg L⁻¹/400 mg L⁻¹, 200 mg L⁻¹/200 mg L⁻¹, 200 mg L⁻¹/400 mg L⁻¹, 200 mg L⁻¹/600 mg L⁻¹, 200 mg L⁻¹/800 mg L⁻¹, 200 mg L⁻¹/1,000 mg L⁻¹, 300 mg L⁻¹/300 mg L⁻¹, 300 mg L⁻¹/600 mg L⁻¹, 300 mg L⁻¹/900 mg L⁻¹, 300 mg L⁻¹/1,200 mg L⁻¹, 300 mg L⁻¹/1,500 mg L⁻¹, 400 mg L⁻¹/400 mg L⁻¹, 400 mg L⁻¹/800 mg L⁻¹, 400 mg L⁻¹/1,200 mg L⁻¹, 400 mg L⁻¹/1,600 mg L⁻¹, and 400 mg L⁻¹/2,000 mg L⁻¹. The ratio between phenol and indole concentrations were 1:1, 1:2, 1:3, 1:4, and 1:5. The PAC dosage was fixed at 1 g/L.

Biodegradation and bioregeneration of PAC loaded with phenol–indole mixture were studied after adsorption equilibrium was reached. The test was conducted with the flasks with initial phenol/indole concentration of 100 mg L⁻¹/100 mg L⁻¹, 100 mg L⁻¹/200 mg L⁻¹, 100 mg L⁻¹/300 mg L⁻¹, and 100 mg L⁻¹/400 mg L⁻¹. Phenol and indole concentrations were determined at different time intervals. Afterwards, the re-adsorption test was conducted with the four flasks above. The PAC was loaded with mixtures, with initial phenol/indole concentrations, i.e. 100 mg L⁻¹/100 mg L⁻¹, 100 mg L⁻¹/200 mg L⁻¹, 100 mg L⁻¹/300 mg L⁻¹, and 100 mg L⁻¹/400 mg L⁻¹,

Table 2
Initial conditions of the flasks in the bioregeneration studies

Flask	Phenol (mg/L)	Indole (mg/L)	Sludge (mL)	PAC (g/L)
1	91.27	–	200	0.2
2	156.5	–	200	0.5
3	–	76.02	200	10
4	–	121.2	200	10
5	91.50	–	200	–
6	156.8	–	200	–
7	–	76.44	200	–
8	–	121.2	200	–
9	100.3	–	0	–
10	–	100.0	0	–
11	100.0	–	200	–
12	–	100.1	100	–

respectively. The re-adsorption capacity was calculated after determining the residual phenol or indole in the supernatant. Then, a second and third regeneration tests were conducted with the same procedures and loading-biodegradation cycles of PAC were carried out to determine the adsorption capacity loss and reusability of PAC. Some particles of spent PAC above were randomly selected and observed under a scanning electron microscopy (SEM, HITACHI S4800 HSD, Japan).

2.5. Effect of pH on the adsorption of indole by PAC

In order to demonstrate the effect of pH on the indole adsorption, five flasks with indole of 1,000 mg/L were mixed with 1 g/L PAC after adjusting pH to 3.06, 5.46, 7.01, 9.82, and 12.25, respectively. The adsorption capacities of PAC for indole at different pH were compared.

2.6. Analytical methods

BET area and pore distribution of the AC were assayed via the BETSORP-mini physicochemical N₂ adsorption analyzer (JW Co. Ltd, China). The analytical method for the mixed liquor suspended solid (MLSS) followed the Standard Methods [16]. Phenol and indole concentrations were quantified by the high-performance liquid chromatography (HPLC) (Agilent 1100) after the samples were filtered 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. TOC was determined with TOC-VCPN analyzer (Shimadzu, Japan). The pH was measured with a pH meter (pHS-3C, Leici, China).

3. Results and discussion

3.1. Adsorption studies for phenol and indole as sole adsorbate

The equilibrium time was determined for estimating the shaking time required for adsorption isotherm tests. Equilibrium time was described as the time when the phenol or concentration reached a constant value, and was determined as 4 h for phenol, and 1 h for indole as seen in Fig. 1. This argument also applied to other initial concentrations and carbon dosages, which were not shown in this figure.

The adsorption isotherm data for phenol and indole are plotted in Fig. 2. The adsorption isotherm data was found to fit the theoretical Freundlich

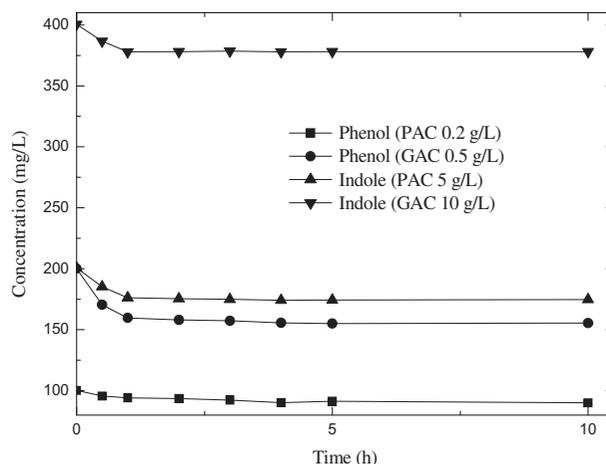


Fig. 1. Concentration profiles of phenol and indole during adsorption by PAC and GAC at certain initial concentrations and dosages.

equation and Langmuir expression defined in Eqs. (1) and (2), respectively.

$$q = K_f C^{1/n} \quad (1)$$

In Eq. (1), q is the adsorption capacity of the AC (mg phenol/indole adsorbed/g AC); C is the equilibrium phenol/indole concentration (mg/L), and K_f and $1/n$ are the Freundlich constants (Freundlich exponent and slope).

$$q = Q_0 bC / (1 + bC) \quad (2)$$

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

Freundlich and Langmuir adsorption isotherm constants obtained by regression analysis for phenol and indole are shown in Tables 3 and 4, respectively. Slightly lower $1/n$ values for the phenol indicated that an increase in the AC dose was more effective for phenol removal rather than in the case of indole with steeper isotherm curves. The K_f value, an indicator of adsorption capacity, was found to be higher for the phenol and PAC. Phenol was more strongly adsorbed onto the carbon in comparison with indole. The PACs were obviously better adsorbent for phenol than GAC. The differences in adsorption capacities between the powdered and GACs were certainly caused by their different surface characteristics [11]. Although PACs had lower macropore volumes than their granular

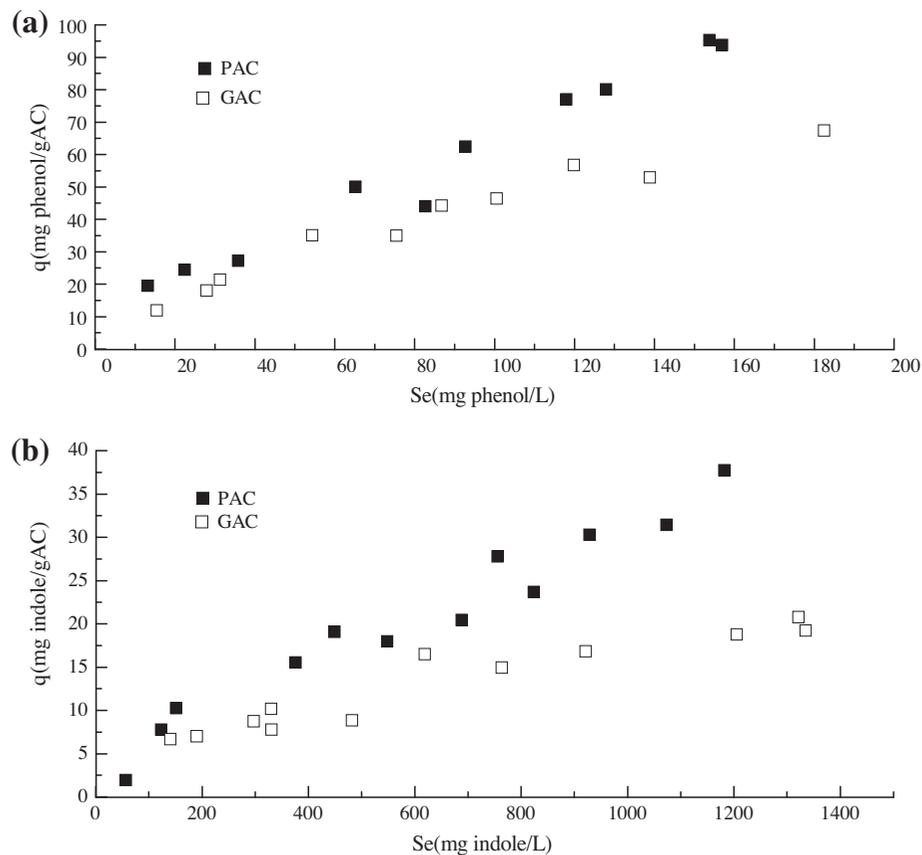


Fig. 2. Adsorption isotherms of powdered and granular activated carbons for (a) phenol and (b) indole.

Table 3
Freundlich isotherm constants for phenol and indole adsorption

Adsorbate	Carbon type	K_f [(mg/g)/(L/mg) ^{1/n}]	1/n	R^2
Phenol	PAC	3.02	0.667	0.952
Phenol	GAC	1.52	0.692	0.980
Indole	PAC	0.121	0.808	0.927
Indole	GAC	0.0401	0.847	0.907

Table 4
Langmuir isotherm constants for phenol and indole adsorption

	Carbon type	Q_0 (mg/g)	b (L/mg)	R^2
Phenol	PAC	103	0.0160	0.913
Phenol	GAC	80.7	0.00860	0.990
Indole	PAC	41.2	0.00200	0.959
Indole	GAC	46.9	0.000400	0.931

countertypes (shown in Table 1), macropores only contributed slightly to interfacial area compared to micropores and mesopores, regardless of the adsorbent.

AC was characterized by a high level of microporosity and various active sites (acidic, alkaline). The differences probably came from these attributes.

3.2. Bioregeneration and reusability of PAC loaded with sole adsorbate

Steady phenol and indole concentrations in flasks 9 and 10 during 10 h aeration period indicated that the volatilization effect could be negligible in this test (Fig. 3). Considering acclimated biomass was used for the batch biodegradation test, it was reasonable that no lag time was observed. For flasks 5, 6, 7, and 8

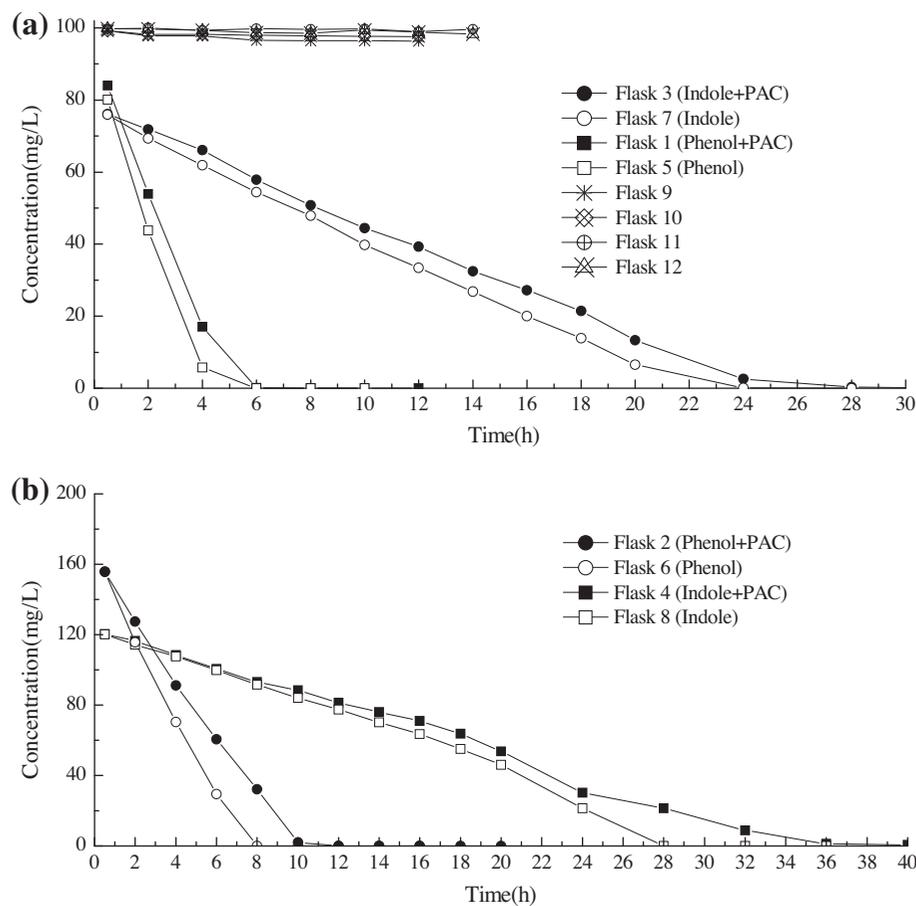


Fig. 3. Concentration profiles of phenol and indole during the bioregeneration process.

Note: The substrate concentrations are referring to the concentration analyzed via HPLC, i.e. the concentration in the liquid bulk.

which contained no PAC, the substrate concentrations were almost constant during the first 5 min, so the “immediate absorption of the organics” was negligible. During 28 h aeration, both the phenol and indole decreased progressively owing to the utilization by the acclimated biomass, although with different degradation rates. Based on the data from flasks without PAC, the phenol and indole removal rates were calculated to be approx. 2.68 mg phenol/(gMLSS h) and 0.44 mg indole/(gMLSS h), respectively. The differences in the biodegradability of phenol and indole were in good agreement with previous studies [17,18]. As shown in Fig. 3, it took more time for the biomass/PAC to consume the substrates, even though the bulk concentrations were the same, e.g. flask 4 and 8. The longer degradation time could be explained by the adsorbates previously loading on the carbons. This fact also indicated that the substrates loading on PAC could be utilized by biomass, allowing PAC in PACT to be bioregenerated, which was also concluded from

the results of re-adsorption studies in Fig. 4. In addition, no obvious biodegradation was observed for flask 11 and 12 (Fig. 3(a)) probably due to short supply of oxygen. This fact also indicated that there was no degradation of phenol/indole during the subsequent reloading process.

In biological systems combined with AC, bioregeneration required that phenol or indole could be initially adsorbed onto the carbon’s surface where microorganisms resided (Fig. 4). Consequently, adsorption concentration rose more than the equilibrium adsorption concentration through the decrease of bulk concentration by biological activity. Then, the adsorbed organic matters were desorbed due to the concentration gradient between the AC surface and bulk liquid. Therefore, more active sites available on ACs surface were obtained for subsequent re-adsorption [19,20].

During mineralization or oxidation of phenol and indole (10–28 h aeration), more significant decrease

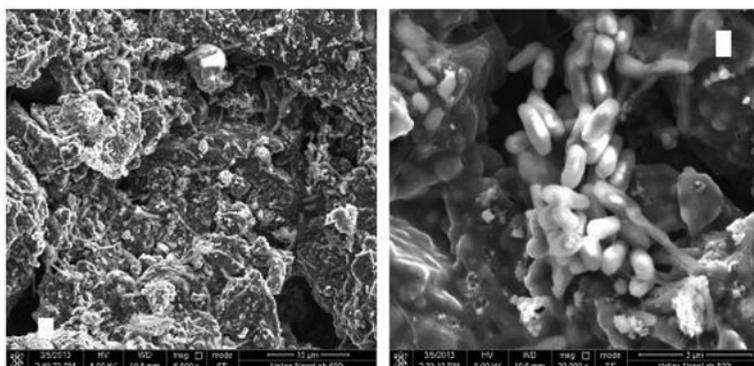


Fig. 4. SEM image of the surface of the spent activated carbons.

in TOC was observed for phenol as compared to indole (data not shown). Therefore, phenol and indole were partly removed and transformed into other organics.

In the re-adsorption test, the bioregeneration capacity can be calculated by using Eq. (3).

$$\omega_i (\%) = Se_i / Se_0 \times 100\% \quad (3)$$

Se_0 is the original adsorption capacity of the AC (mg substrate adsorbed/g AC); Se_i is the adsorption capacity of AC (mg phenol adsorbed/g AC) after i cycle(s) of loading biodegradation ($i = 1, 2, 3, 4, \dots$), e.g. Se_1 and Se_2 means the adsorption capacity after a second and third bioregeneration steps.

In this bioregeneration study, ω_1 were 95.28 ± 0.47 , 94.94 ± 0.56 , 82.75 ± 0.08 , and $79.66 \pm 0.38\%$ for flasks 1–4, respectively. Therefore, the indole-loaded PAC seemed more difficult to be bioregenerated, indicating that the reusability of PAC was closely related with the biodegradability of adsorbates. In addition, PAC could not be retrieved completely, even though the adsorbates in bulk solution decreased to low concentrations.

After a second and third bioregeneration steps, ω_2 were 89.63 ± 2.03 , 88.53 ± 0.94 , 78.51 ± 0.74 , and $67.17 \pm 1.90\%$ and ω_3 were 81.44 ± 1.83 , 79.53 ± 0.34 , 58.21 ± 0.85 , and $48.26 \pm 2.00\%$, respectively. The progressive loss of adsorption capacity with the cycles of use could be explained by the chemical fouling and the biofouling by the blockage of pores of adsorbent, which was caused by the bacteria debris and/or the adsorption of soluble microbial products onto the surface of PAC. In addition, extending the biodegradation time to 36 h was not effective to improve the regeneration of adsorption sites and reusability of PAC (data not shown).

3.3. Adsorption of PAC for phenol–indole mixture and bioregeneration of PAC

In the dual-adsorbate adsorption study, the adsorptive preference of PAC can be evaluated by the parameters— γ_{phenol} and γ_{indole} , which are defined by Eqs. (4) and (5):

$$\gamma_{\text{phenol}} = q'_{\text{phenol}} / q_{\text{phenol}} \quad (4)$$

$$\gamma_{\text{indole}} = q'_{\text{indole}} / q_{\text{indole}} \quad (5)$$

q'_{phenol} —Adsorption capacity for phenol when AC was loaded with phenol–indole mixture. q_{phenol} —The equilibrium adsorption capacity for phenol as sole adsorbate. q'_{indole} —Adsorption capacity for indole when AC was loaded with phenol–indole mixture. q_{indole} —The equilibrium adsorption capacity for indole as sole adsorbate.

Fig. 5 presents the unexpected results of γ_{phenol} and γ_{indole} in the dual-adsorbate adsorption study. γ_{phenol} was in the range of 0.022–0.040, indicating low adsorption capacity for phenol in the presence of indole. The γ_{phenol} stayed at low value regardless of the ratio and indole concentrations. In contrast, the γ_{indole} was all above 1 in the presence of phenol. This fact suggested that the phenol in the bulk solution contributed to higher indole-reloading capacity. And it seemed that this capacity could be improved especially by phenol at low concentrations, e.g. 100 and 200 mg/L (shown in Fig. 5). γ_{indole} reached high to 3.95 with initial phenol/indole of 100 mg L⁻¹/100 mg L⁻¹. The ionization of phenol was supposed to explain the seemingly weird phenomenon. According to the previous reports, the surface characteristics of the AC in terms of acidity/alkalinescence [11,21] and surface charge significantly determined the adsorption

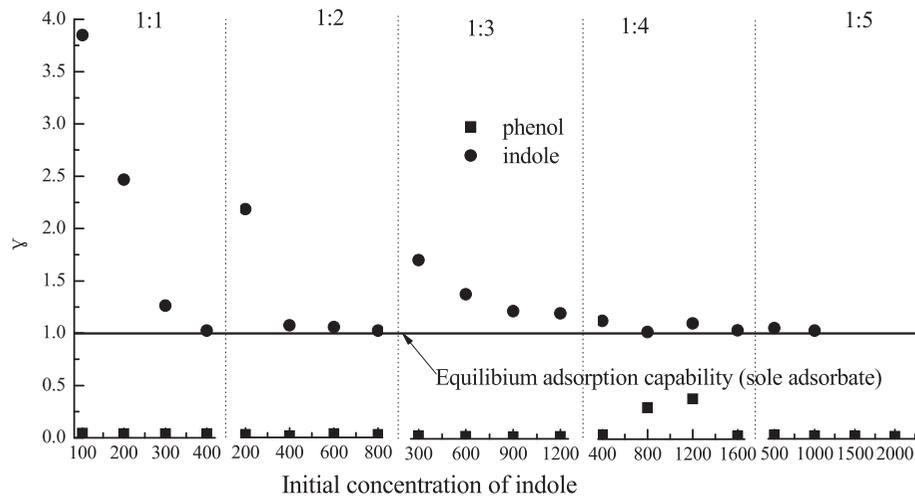


Fig. 5. Profiles of γ_{phenol} and γ_{indole} in the dual-adsorbates adsorption.

capacity for the pollutants [22]. Since the phenol was weakly acidic and the thermally AC was basic, and the release of ionized H^+ from phenol might change the attributes of the original surface, which therefore influenced the adsorption capacity for indole. However, this explanation contradicted with the study on the effect of pH on equilibrium bulk indole concentrations. At a pH of 3.06, 5.46, 7.01, 9.82, and 12.25, the equilibrium adsorption capacities for indole were 24.54, 23.06, 24.18, 23.25, and 25.40 mg/g, which were almost unvaried with pH. Therefore, H^+ could not be the reason for the increase of adsorption capacity for indole in the presence of phenol. The preferential adsorption for indole was probably caused by higher energy bonding of indole molecules to specific functional groups on the active sites [8,10,23].

In the subsequent bioregeneration study, the phenol was almost completely degraded after 28 h aeration in all the flasks while the indole of 300, 400, and 500 mg/L seemed surplus for the biomass (data now shown). And it was noteworthy that the indole removal rate was approx. 3.10–3.2 mg indole/(gMLSS h), compared to the rate of 2.5 mg indole/(gMLSS h) in Section 3.2, indicating that more indole could be removed in the presence of phenol as co-substrate.

For indole, ω_{indole} were 90.38 ± 1.15 and $87.36 \pm 0.74\%$ at phenol/indole ratio of 1:1, 1:2, i.e. at the initial indole concentrations of 100 and 200 mg/L, respectively, compared to ω_{indole} of 82.75 ± 0.08 and $79.66 \pm 0.38\%$ described in Section 3.2 when indole was the sole substrate. After a second and third regeneration steps, ω_{2indole} were 88.12 ± 1.45 and $84.07 \pm 0.66\%$ and ω_{3indole} were 82.51 ± 0.35 and $79.78 \pm 2.94\%$. In contrast, ω_{2indole} were 78.51 ± 0.74 and $67.17 \pm 1.90\%$ and ω_{3indole} were 58.21 ± 0.85 and $48.26 \pm 2.00\%$ in the sole-

substrate re-adsorption test in Section 3.2. Therefore, the phenol enhanced the biodegradation of indole, which generated more available adsorption sites for the accommodation of more indole molecules in the re-adsorption process. Similarly, other refractory compounds, e.g. monochlorophenols and cresols were more efficiently removed by a cometabolic pathway in the presence of phenol [24–26]. At initial indole concentration of 300, 400, and 500 mg/L, ω_{indole} were only 42.66 ± 0.57 , 31.64 ± 0.15 , and $18.28 \pm 0.32\%$, respectively, probably due to the inadequate degradation of indole with relatively high concentrations.

Theoretically, the findings about selective adsorption for phenol–indole mixture revealed that PACT was suitable for the treatment of the wastewater containing phenol and indole. PACs preferentially adsorbed the recalcitrant indole while the relatively easily degradable phenol was utilized by the biomass in the bulk solution. Besides, phenol enhanced the degradation of indole and the reusability of PACs, thereby resulting in a stable and efficient performance of PACT.

4. Conclusions

The adsorption isotherm data suggested that PAC was a better adsorbent for phenol than GAC. The bioregeneration of indole-loaded PAC was more difficult due to the higher recalcitrant nature of indole. In the dual-substrate adsorption test, PAC exhibited much higher adsorption capacity for the indole, especially when the phenol was of low concentration. In addition, the biodegradation of indole could be enhanced in the presence of phenol as co-substrate, leading to a high reusability of indole-loaded PAC. Therefore, the

findings in this study reflected the superiority of PACT system for the treatment CGW. Within the system, the recalcitrant indole could be removed via adsorption while the relatively easily degradable phenol could be utilized by the biomass.

Acknowledgments

This work was supported by the Sino-Dutch Research Program (SDRP-WRZ) and the independent subject sponsored by the State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology (No. 2013DX10).

References

- [1] W. Wang, H.J. Han, M. Yuan, H.Q. Li, F. Fang, K. Wang, Treatment of coal gasification wastewater by a two-continuous UASB system with step-feed for COD and phenols removal, *Bioresour. Technol.* 102 (2011) 5454–5460.
- [2] H.Q. Li, H.J. Han, M.A. Du, W. Wang, Inhibition and recovery of nitrification in treating real coal gasification wastewater with moving bed biofilm reactor, *J. Environ. Sci.* 23 (2011) 568–574.
- [3] H.J. Gai, Y.B. Jiang, Y. Qian, A. Kraslawski, Conceptual design and retrofitting of the coal-gasification wastewater treatment process, *Chem. Eng. J.* 138 (2008) 84–94.
- [4] W. Wang, W.C. Ma, H.J. Han, H.Q. Li, M. Yuan, Thermophilic anaerobic digestion of Lurgi coal gasification wastewater in a UASB reactor, *Bioresour. Technol.* 102 (2011) 2441–2447.
- [5] Z.X. Wang, X.C. Xu, Z. Gong, F.L. Yang, Removal of COD, phenols and ammonium from Lurgi coal gasification wastewater using A₂O-MBR system, *J. Hazard. Mater.* 235–236 (2012) 78–84.
- [6] Q. Zhao, H.J. Han, C. Xu, H.F. Zhuang, F. Fang, L.H. Zhang, Effect of powdered activated carbon technology on short-cut nitrogen removal for coal gasification wastewater, *Bioresour. Technol.* 142 (2013) 179–185.
- [7] K.M. Lee, P.E. Lim, Bioregeneration of powdered activated carbon in the treatment of alkyl-substituted phenolic compounds in simultaneous adsorption and biodegradation processes, *Chemosphere* 58 (2005) 407–416.
- [8] R.J. de Jonge, A.M. Breure, J.G. van An del, Bioregeneration of powdered activated carbon (PAC) loaded with aromatic compounds, *Water Res.* 30 (1996) 875–882.
- [9] W. Tri, M. Tomonori, N. Yoichi, N. Wataru, O. Mitsumasa, Adsorption capacity of powdered activated carbon for 3,5-dichlorophenol in activated sludge, *Chemosphere* 57 (2004) 1219–1224.
- [10] D.M. Nevskaja, A. Santianes, V. Muñoz, A. Guerrero-Ruiz, Interaction of aqueous solutions of phenol with commercial activated carbons: An adsorption and kinetic study, *Carbon* 37 (1999) 1065–1074.
- [11] A. Ozgur, C. Ferhan, Adsorption, desorption and bioregeneration in the treatment of 2-chlorophenol with activated carbon, *J. Hazard. Mater.* 141 (2007) 769–777.
- [12] R.H. Bradley, Recent developments in the physical adsorption of toxic organic vapours by activated carbons, *Adsorpt. Sci. Technol.* 29 (2011) 1–28.
- [13] I.P.P. Cansado, C. Galacho, A.S. Nunes, M.M.L.R. Carrott, P.J.M. Carrott, Adsorption properties of activated carbons prepared from recycled PET in the removal of organic pollutants from aqueous solutions, *Adsorpt. Sci. Technol.* 28 (2010) 807–821.
- [14] O. Hamdaoui, E. Naffrechoux, Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon Part I. Two-parameter models and equations allowing determination of thermodynamic parameters, *J. Hazard. Mater.* 147 (2007) 381–394.
- [15] P.A.M. Mourão, P.J.M. Carrott, M.M.L. Ribeiro Carrott, Application of different equations to adsorption isotherms of phenolic compounds on activated carbons prepared from cork, *Carbon* 44 (2006) 2422–2429.
- [16] APHA-AWWA-WPCF, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington, DC, 1998.
- [17] M. Bajaj, C. Gallert, J. Winter, Biodegradation of high phenol containing synthetic wastewater by an aerobic fixed bed reactor, *Bioresour. Technol.* 99 (2008) 8376–8381.
- [18] P. Li, L. Tong, K. Liu, Y.H. Wang, Y.X. Wang, Indole degrading of ammonia oxidizing bacteria isolated from swine wastewater treatment system, *Water Sci. Technol.* 59 (2009) 2405–2410.
- [19] A.W.M. Ip, J.P. Barford, G. McKay, Biodegradation of Reactive Black 5 and bioregeneration in upflow fixed bed bioreactors packed with different adsorbents, *J. Chem. Technol. Biotechnol.* 85 (2010) 658–667.
- [20] W.A. Al-Amrani, P.E. Lim, C.E. Seng, W.N. Wan Ngah, Bioregeneration of mono-amine modified silica and granular activated carbon loaded with acid orange 7 in batch system, *Bioresour. Technol.* 118 (2012) 633–637.
- [21] F. Julien, M. Baudu, M. Mazet, Relationship between chemical and physical surface properties of activated carbon, *Water Res.* 32 (1998) 3414–3424.
- [22] M. Mazet, B. Farkhani, M. Baudu, Influence d'un traitement thermique ou chimique des charbons actifs sur l'adsorption de composés organiques [Influence of heat or chemical treatment of activated carbon onto the adsorption of organic compounds], *Water Res.* 28 (1994) 1609–1617.
- [23] D.R. Yonge, T.M. Keinath, K. Poznanska, Z.P. Jiang, Single-solute irreversible adsorption on granular activated carbon, *Environ. Sci. Technol.* 19 (1985) 690–694.
- [24] Z. Alexieva, H. Yemendzhiev, P. Zlateva, Cresols utilization by *Trametes versicolor* and substrate interactions in the mixture with phenol, *Biodegradation* 21 (2010) 625–635.
- [25] D.J. Lee, K.L. Ho, Y.Y. Chen, Degradation of cresols by phenol-acclimated aerobic granules, *Appl. Microbiol. Biotechnol.* 89 (2011) 209–215.
- [26] P. Saravanan, K. Pakshirajan, P. Saha, Biodegradation of phenol and m-cresol in a batch and fed batch operated internal loop airlift bioreactor by indigenous mixed microbial culture predominantly *Pseudomonas* sp., *Bioresour. Technol.* 99 (2008) 8553–8558.