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Advanced treatment of printing and dyeing wastewater by activated coke and thermal regeneration of spent activated coke

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ABSTRACT

The advanced treatment of printing and dyeing wastewater by adsorption using activated coke was studied. Specifically, the effects of adsorption conditions on wastewater treatment were examined by adsorption experiments. Meanwhile, the adsorption behaviors of organic pollutants by activated coke were investigated by the adsorption kinetics and isotherms. The chemical oxygen demand (COD) removal met the printing and dyeing wastewater discharge requirement under the conditions of initial COD concentration 158 mg/L, adsorption time 360 min, activated coke concentration 30 g/L and adsorption temperature 308 K. After adsorption, 53.86% of COD was removed. The adsorption kinetics of COD by activated coke followed the pseudo-second-order model and the adsorption isotherms could be expressed by the Freundlich model. Moreover, thermal regeneration of spent activated coke was studied. Specifically, the effects of regeneration conditions on the thermal regeneration efficiency of spent activated coke were examined by thermal regeneration experiments. Meanwhile, the reusability of activated coke for organic pollutants removal was evaluated by the successive adsorption-regeneration cycles. 98.13% of thermal regeneration efficiency could be achieved under the conditions of regeneration temperature 1,073 K, regeneration time 30 min and CO_2 flow rate 150 mL/min, and activated coke still maintained 92.54% of regeneration efficiency after ten adsorption-regeneration cycles.

Keywords: Activated coke; Adsorption; Advanced treatment; Printing and dyeing wastewater; Thermal regeneration

1. Introduction

The printing and dyeing industry is one of the most water pollution-intensive industries in China [1]. The printing and dyeing wastewater contains a large number of organic pollutants that must be treated prior to discharge into the aquatic environments to prevent serious ecological and health risks [2,3]. After the conventional biochemical treatment, degradable organic pollutants can be removed from wastewater, however, non-degradable organic pollutants remain in wastewater [4,5]. As the stringency of effluent discharge standard for printing and dyeing industry, it is necessary to remove these refractory compounds to meet more stringent discharge standards. Adsorption is an effective technology for refractory compound removal with economic viability, easy operation and versatility for a wide range of chemical compounds [6,7].

A suitable and economical adsorbent is the prerequisite for the application of adsorption technologies to advanced treatment of wastewater [8,9]. Activated carbon is often used to remove different organic compounds from wastewater [10,11]. However, activated carbon with abundant micropores has low adsorption capacity for non-degradable organic pollutants which are characterized by high

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molecular weight, due to the mismatch between micropore size and molecular size of pollutants [12]. Based on the molecular sieve effects, big molecular pollutants are mostly well adsorbed on the surface of the mesopore [13,14]. Therefore, activated coke with high mesopore volumes has become an alternative to activated carbon in the treatment of refractory organic pollutants.

Recently, activated coke has begun to be applied to remove refractory organic pollutants from wastewater [15,16]. Tong et al. [17] investigated the adsorption of refractory organic pollutants from super heavy oil wastewater by activated coke and examined the effects of activated coke adsorption on pH, biodegradability and main pollutants of wastewater. Zheng et al. [18] used activated coke to remove typical cyclic organics from coal pyrolysis wastewater and analyzed the mechanisms for selective adsorption of typical cyclic organics by activated coke. They found that the selectivity of activated coke was dominated by chemical interaction and its mesoporous, and was enhanced by the hydrophobicity effect. However, compared with the extensive application of activated coke in flue gas treatment [19–21], the application of activated coke in wastewater treatment is just in its infancy and the types of wastewater treated by activated coke are also very limited [22,23]. In order to extend the application of activated coke in wastewater treatment, it is necessary to carry out the research on the treatment of various organic wastewater by activated coke. To the best of our knowledge, few studies on the treatment of printing and dyeing wastewater by activated coke were reported before.

In addition, activated coke is saturated after sustained use in wastewater and becomes the waste called spent activated coke [24,25]. Subsequently, spent activated coke must be replaced by fresh or regenerated activated coke in order to achieve effective adsorption [26]. The second option is preferred taking economic costs and environmental benefits into consideration [27]. Meanwhile, the extensive application of activated coke in wastewater treatment greatly depends on the reuse of spent activated coke [28,29]. Therefore, it is important to reuse spent activated coke using the regeneration techniques. Thermal regeneration is considered as one of the most effective methods for regeneration of spent adsorbent because of its some exciting advantages such as high regeneration efficiency, short regeneration time and wide application range [30–32]. Recently, thermal regeneration has been applied to reuse activated carbon saturated with wastewater [33,34] and activated coke saturated with flue gas [35,36]. However, as the application of activated coke in wastewater treatment is just in its infancy, the subsequent thermal regeneration of spent activated coke is rarely studied.

Therefore, activated coke is used to remove organic pollutants from printing and dyeing wastewater and spent activated coke is reused by thermal regeneration in this study. Firstly, static adsorption experiments are carried out to study the effects of adsorption time, activated coke concentration and adsorption temperature on printing and dyeing wastewater treatment. Meanwhile, the adsorption kinetics and adsorption isotherms theories are used to study the adsorption behaviors of organic pollutants from printing and dyeing wastewater by activated coke. Then, thermal regeneration experiments are conducted to study the effects of regeneration temperature, regeneration time and flow rate of activation agent (CO_2) on the thermal regeneration efficiency of spent activated coke. Finally, the successive adsorption-regeneration cycles are carried out to evaluate the reusability of activated coke for organic pollutants removal from printing and dyeing wastewater. It is expected that this study can provide technical support and theoretical basis for full-scale usage of activated coke in advanced treatment of printing and dyeing wastewater and thermal regeneration in reuse of spent activated coke.

2. Materials and methods

2.1. Experiment materials

The printing and dyeing wastewater used in this study was obtained from a printing and dyeing plant in Liaoyang, Liaoning Province, China, which had already been treated by the traditional secondary wastewater treatment methods. The wastewater was a brown liquid with peculiar smell. And the general characteristics of the wastewater were as following: chemical oxygen demand (COD) (158 mg/L), pH (8.0), total salt (500 mg/L) and Chroma (350 times).

Activated coke was purchased from the Henan Bafang Water Purification Material Co., Ltd., and its main technical indexes are shown in Table 1. Before the experiments, activated coke was sieved into a uniform size of 0.60–0.85 mm. Then, activated coke was washed with distilled water in order to remove fine particles and organics attached to it. Finally, activated coke was dried in an oven at 378 K for 12 h. The activated coke after pretreatment was stored in an airtight glass bottle until needed.

The spent activated coke used in thermal regeneration experiments was prepared from fresh activated coke and real printing and dyeing wastewater. Firstly, 1.5 g of activated coke was added into 200 mL triangular flask with a stopper, which contained 50 mL of printing and dyeing wastewater. Then, this flask was placed in a water-bath shaker at 150 rpm and 308 K for 360 min. Finally, the spent activated coke was filtered and dried at 378 K for 12 h. These experimental conditions were chosen based on adsorption experiments, which could guarantee the saturation and adsorption equilibrium.

Table 1
Technical indexes of activated coke

Parameter	
Particle diameter (mm)	0.60–0.85
Pore volume (mL/g)	0.28
Surface area (m^2/g)	468
Iodine value (mg/g)	427
Methylene blue value (mg/g)	96
Fixed carbon (%)	>67
Ash content (%)	<20
Water content (%)	<4

2.2. Adsorption experiments

The same dose of activated coke was added into eight 200 mL triangular flasks with stoppers, respectively, which contained 50 mL of printing and dyeing wastewater. Then these flasks were placed in a water-bath shaker at 150 rpm and 308 K for different times (60, 120, 180, 240, 300, 360, 420 and 480 min). The activated coke was subsequently filtered and the resulting filtrate was analyzed.

Different doses of activated coke (0.5, 0.75, 1, 1.25, 1.5 and 1.75 g) were added to six 200 mL triangular flasks with stoppers, respectively, which contained 50 mL of printing and dyeing wastewater. Then these flasks were placed in a water-bath shaker at 150 rpm and different temperatures (308, 318, 328 and 338 K) for 360 min. The activated coke was subsequently filtered and the resulting filtrate was analyzed.

2.3. Thermal regeneration experiments

According to the desorption of different substances, thermal regeneration generally involves three processing steps: evaporation, pyrolysis and activation. The first step is drying, resulting in the elimination of residual moisture. The second step is the thermal decomposition of organic pollutants under an inert atmosphere, producing gas products that can be desorbed and charred residues that remain in the adsorbent. The third step is the controlled activation of the adsorbent under a mildly oxidizing atmosphere, resulting in the elimination of the charred residues. Based on this regeneration mechanism, thermal regeneration experiments were conducted in the laboratory-scale apparatus consisting of a horizontal tube furnace, temperature controller, and gas-flow devices (Fig. 1).

The dried spent activated coke (5 g) was loaded into the furnace as the precursor sample of thermal regeneration experiments. And the system was heated from room temperature to different target temperatures (773–1,273 K) at a rate of 10 K/min under 150 mL/min nitrogen flow. Upon reaching the target temperature, CO_2 was injected into the system at the different flow rates (50–250 mL/min). And the system was held at target temperature for different reaction times (10–50 min) under CO_2 atmosphere. After that, injection of CO_2 was halted and the treated sample was allowed to cool down under flowing nitrogen to obtain activated coke regenerated under different regeneration conditions (regeneration temperature, regeneration duration and flow rate of activation agent (CO_2)). Finally, regenerated sample was used to carry out readsorption experiment under the same conditions as the adsorption experiment.

2.4. Evaluation methods

In this study, the COD is used as the index for exploring the wastewater treatment efficiency by activated coke and the thermal regeneration efficiency of spent activated coke. The COD is determined according to the Chinese standard method (Water Quality-Determination of the Chemical Oxygen Demand-Dichromate method, GB11914-89). Meanwhile, in order to avoid experimental errors, all of the experiments are repeated three times and the average values of COD are used in the analysis.

The wastewater treatment efficiency by activated coke can be evaluated by the removal rate of COD, which can be calculated according to the following formula:

$$\phi = \frac{\left(C_0 - C_t\right)}{C_0} \times 100\% \tag{1}$$

where ϕ (%) is the removal rate of COD by activated coke, C_0 (mg/L) is the COD concentration in the raw printing and dyeing wastewater, and C_t (mg/L) is the COD concentration of wastewater after adsorption.

The thermal regeneration efficiency of spent activated coke can be assessed by the ratio of the COD adsorption capacity of regenerated activated coke to that of fresh activated coke at equilibrium, which can be calculated according to the following formula:

$$\mathrm{RP} = \frac{q_{\mathrm{er}}}{q_{\mathrm{ef}}} \times 100\% \tag{2}$$

where RP is the thermal regeneration efficiency of spent activated coke, q_{ef} (mg/g) is the COD adsorption capacity of fresh activated coke at equilibrium, that is, the equilibrium amount of COD adsorbed per unit mass of fresh

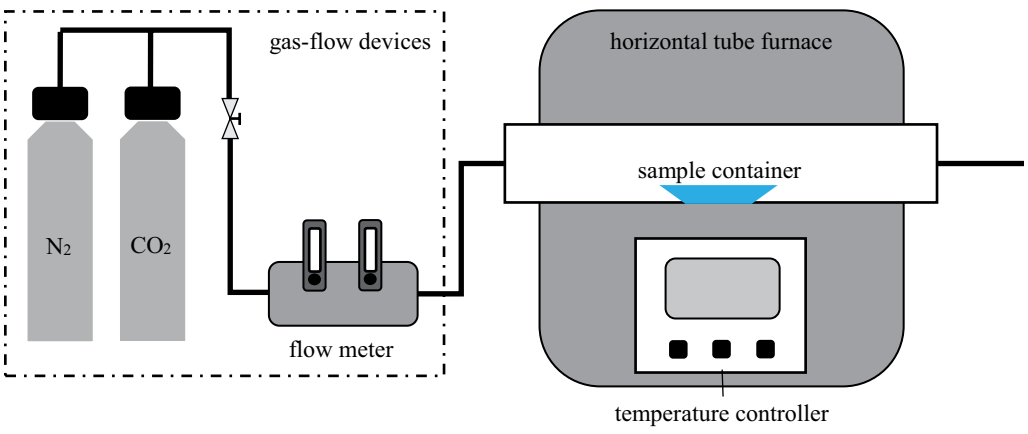

Fig. 1. Thermal regeneration apparatus for the reuse of spent activated coke.

activated coke, and q_{er} (mg/g) is the COD adsorption capacity of regenerated activated coke after the readsorption equilibrium, that is, the equilibrium amount of COD adsorbed per unit mass of regenerated activated coke.

Both q_{ef} and q_{er} can be calculated according to the following formula:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{3}$$

where q_e (mg/g) is the adsorption capacity of activated coke for COD at equilibrium, C_e (mg/L) is the COD concentration of wastewater after adsorption equilibrium, V (L) is the volume of the printing and dyeing wastewater, and W (g) is the activated coke weight.

3. Results and discussion

3.1. Effects of the absorption conditions

The effects of adsorption time, activated coke concentration and adsorption temperature on printing and dyeing wastewater treatment are studied to determine suitable adsorption conditions and to demonstrate the feasibility of activated coke removing organic pollutants from printing and dyeing wastewater.

3.1.1. Effect of the adsorption time

Adsorption time is one of the most important factors influencing the wastewater treatment efficiency by activated coke. The effect of adsorption time can provide important information for measuring the adsorption equilibrium of activated coke. The effect of adsorption time on the treatment of printing and dyeing wastewater by activated coke at temperature 308 K is shown in Fig. 2.

It can be seen that the COD concentration of printing and dyeing wastewater decreases gradually from 158 mg/L initially to 69.74–110.95 mg/L with increasing adsorption time up to 360 min and then is not changed by further increase in adsorption time. Accordingly, the removal efficiency of COD increases gradually from 0 initially to 29.78%–55.86% with increasing adsorption time up to 360 min and then is not changed by further increase in adsorption time. It is readily understood that at the initial stage of adsorption, there are a large number of sorption sites of organic pollutants on activated coke and there is a high concentration difference of organic pollutants between wastewater and activated coke, which promotes the rapid adsorption of organic pollutants on activated coke. As adsorption continues, the sorption sites are gradually occupied by organic pollutants and the concentration difference between wastewater and activated coke decreases gradually and it, therefore eventually results in adsorption equilibrium. Therefore, it can be inferred that the adsorption system reaches equilibrium after contact between activated coke and printing and dyeing wastewater for 360 min. And contact time of 360 min is used in the subsequent adsorption experiments.

3.1.2. Effect of the activated coke concentration

The activated coke concentration is one of the most important factors influencing the treatment of printing and dyeing wastewater. The effect of activated coke concentration can provide theoretical support for the design and operation of printing and dyeing wastewater treatment system. The effect of activated coke dosage on the treatment of printing and dyeing wastewater by activated coke at 360 min is shown in Fig. 3. It can be seen that the COD concentration of printing and dyeing wastewater decreases gradually from 104.61–110.95 to 64.99–69.74 mg/L when the activated coke dosage is increased from 10 to 35 g/L. Accordingly, the removal efficiency of COD increases gradually from 29.78%–33.79% to 55.86%–58.87% with increasing the activated coke dosage from 10 to 35 g/L. This can be explained that the sorption sites of organic pollutants increase with an increase

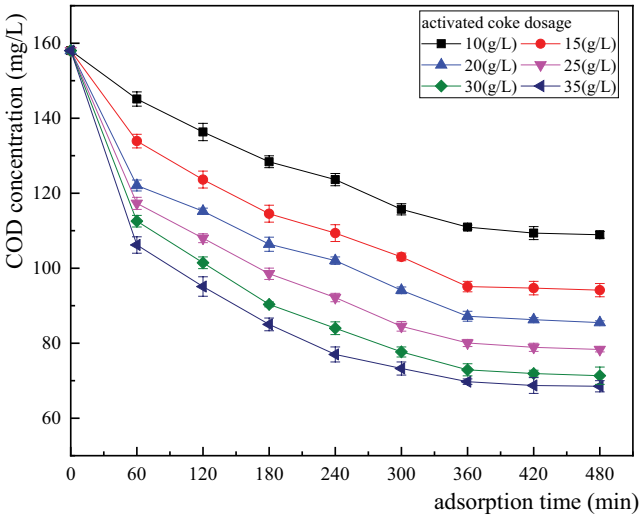

Fig. 2. The effect of adsorption time on the treatment of printing and dyeing wastewater by activated coke.

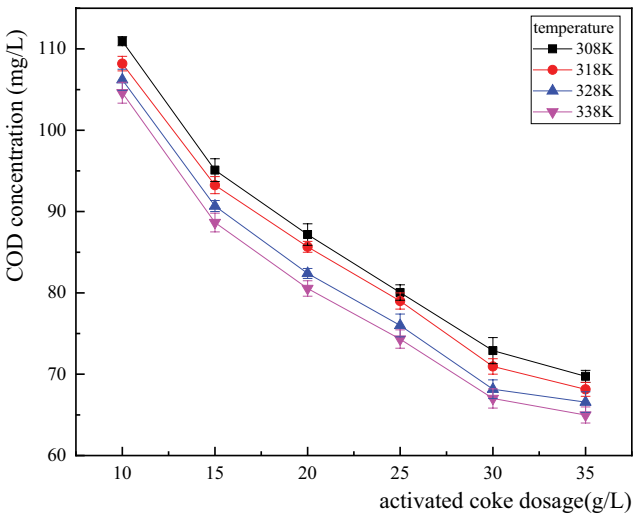

Fig. 3. The effect of activated coke dosage on the treatment of printing and dyeing wastewater by activated coke.

in activated coke dosage and it, therefore results in the decrease of COD concentration and the increase of COD removal efficiency. In addition, it is worth noting that the COD concentration of printing and dyeing wastewater at adsorption equilibrium is less than 80 mg/L at activated coke dosage of 30 g/L, which meets the direct discharge requirement for printing and dyeing wastewater.

3.1.3. Effect of the adsorption temperature

The effect of adsorption temperature on the treatment of printing and dyeing wastewater by activated coke at 360 min is shown in Fig. 4. It can be seen that the COD concentration of printing and dyeing wastewater decreases slightly from 69.74–110.95 to 64.99–104.61 mg/L when the adsorption temperature is increased from 308 K to 338 K. Accordingly, the removal efficiency of COD increases slightly from 29.78%–55.86% to 33.79%–58.87% with the increasing of adsorption temperature from 308 K to 338 K. This can be explained that molecular thermal motion increases with an increase in adsorption temperature, which accelerates the collision between organic pollutants in printing and dyeing wastewater and activated coke. However, an adsorption process involving low adsorption temperature may be suggested in practical application since adsorption temperature has weak effect on printing and dyeing wastewater treatment and low economic cost is obtained at low adsorption temperature.

In summary, considering the direct discharge requirement for printing and dyeing wastewater and economic cost, the absorption conditions for printing and dyeing wastewater treatment by activated coke are identified to be absorption time of 360 min, activated coke concentration of 30 g/L and absorption temperature of 308 K. And these absorption conditions can be used as the experiment conditions for the subsequent adsorption kinetics and isotherms experiments.

In addition, as mentioned earlier, the regeneration of spent activated coke can be evaluated via equilibrium adsorption test followed by regeneration and readsorption. Therefore, the absorption conditions determined in this section can also be used as the experiment conditions for reabsorption of regenerated activated coke.

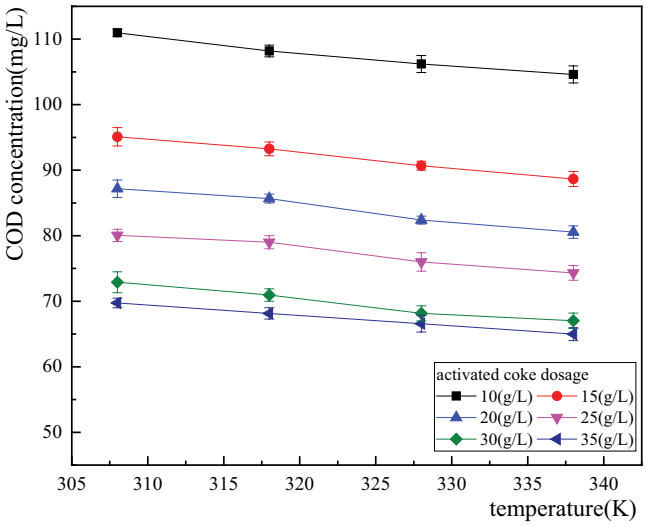

Fig. 4. The effect of adsorption temperature on the treatment of printing and dyeing wastewater by activated coke.

3.2. Adsorption behaviors

The adsorption kinetics and adsorption isotherms theories are used to study the adsorption behaviors of organic pollutants from printing and dyeing wastewater by activated coke.

3.2.1. Adsorption kinetics

Adsorption kinetics is a theory for studying adsorption rate, which can be used to evaluate adsorption process (including boundary layer diffusion, intraparticle diffusion and adsorption reaction). In order to evaluate the adsorption kinetics, the experimental data is fitted by two typical models: pseudo-first-order and pseudo-second-order kinetic models. The readership can refer to [37,38] to learn the specific theoretical methods of these models.

The linear fitting of adsorption kinetics data using two types of kinetic models is shown in Fig. 5. It can be found that the R^2 value for pseudo-first-order model is 0.9333, while the R^2 value for pseudo-second-order model

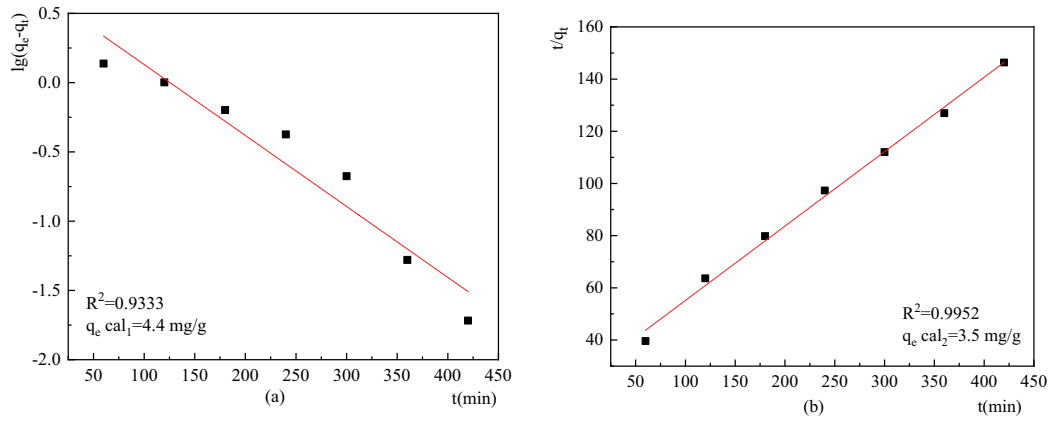

Fig. 5. The linear fitting of adsorption kinetics data using pseudo-first-order (a) and pseudo-second-order (b) kinetic models.

is 0.9952. The latter is significantly higher than the former and closer to unity. Moreover, the adsorption capacity of activated coke for COD determined by experiment ($q_{e,\exp}$) is 2.8 mg/g, while the values calculated by pseudo-first-order ($q_{e,cal1}$) and pseudo-second-order ($q_{e,cal2}$) kinetic models are 4.4 and 3.5 mg/g, respectively, indicating the agreement between calculated and experimental values in the pseudo-second-order kinetic model is better than that in the pseudo-first-order kinetic model. Therefore, it can be inferred that the adsorption process of organic pollutants in printing and dyeing wastewater by activated coke might follow the pseudo-second-order kinetic model, which indirectly indicates that the whole adsorption process is controlled by multiple steps.

3.2.2. Adsorption isotherms

The adsorption isotherm is a theory for studying adsorption equilibrium, which can be used to describe equilibrium relationships between adsorbent and adsorbate in the system. In order to evaluate the adsorption isotherms, the experimental data is fitted by two typical models: Langmuir and Freundlich models. The readership can refer to [39,40] to learn the specific theoretical methods of these models.

The linear fitting of adsorption isotherms data using two types of isotherms models is shown in Fig. 6. It can be found that the R^2 value for Langmuir model is 0.7014, while the R^2 value for Freundlich model is 0.9776. The latter is significantly higher than the former and closer to unity, which indicates the applicability of Freundlich model to adsorption of organic pollutants in printing and dyeing wastewater by activated coke.

3.3. Effects of the thermal regeneration conditions

The effects of regeneration temperature, regeneration time and flow rate of activation agent (CO_2) on the thermal regeneration efficiency of spent activated coke are studied to determine suitable thermal regeneration conditions and to demonstrate the feasibility of reusing spent activated coke by thermal regeneration.

3.3.1. Effect of the regeneration temperature

The effect of regeneration temperature on the thermal regeneration efficiency of spent activated coke under experiment conditions of regeneration time 30 min and flow rate of CO_2 150 mL/min is shown in Fig. 7. It can be found that the thermal regeneration efficiency of spent activated coke increases rapidly from 66.32% to 98.13% as the regeneration temperature increases from 773 K to 1073 K, and then the regeneration efficiency decreases with increasing temperature. This observation indicates that higher temperature has a negative effect on regeneration of spent activated coke. Because higher regeneration temperature can lead to the collapse of the original carbon pore structure, which reduces the adsorption capacity of the activated coke regenerated. Therefore, the regeneration temperature of spent activated coke is identified to be 1,073 K, which is selected in the subsequent thermal regeneration experiments.

3.3.2. Effect of the regeneration time

The effect of regeneration time on the thermal regeneration efficiency of spent activated coke under experiment conditions of regeneration temperature 1,073 K and flow rate of CO_2 150 mL/min is shown in Fig. 8. It can be found that at the regeneration time below 30 min, the thermal regeneration efficiency of spent activated coke increases from 77.64% to 98.13% with increasing regeneration time. It is readily understood that CO_2 is used to eliminate the

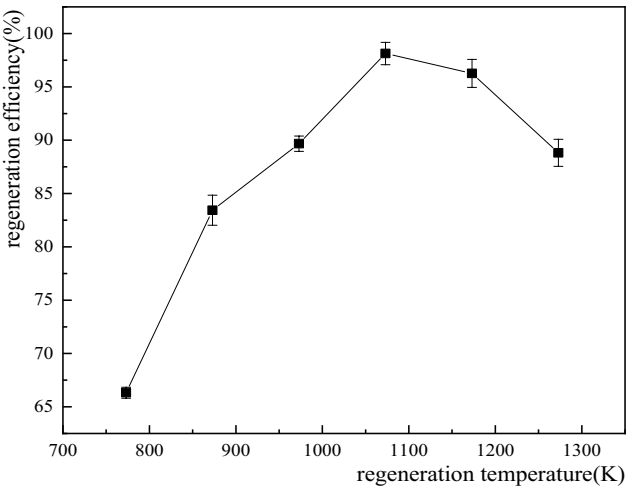

Fig. 7. The effect of regeneration temperature on the thermal regeneration efficiency of spent activated coke.

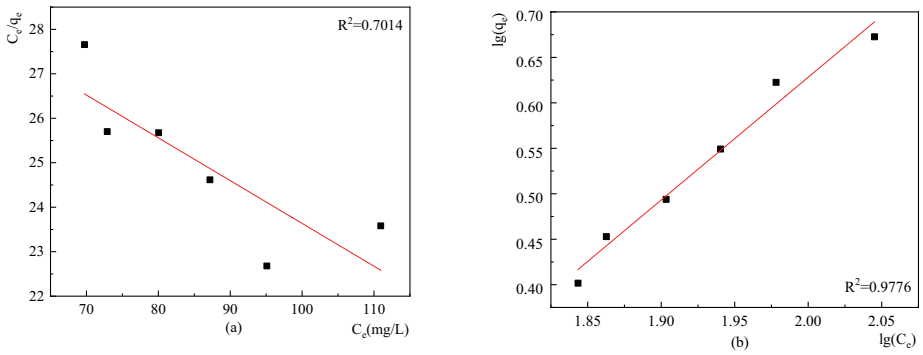

Fig. 6. The linear fitting of adsorption isotherms data using Langmuir (a) and Freundlich (b) models.

charred residues derived from the adsorbed organic matter so that the original carbon pore is exposed. The charred residues removed by CO_2 increase with an increase in regeneration time, which eventually results in maximum recovery of original carbon pore. However, the thermal regeneration efficiency of spent activated coke decreases from 98.13% to 86.26% with increasing regeneration time from 30 min to 50 min. This can be explained that if the thermal regeneration time is too long, the activation agent CO_2 will react with the carbon-based material of the activated coke itself, thus damaging the original carbon pore structure. Therefore, the regeneration time of spent activated coke is identified to be 30 min, which is selected in the subsequent thermal regeneration experiments.

3.3.3. Effect of the flow rate of CO_2

The effect of flow rate of CO_2 on the thermal regeneration efficiency of spent activated coke under experiment conditions of regeneration temperature 1,073 K and regeneration time 30 min is shown in Fig. 9. It can be found that with the increase of flow rate, the thermal regeneration efficiency of spent activated coke increases and reaches the maximum value at flow rate of CO_2 150 mL/min, and then the thermal regeneration efficiency decreases with increasing flow rate of CO_2. Similar to the effect of regeneration time, the use of less CO_2 results in the incomplete elimination of accumulated charred residues and recovery of original carbon pore cannot be maximized. On the contrary, the use of more CO_2 leads to damage to the original carbon pore structure. Therefore, it is important to identify the flow rate of CO_2 for the thermal regeneration. And the flow rate of CO_2 is set at 150 mL/min in thermal regeneration experiments.

In summary, in order to achieve the maximum regeneration of spent activated coke, the thermal regeneration conditions are identified to be regeneration temperature of 1,073 K, regeneration time of 30 min and flow rate of CO_2 of 150 mL/min.

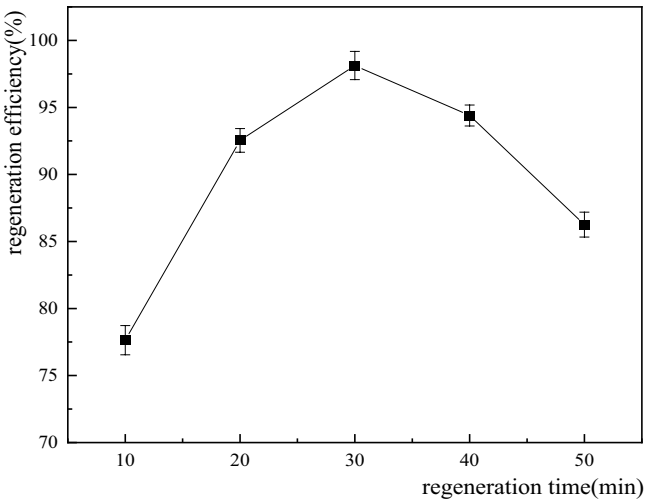

Fig. 8. The effect of regeneration time on the thermal regeneration efficiency of spent activated coke.

3.4. Adsorption-regeneration cycles of activated coke

As it is well known, the cyclic reusability of activated coke plays a key role in its practical application. Thus, based on the previously determined absorption conditions (absorption time of 360 min, activated coke concentration of 30 g/L and absorption temperature of 308 K) and thermal regeneration conditions (regeneration temperature of 1,073 K, regeneration time of 30 min and flow rate of CO_2 of 150 mL/min), the successive adsorption-regeneration cycles are carried out to evaluate the reusability of activated coke for organic pollutants removal from printing and dyeing wastewater. The regeneration efficiency of activated coke in ten successive adsorption-regeneration cycles is shown in Fig. 10. It can be found that the regeneration efficiency of activated coke decreases slightly with the increasing of cycle time, however, it remains very high in ten successive adsorption-regeneration cycles. The regeneration efficiency after the tenth cycle is 92.54%, which is only 5.7% lower than that of the first cycle. The results indicate

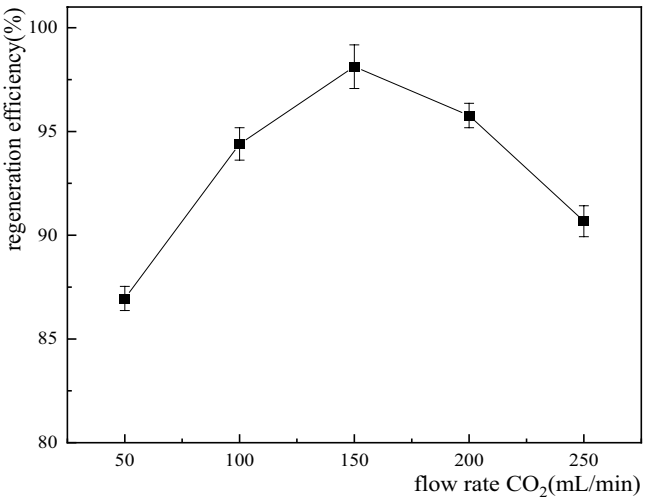

Fig. 9. The effect of flow rate of CO_2 on the thermal regeneration efficiency of spent activated coke.

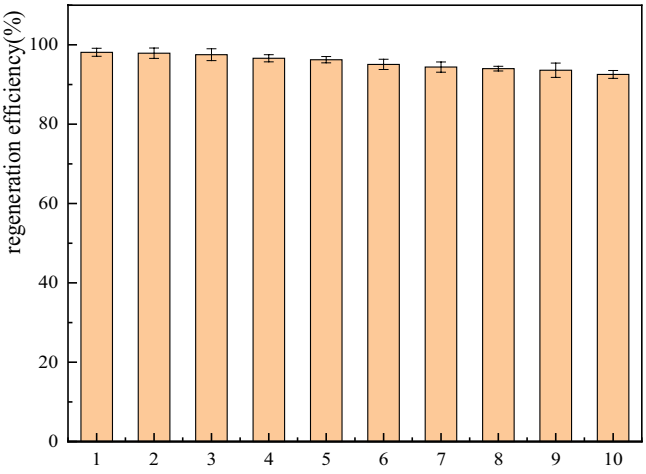

Fig. 10. Regeneration efficiency of activated coke in ten successive adsorption-regeneration cycles.

that activated coke exhibits high reusability for organic pollutants removal in the successive adsorption-regeneration cycles and thermal regeneration is a feasible way for reusing the spent activated coke.

4. Conclusions

In this study, activated coke is used to remove organic pollutants from printing and dyeing wastewater and spent activated coke is reused by thermal regeneration. The following conclusions can be drawn from the present work:

Activated coke is effective for the removal of organic pollutants from printing and dyeing wastewater (initial COD concentration 158 mg/L). The absorption conditions for printing and dyeing wastewater treatment by activated coke are identified to be absorption time of 360 min, activated coke concentration of 30 g/L and absorption temperature of 308 K. And the COD removal can meet the printing and dyeing wastewater discharge requirement under these absorption conditions. After absorption, the COD concentration is 72.9 mg/L and 53.86% of COD can be removed.

The adsorption kinetics analysis indicates that the pseudo-second-order kinetic model describes the adsorption process of organic pollutants in printing and dyeing wastewater by activated coke with a good fitting. The adsorption isotherms analysis discloses that the absorption data of organic pollutants in printing and dyeing wastewater by activated coke fits well to Freundlich isotherm model.

The thermal regeneration is a feasible way for reusing the spent activated coke. The thermal regeneration conditions for spent activated coke are identified to be regeneration temperature of 1,073 K, regeneration time of 30 min and flow rate of CO_2 of 150 mL/min, under which the highest thermal regeneration efficiency (98.13%) of spent activated coke is obtained. In addition, activated coke exhibits high reusability for organic pollutants removal in the successive adsorption-regeneration cycles and the regeneration efficiency after the tenth cycle is 92.54%.

Acknowledgments

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References

[1] Y. Zhu, J. Xu, X. Cao, Y. Cheng, Characterization of functional microbial communities involved in different transformation stages in a full-scale printing and dyeing wastewater treatment plant, Biochem. Eng. J., 137 (2018) 162–171.
[2] J. Wang, T. Zhang, Y. Mei, B. Pan, Treatment of reverse-osmosis concentrate of printing and dyeing wastewater by electro-oxidation process with controlled oxidation-reduction potential (ORP), Chemosphere, 201 (2018) 621–626.
[3] R. Wang, X. Jin, Z. Wang, W. Gu, Z. Wei, Y. Huang, Z. Qiu, P. Jin, A multilevel reuse system with source separation process for printing and dyeing wastewater treatment: a case study, Bioresour. Technol., 247 (2018) 1233–1241.
[4] A.K. Swain, A. Sahoo, H.M. Jena, H. Patra, Industrial wastewater treatment by Aerobic Inverse Fluidized Bed Biofilm Reactors (AIFBBRs): a review, J. Water Process Eng., 23 (2018) 61–74.
[5] M.H. Zhang, H. Dong, L. Zhao, D.X. Wang, D. Meng, A review on Fenton process for organic wastewater treatment based on optimization perspective, Sci. Total Environ., 670 (2019) 110–121.
[6] R. Mailler, J. Gasperi, Y. Coquet, S. Deshayes, S. Zedek, C.C. Olive, N. Cartiser, V. Eudes, A. Bressy, E. Caupos, R. Moilleron, G. Chebbo, V. Rocher, Study of a large scale powdered activated carbon pilot: removals of a wide range of emerging and priority micropollutants from wastewater treatment plant effluents, Water Res., 72 (2015) 315–330.
[7] A.S. Ruhl, F. Zietzschmann, I. Hilbrandt, F. Meinel, J. Altmann, A. Sperlich, M. Jekel, Targeted testing of activated carbons for advanced wastewater treatment, Chem. Eng. J., 257 (2014) 184–190.
[8] W. Wang, S. Deng, D. Li, L. Ren, D. Shan, B. Wang, J. Huang, Y. Wang, G. Yu, Sorption behavior and mechanism of organophosphate flame retardants on activated carbons, Chem. Eng. J., 332 (2018) 286–292.
[9] F. Meinel, F. Zietzschmann, A.S. Ruhl, A. Sperlich, M. Jekel, The benefits of powdered activated carbon recirculation for micropollutant removal in advanced wastewater treatment, Water Res., 91 (2016) 97–103.
[10] W. Wang, A. Maimaiti, H. Shi, R. Wu, R. Wang, Z. Li, D. Qi, G. Yu, S. Deng, Adsorption behavior and mechanism of emerging perfluoro-2-propoxypropanoic acid (GenX) on activated carbons and resins, Chem. Eng. J., 364 (2019) 132–138.
[11] H. Javed, D.X. Luong, C.G. Lee, D. Zhang, J.M. Tour, P.J.J. Alvarez, Efficient removal of bisphenol-A by ultra-high surface area porous activated carbon derived from asphalt, Carbon, 140 (2018) 441–448.
[12] S.J. Zhang, T. Shao, H.S. Kose, T. Karanfil, Adsorption of aromatic compounds by carbonaceous adsorbents: a comparative study on granular activated carbon, activated carbon fiber, and carbon nanotubes, Environ. Sci. Technol., 44 (2010) 6377–6383.
[13] W. Zhang, Q.G. Chang, W.D. Liu, B.J. Li, W.X. Jiang, L.J. Fu, W.C. Ying, Selecting activated carbon for water and wastewater treatability studies, Environ. Prog., 26 (2007) 289–298.
[14] G.S. Miguel, S.D. Lambert, N.J.D. Graham, The regeneration of field-spent granular activated carbons, Water Res., 35 (2001) 2740–2748.
[15] M.H. Zhang, Q.L. Zhao, X. Bai, Z.F. Ye, Adsorption of organic pollutants from coking wastewater by activated coke, Colloids Surf., A, 362 (2010) 140–146.
[16] K. Tong, Y. Zhang, D. Fu, X. Meng, Q. An, P.K. Chu, Removal of organic pollutants from super heavy oil wastewater by lignite activated coke, Colloids Surf., A, 447 (2014) 120–130.
[17] K. Tong, A. Lin, G. Ji, D. Wang, X. Wang, The effects of adsorbing organic pollutants from super heavy oil wastewater by lignite activated coke, J. Hazard. Mater., 308 (2016) 113–119.
[18] M. Zheng, Y. Han, C. Xu, Z. Zhang, H. Han, Selective adsorption and bioavailability relevance of the cyclic organics in anaerobic pretreated coal pyrolysis wastewater by lignite activated coke, Sci. Total Environ., 653 (2019) 64–73.
[19] Y. Itaya, K. Kawahara, C.W. Lee, J. Kobayashi, N. Kobayashi, S. Hatano, S. Mori, Dry gas cleaning process by adsorption of H_2S into activated cokes in gasification of carbon resources, Fuel, 88 (2009) 1665–1672.
[20] Z. Qie, Z. Zhang, F. Sun, L. Wang, X. Pi, J. Gao, G. Zhao, Effect of pore hierarchy and pore size on the combined adsorption of SO_2 and toluene in activated coke, Fuel, 257 (2019) 116090, doi: 10.1016/j.fuel.2019.116090.
[21] P. Lu, R. Li, Y. Xing, Y. Li, T. Zhu, H. Yue, W. Wu, Low temperature selective catalytic reduction of NO_X with NH_3 by activated coke loaded with $Fe_xCo_yCe_zO_m$: the enhanced activity, mechanism and kinetics, Fuel, 233 (2018) 188–199.
[22] H. An, Z. Liu, X. Cao, J. Teng, W. Miao, J. Liu, R. Li, P. Li, Mesoporous lignite-coke as an effective adsorbent for coal gasification wastewater treatment, Environ. Sci.-Water Res., 3 (2017) 169–174.
[23] P. Li, N. Ailijiang, X. Cao, T. Lei, P. Liang, X. Zhang, X. Huang, J. Teng, Pretreatment of coal gasification wastewater by adsorption using activated carbons and activated coke, Colloids Surf., A, 482 (2015) 177–183.

[24] J. Zhan, H. Wang, X. Pan, J. Wang, G. Yu, S. Deng, J. Huang, B. Wang, Y. Wang, Simultaneous regeneration of p-nitrophenol-saturated activated carbon fiber and mineralization of desorbed pollutants by electro-peroxone process, Carbon, 101 (2016) 399–408.
[25] R.M. Narbaitz, J. McEwen, Electrochemical regeneration of field spent GAC from two water treatment plants, Water Res., 46 (2012) 4852–4860.
[26] J. Zhan, Y. Wang, H. Wang, W. Shen, X. Pan, J. Wang, G. Yu, Electro-peroxone regeneration of phenol-saturated activated carbon fiber: the effects of irreversible adsorption and operational parameters, Carbon, 109 (2016) 321–330.
[27] L. Dong, W. Liu, R. Jiang, Z. Wang, Physicochemical and porosity characteristics of thermally regenerated activated carbon polluted with biological activated carbon process, Bioresour. Technol., 171 (2014) 260–264.
[28] F.S. Cannon, V.L. Snoeyink, R.G. Lee, G. Dagois, Reaction mechanism of calcium-catalysed thermal regeneration of spent granular activated carbon, Carbon, 32 (1994) 1285–1301.
[29] R.A. Hutchins, Economic factors in granular carbon thermal regeneration, Chem. Eng. Prog., 69 (1973) 48–55.
[30] C.T. Murunaka, C. Julcour, A.M. Wilhelm, H. Delmas, C.A.O. Nascimento, Regeneration of activated carbon by (photo)-fenton oxidation, Ind. Eng. Chem. Res., 49 (2010) 989–995.
[31] A.H. Gorji, A. Sayari, Thermal, oxidative, and CO_2-induced degradation of supported polyethylenimine adsorbents, Ind. Eng. Chem. Res., 51 (2012) 6887–6894.
[32] X.H. Duan, C. Srinivasakannan, J.S. Liang, Process optimization of thermal regeneration of spent coal based activated carbon using steam and application to methylene blue dye adsorption, J. Taiwan Inst. Chem. Eng., 45 (2014) 1618–1627.
[33] R. Berenguer, J.P.M. Lozar, C. Quijada, D.C. Amorós, E. Morallón, Comparison among chemical, thermal, and electrochemical regeneration of phenol-saturated activated carbon, Energy Fuel, 24 (2010) 3366–3372.
[34] A.L. Cazetta, O.P. Junior, A.M.M. Vargas, A.P. Silva, X.X. Zou, T. Asefa, V.C. Almeida, Thermal regeneration study of high surface area activated carbon obtained from coconut shell: characterization and application of response surface methodology, J. Anal. Appl. Pyrolysis, 101 (2013) 53–60.
[35] Y. Li, Y. Lin, B. Wang, S. Ding, F. Qi, T. Zhu, Carbon consumption of activated coke in the thermal regeneration process for flue gas desulfurization and denitrification, J. Cleaner Prod., 228 (2019) 1391–1400.
[36] X. Cui, H. Yi, X. Tang, S. Zhao, K. Yang, B. Yan, C. Li, X. Yang, T. Feng, Y. Ma, Study of the properties of adsorption of SO_2-thermal regeneration cycle of activated coke modified by oxidization, J. Chem. Technol. Biotechnol., 93 (2018) 720–729.
[37] Ö. Ayla, A. Gönül, T. Meral, The biosorption of acid red 337 and acid blue 324 on *Enteromorpha prolifera*: the application of nonlinear regression analysis to dye biosorption, Chem. Eng. J., 112 (2005) 181–190.
[38] Y. Yao, F. Xu, M. Chen, Z. Xu, Z. Zhu, Adsorption behavior of methylene blue on carbon nanotubes, Bioresour. Technol., 101 (2010) 3040–3046.
[39] Ö. Ayla, A. Gönül, T. Meral. Biosorption of acid blue 290 (AB 290) and acid blue 324 (AB 324) dyes on spirogyra rhizopus, J. Hazard. Mater., 135 (2006) 355–364.
[40] P. Hadi, M. Xu, C. Ning, C.S.K. Lin, G. McKay, A critical review on preparation, characterization and utilization of sludge-derived activated carbons for wastewater treatment, Chem. Eng. J., 260 (2015) 895–906.