



Insight into the effects of biochar as adsorbent and microwave receptor from one-step microwave pyrolysis of sewage sludge

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Abstract

The effect of biochar, derived from one-step microwave pyrolysis of sewage sludge (OMPSS), on the removal of industrial wastewater (eosin and safranin T) was investigated in this study. Meanwhile, the multiple-reuse potential of biochar as microwave receptor to raise the pyrolysis temperature was also tested during the pyrolysis process. The results showed that OMPSS prepared adsorbents had excellent adsorption performance, achieving the highest removal efficiencies of 97.3 and 95.9% for eosin and safranin T, respectively. Further analysis indicated that this was due to its appropriate porous structure and surface chemistry characteristics, where the S_{BET} and pore volume of adsorbent AC-1 reached 459 m²/g and 0.23 cm³/g, respectively. The multiple reuses of biochar adsorbents after five times as microwave receptor was feasible, where the pyrolysis temperature could increase sharply from room temperature to 800 °C within 5 min. The mechanism analysis revealed that the limiting stage of adsorption was chemical sorption. This research provided an alternative way for the preparation of functional adsorbent and microwave receptor.

Keywords OMPSS · Microwave receptor · Sewage sludge · Adsorbent · Dual effect

Introduction

Municipal sewage sludge is generated in wastewater treatment plants in the process of sewage treatment, and the waste stream of sewage sludge is rapidly growing worldwide. In China, for example, over 30 million tons (dry solids) of treated sludge is produced with the increasing rate of 10–15% each year (Tian et al. 2013; Zhang et al. 2014, 2017a, b). Moreover, sewage sludge is composed of organic, pathogenic, and toxic substances. If not disposed of properly, serious pollution problem would follow. Thus, the handling of sewage sludge is one

of the most significant challenges in wastewater management. The conventional application of sewage sludge on agricultural land, landfill, and incineration faces significant difficulty due to health, environmental, and social concerns (Smith et al. 2009). Consequently, it is of interest to search for innovative approaches for beneficial use of sewage sludge.

Since sewage sludge contains the high content of organic matter, it is reasonable to use this carbonaceous matter as raw material in the preparation of carbonaceous adsorbents. This would not only solve the pollution problem of sewage sludge but provide a sustainable waste-to-resource way of producing adsorbent for wastewater treatment. Recently, the feasibility of using sludge to produce adsorbent has been demonstrated by chemical and physical activation methods. For adsorbents produced by carbonization, the highest BET surface areas from the carbonization of sewage sludge were reported to be 359 m²/g (Zhai et al. 2004) and 141 m²/g (Seredych and Bandosz 2007), respectively. The optimum carbonization temperature for maximizing the BET surface area was mainly depended on the composition of different sewage sludge (Smith et al. 2009). Physical activation produced adsorbents typically exhibit relatively low surface areas. Ros (Ros et al. 2006) reported a surface area of only 55 m²/g through the air/N₂ mixture activation, and the highest BET surface area

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was 226 m²/g obtained by a two-stage procedure consisting of carbonization followed by activation (Rio et al. 2006). It should be noted that the adsorbent produced after an activation step was generally referred to as activated carbon. As regards adsorbents produced by chemical activation, the BET surface areas reported in the studies were usually in the ranges of 658–1882 m²/g, where KOH, NaOH, ZnCl₂, H₂SO₄, and H₃PO₄ were reported as the most effective activation reagents (Smith et al. 2009).

Based on the above analysis, it was noted that the large surface areas of prepared adsorbents were all produced by a two-stage procedure, whereby the sludge was carbonized first and then impregnated and activated with chemical reagents or gas mixture. This two-step procedure makes the production of adsorbent complex and difficult because many issues need to be considered during the process. In addition, although chemical activation achieves larger BET surface area compared with other methods, a large number of chemical agents are required leading to the high cost of adsorbent production (Li et al. 2011).

In this study, a one-step microwave pyrolysis method (OMPSS) was proposed to prepare biochar adsorbent and microwave receptor simultaneously. Microwave pyrolysis has distinctive advantages of rapid heating, low temperature of reactor wall, and less PAH release than the conventional pyrolysis, which is regarded as a potential technology for sludge pyrolysis to recover energy efficiently. The cost of producing sludge-based activated carbon was reduced significantly since the microwave pyrolysis time was usually less than 10 min, in which the carbonization and activation steps proceeded simultaneously. Additional benefit would be generated from the application of this carbon adsorbent for wastewater treatment where no chemical agents were introduced. Therefore, the objective of the present work was to investigate the feasibility of OMPSS method to prepare sludge-based adsorbent. The surface area and porous structure, surface morphology, and chemistry structure of prepared adsorbents were characterized. Besides, the reuse potential of prepared adsorbents during microwave pyrolysis process was explored. Moreover, the adsorption performance and mechanism of dye wastewater such as eosin and safranin T on prepared adsorbents were investigated. This work could provide an alternative way for production of sewage sludge-based biochar adsorbents and microwave receptors.

Materials and methods

Adsorbents preparation

The raw sewage sludge was collected from a municipal wastewater treatment plant in Harbin, China. Sludge sample was

first dried at 105 °C up to constant weight and then ground and sieved to a desired particle size.

Microwave pyrolysis of sewage sludge was conducted in a fixed-bed device, and its detailed operation information was given in previous studies (Zhang et al. 2017a, b). The one-step preparation of carbon adsorbents (OMPSS) was conducted under the optimum conditions with microwave power of 1200 W, irradiation time of 10 min, and dosing ratio of 1:3.5 (microwave receptor/sludge, wt.%) according to our previous study (Zuo et al. 2011). Since the sewage sludge was transparent to microwave irradiation. Thus, before pyrolysis, sewage sludge using as precursor was impregnated with commercial activated carbon (AC-C, Tianjin Benchmark Chemical Reagent Co. Ltd., China) which played the roles as microwave receptor. Furthermore, the obtained biochar adsorbent (activated carbon product) after one-time pyrolysis, namely AC-1, was recycled as microwave receptor to evaluate its reuse potential during microwave pyrolysis. Consequently, the adsorbents of AC-2 to AC-5 were prepared after two-time to five-time pyrolysis reactions based on the method mentioned above.

Adsorption experiments

Adsorption tests of eosin and safranin T were conducted in a thermostated shaker at 25 °C and stirred at 150 rpm for adsorption. The concentrations of eosin and safranin T solutions were determined in a UV-Vis spectrophotometer by measuring the light absorbance at a wavelength of 516 and 553 nm, respectively.

For the kinetic studies, 200 mg of prepared adsorbents was mixed in stoppered flasks with 100 mL of dye solutions under their optimum pH of 3 and 8, respectively. During adsorption experiments, pH of aqueous solutions was adjusted and maintained by HNO₃ or NH₃·H₂O. The initial eosin and safranin T concentrations were 100 mg/L, respectively. The concentrations of eosin and safranin T solutions were measured at different sampling times. The adsorption efficiency (%) of dyes was calculated by Eq. (1):

$$D = \frac{(C_0 - C)}{C_0} \times 100\% \quad (1)$$

where C₀ (mg/L) and C (mg/L) are the solute concentrations of eosin and safranin T at initial and sampling time, respectively.

For the isotherm experiments at 25 °C, different flasks containing 100 mL of solutions and different amounts of adsorbent were stirred during the equilibrium time and the amounts of adsorbates retained in equilibrium (q_e) were calculated. All the above experiments were duplicated under the same experimental conditions.

Characterization of prepared adsorbents

The iodine value for the prepared adsorbents was measured according to Chinese standard (GB/T 12496.8–1999). The surface area (S_{BET}) and porosity of adsorbents were characterized by nitrogen adsorption at 77 K in a sorptometer (Nowa 4000, Quantachrome, USA). Prior to analysis, the samples were degassed at 150 °C for 8 h until a pressure below 10^{-3} Torr was reached. The surface morphology of adsorbents was observed by a scanning electron microscopy (SEM, JSM-6700F, Japan), and the types of the crystalline phases were characterized by X-ray with Cu K α radiation (XRD: P|max- $\gamma\beta$, Rigaku, Japan). The range of 2-theta used for the XRD analysis was ranged between 10° and 90°. For FTIR characterization, a fixed weight of each sample was mixed with KBr before analysis. Transmission measurements were carried out in the 4000–400 cm^{-1} region with a spectrometer (Perkin Elmer Spectrum, GX, USA) at a resolution of 4 cm^{-1} .

Results and discussion

Characterization of prepared adsorbents

Surface area and porous structure

The main factors affecting the adsorption performance of adsorbents were the specific surface area, pore volume, and pore size distribution (Marques et al. 2011; Monsalvo et al. 2011). The values of the BET surface area and porous parameters of different carbon adsorbents are shown in Table 1. It can be found that S_{BET} and pore volume of AC-1 reached 459 m^2/g and 0.23 cm^3/g , respectively, accounting for about 70% of the BET surface area of commercial adsorbent (AC-C). This result indicated that the pore structure of AC-1 developed well during microwave pyrolysis. However, the S_{BET} and pore volume of AC-5 were reduced significantly after multiple reuses in the pyrolysis process, suggesting the porous structure in the AC-5 was destroyed and sintered contributing to the decline of adsorption capacity finally. With respect to the BET surface area, the adsorbents prepared by the one-step microwave pyrolysis presented competitive advantage compared with the

conventional pyrolysis methods. The maximum S_{BET} reached 141 m^2/g when sewage sludge was used as the single precursor to produce adsorbents during conventional pyrolysis (Seredych and Bandosz 2007). Marques (Marques et al. 2011) reported that the highest S_{BET} attained by CO_2 activation and carbonization was 228 and 153 m^2/g , respectively, both of which were less than 459 m^2/g of AC-1 obtained in this study. Through the literatures (Bagreev and Bandosz 2004; Smith et al. 2009), it was found that the carbon adsorbents produced by physical activation or carbonization did not exhibit S_{BET} in excess of 300 m^2/g for the sewage sludge-based adsorbents.

The pore size distribution of adsorbent determined its selective adsorption capacity. From Table 1, the average pore size of 3.1 and 8.6 nm was obtained for the adsorbents of AC-1 and AC-5, which was located in the mesopore range (2–50 nm), while the AC-C pore size was less than 2 nm indicating the micropore structures were the dominating pores in this adsorbent. The major mesopore structure of sludge adsorbent was also reported by other researches (Liu et al. 2010; Stüber et al. 2011). The capillary condensation of mesopores under certain relative pressure would contribute to the adsorption of some molecules that could not enter the micropores (Wen et al. 2011). Thus, the mesopore structure of adsorbents displayed an important effect on the adsorption of macromolecules. It was believed that the predominant mesoporous adsorbents were derived from the evolution of organic matter during pyrolysis. Based on the above analysis, it was supposed that the competitive S_{BET} and dominating mesoporous structures of AC-1 adsorbent might arise from the special heating characteristic of microwave pyrolysis process. Different from the conventional pyrolysis, sewage sludge in the microwave heating system was heated inside and outside synchronously leading to the sharp decrease of residence time during microwave pyrolysis (Zhang et al. 2017c).

Surface morphology

SEM analysis on the different adsorbents is shown in Fig. 1. The results presented that AC-1 had rough areas containing various irregular-shaped porous structures including both the macropores and more transitional pores internally, and AC-C possessed mainly the abundant micropores. However, the adsorbent surface of AC-5 was quite dense and even no pores existing, indicating multiple reuses of this biochar adsorbent resulted in the destruction of porous structure during pyrolysis. Those pores with different size and shape could influence the adsorption performances of carbon adsorbents in different degrees because the adsorbate would firstly pass through them before reaching the adsorptive site (Wen et al. 2011). From Fig. 1, some impurities on the surface and wall of the pores were also found which might contribute to the negative effect on the adsorption capacity of adsorbents.

Table 1 BET surface area of different adsorbents

Sample	S_{BET} (m^2/g)	D_p (nm)	V_t (cm^3/g)
AC-1	459	3.10	0.23
AC-2	378	4.66	0.18
AC-3	265	5.18	0.13
AC-4	106	7.82	0.05
AC-5	85	8.60	0.03
AC-C	650	1.95	0.38

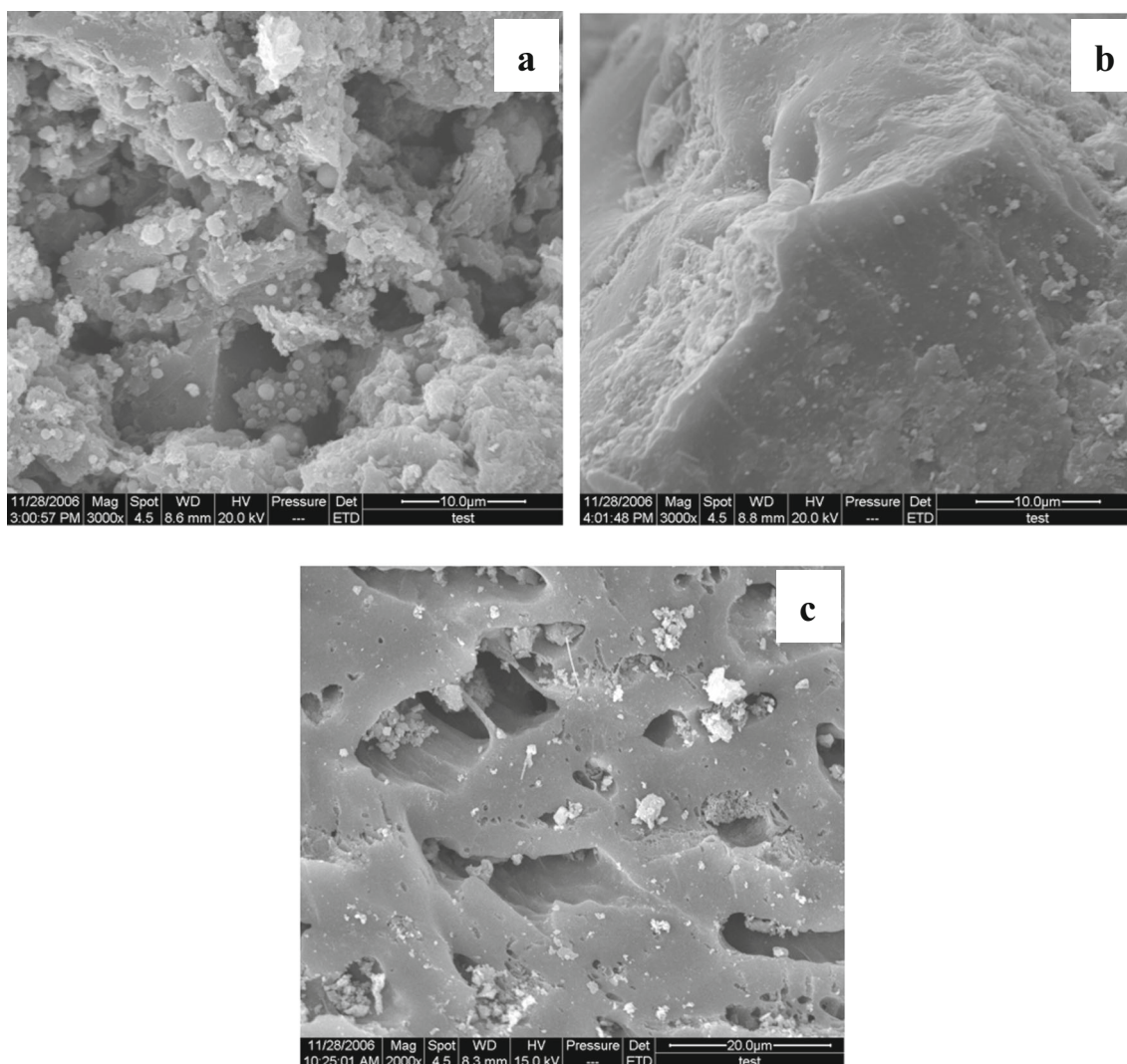


Fig. 1 SEM images of different adsorbents: **a** AC-1, **b** AC-5, **c** AC-C

Surface chemistry structure

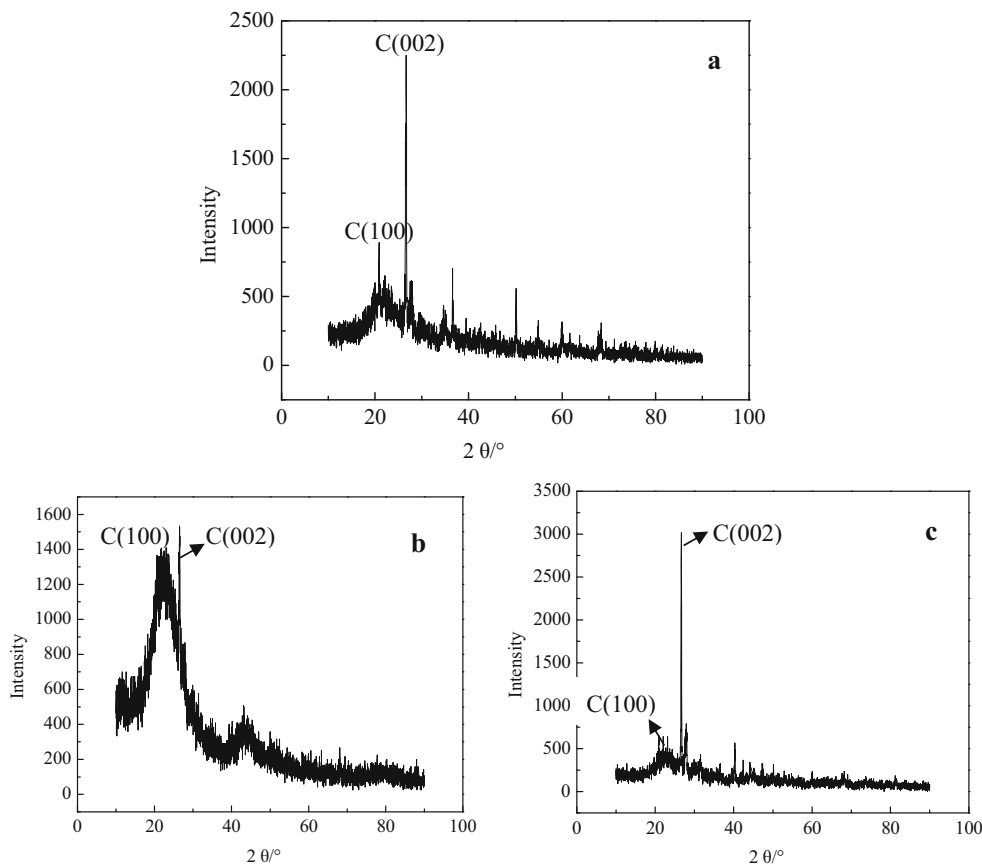
The crystallization conditions of dried sludge and adsorbents prepared by pyrolysis were characterized by XRD. The XRD patterns of samples are shown in Fig. 2. It can be seen that all the samples displayed certain degree of microcrystalline structures, but the arrangement of these carbon crystallites was irregular in the form of amorphous structure. For the sewage sludge-based adsorbents, the sludge carbon exhibited two peaks at around $2\theta = 23^\circ$ and 26° , corresponding to the (100) and (002) planes of the typical carbon materials, respectively (Martins et al. 2007). The result demonstrated that the carbon structure was not destroyed after microwave pyrolysis. It was noted that a significant increase of peak intensity at $2\theta = 23^\circ$ was observed for the adsorbent AC-1, which was consistent with the newly generated porous structure of AC-1 during the pyrolysis.

Multiple-reuse potential of prepared adsorbents

Heating characteristics during microwave pyrolysis

At normal condition, the pyrolysis temperature did not exceed 300°C by direct pyrolysis of sewage sludge without microwave receptor, because most of sludge compositions were transparent to microwave irradiation (Domínguez et al. 2006, 2003) and could not absorb this kind of energy. Thus, it was important to impregnate microwave receptor in the sludge to achieve high temperature during pyrolysis. The temperature rising curves of sewage sludge impregnated with different adsorbents (AC-1 to AC-5) as microwave receptors are shown in Fig. 3. The temperature rising curves showed the similar trends, where the temperatures of sludge increased sharply to reach 800°C at 5 min and then maintained the steady state until the end. The results indicated that the multiple reuses of biochar products (adsorbents) as microwave

Fig. 2 The XRD spectrum of dried sludge (a), AC-1 (b), and AC-5 (c)



receptor was feasible during microwave pyrolysis of sewage sludge, which provided a cost-effective way for the application of prepared adsorbents.

Particle size and iodine value of adsorbents

The carbon adsorbents obtained after pyrolysis were sieved into four groups including 20, 40, 60, and > 60 mesh. The variations of particle size and their corresponding iodine value

of different adsorbents were examined, and results are shown in Figs. 4 and 5. It was seen that the masses of 20 mesh and 40 mesh particles gradually decreased with the increase of reuse times, while the former changed slightly after three times of reuse possibly resulting from the bulk aggregation. Different from the stable state of 60 mesh, the mass of > 60 mesh particle increased gradually with the increasing reuse time. It was also noted that 40-mesh particles dominated in the AC-1 and AC-2, while the > 60 mesh played the leading role for AC-3 to AC-5. As for the iodine values of different adsorbents, it was

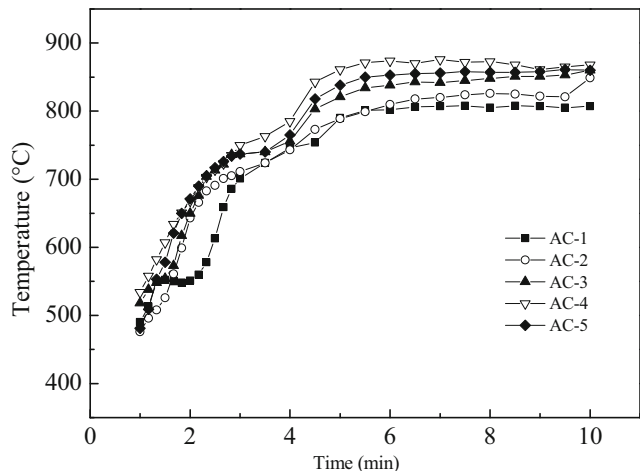


Fig. 3 Temperature rising curve of sewage sludge impregnated with different adsorbents as microwave receptors

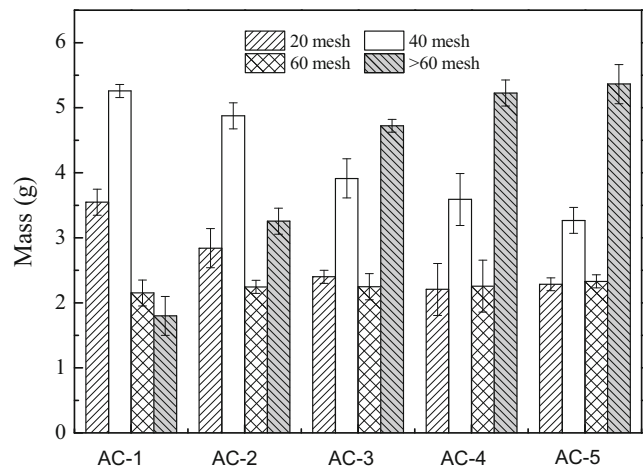


Fig. 4 Particle size distribution of multiple-reuse adsorbents

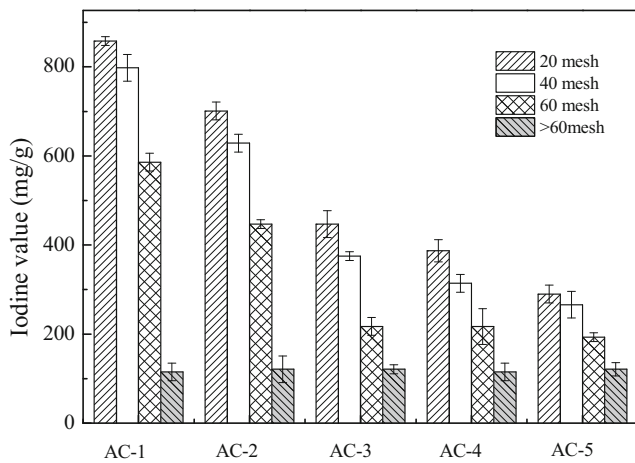


Fig. 5 The effect of particle size on the iodine values of different adsorbents

found that the total iodine value of each adsorbent decreased with the rise of reuse time. In detail, the iodine value contribution of 20-, 40-, and 60-mesh particles declined with multiple reuses. However, it remained stable for the particle size of > 60 mesh. Considering the changing trend of surface area of adsorbents, the iodine value displayed a positive relationship with the surface area. It was reported that iodine value can represent the surface area contributed by pores larger than 1 nm and was a good indication of the adsorption capacity of a carbonaceous adsorbent for water pollutant removal (Lin et al. 2012; Satya Sai et al. 1997). Therefore, based on the above analysis on the surface area, porous structure, heating characteristic, and iodine value of each adsorbent, the AC-1 was supposed to be the better one among all the adsorbents and will be used for the industrial wastewater adsorption in the following studies.

Adsorption performance of prepared adsorbents

Adsorption capacity

To investigate the adsorption performance of eosin and safranin T, AC-1 and AC-C were selected as the adsorbents for the dye wastewater removal in this section. The removal efficiency curve of AC-1 with different adsorption times under the optimum pH and dosage was presented in Fig. 6. It can be seen that both the removal rate of eosin and safranin T increased rapidly with the adsorption time at the initial stage and then gradually stabilized. The highest removal efficiency of eosin and safranin T achieved 97.3 and 95.9% respectively under their optimum adsorption time of 320 and 490 min. It was reported that under the optimum pH of acidic (eosin) and basic (safranin T) conditions, the competitive influence of OH⁻ in the acidic solution and H⁺ in the basic solution was inhibited

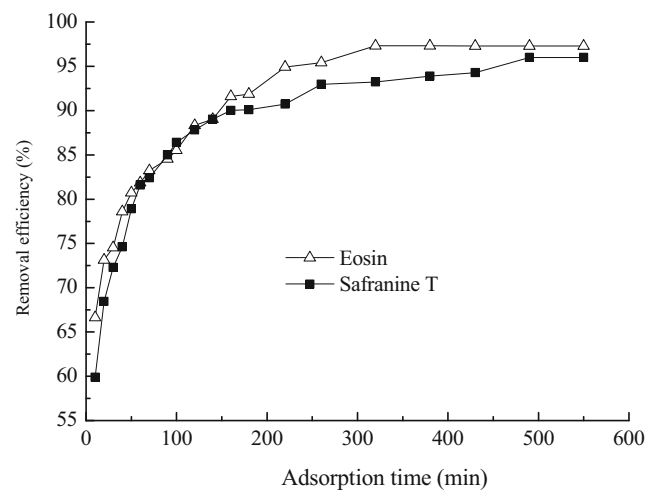


Fig. 6 The effects of adsorption time on the removal efficiency of Eosin and Safranin T by AC-1

significantly respectively, contributing to the high removal of the two dyes (Ngulube et al. 2017).

For comparison purpose, the effect of different adsorbents on the removal of eosin and safranin T dye wastewater is shown in Table 2. It can be seen that the commercial activated carbon (AC-C) had better adsorption capacity than the prepared carbon adsorbent AC-1. For the eosin wastewater, the adsorption capacity of AC-C and AC-1 was 43.66 and 24.33 mg/g, respectively. Regarding the safranin T dye, the adsorption capacities of AC-C and AC-1 were 70.78 and 48 mg/g, respectively. It was noticed that the adsorption capacity of AC-1 contributed to 55.7 and 67.8% of those of AC-C for the two dyes, which was resulting from the different BET surface area of the two adsorbents. This was consistent with other researchers, who reported that the highest BET surface area also led to the largest phenol uptake in the investigated range of concentration (Julcour Lebigue et al. 2010). Besides, the adsorption performance of prepared sludge adsorbent was comparable to other activated carbons from rice straw (Johns et al. 1998), peanut hull (Brown et al. 2000), and wood sawdust (Kalavathy et al. 2005). The disparity in the adsorption capacities of AC-1 and other adsorbents probably was resulted from the amounts of polar functional groups on the adsorbent surface induced by the difference in carbonization degree (Lin et al. 2012; Liu et al. 2010). Thus, considering the high cost and the difficulty for regeneration of the

Table 2 Comparison of adsorption capacity of adsorbents

Sample	Initial concentration (mg/L)	Adsorption capacity (mg/g)	
		AC-C	AC-1
Eosin	100	43.66	24.33
Safranin T	100	70.78	48

commercial activated carbon, the multiple reuses of sludge prepared adsorbents provided a cost-effective solution for pollutant removal. This replacement can not only achieve a certain degree of wastewater treatment but also solve the problem of high cost present in the current wastewater treatment by physical adsorption.

FTIR characterization

To elucidate the changes of functional groups of AC-1 before and after the adsorption of dye wastewater, the FTIR analysis was conducted and the result is shown in Fig. 7. The difference of adsorbent adsorption did not give rise to a significant change in peak position of FTIR spectrums, indicating that the same species of functional groups were contained on the adsorbent surface. The broadband at wavelength of 3425 cm^{-1} was corresponded to the stretching vibration ($3700\text{--}3200\text{ cm}^{-1}$) of hydroxyl groups (O–H), and the band at about 1634 cm^{-1} was assigned to the C=O stretching vibration (Lin et al. 2012). The broad peak at 1042 cm^{-1} was mainly related to C–O stretching vibration of alcoholic, phenolic, and carboxylic groups or possibly Si–O–C and Si–O–Si structures (Duggan and Allen 1997).

The peak intensities of O–H, C–O, and C=O groups on the surface of AC-1 were reduced significantly after adsorption, suggesting that the positive role of sludge-based adsorbent on dye removal can be associated with its surface chemistry.

Despite a lot of studies investigated the adsorption of organic compounds by activated carbons, the mechanism by which these compounds were adsorbed was still not completely well understood. It was believed that the mechanism was not only determined by donor–acceptor complex interaction but also by the solvent effect (Monsalvo et al. 2011). Yin et al. (2007) reported that the significant adsorption of phenols could be attributed to the synergy effect of physic-sorption and surface chemical polymerization induced by the oxygen-containing functional surface groups. The decline of peak intensities of oxygen-containing groups was also observed in this study. Our previous study on the effect of temperature on the adsorption capacity of adsorbents also confirmed this point (Zhang et al. 2017b). Therefore, it was inferred that the adsorption of acidic and basic dyes on the surface of AC-1 adsorbent was caused by both physical adsorption and surface chemistry process.

Adsorption kinetics and isotherm analysis

Adsorption kinetics has been widely studied to describe the adsorption process and mechanism of organic contaminants adsorption (Liao et al. 2012; Zhao et al. 2008). In this study, kinetic analysis was conducted by using the Lagergren first-order and Lagergren second-order model.

The equation of Lagergren first-order kinetic model could be expressed as follows (Rozada et al. 2005;

Fig. 7 FTIR spectra of sludge-based adsorbent (AC-1) before and after the adsorption of eosin and safranin T

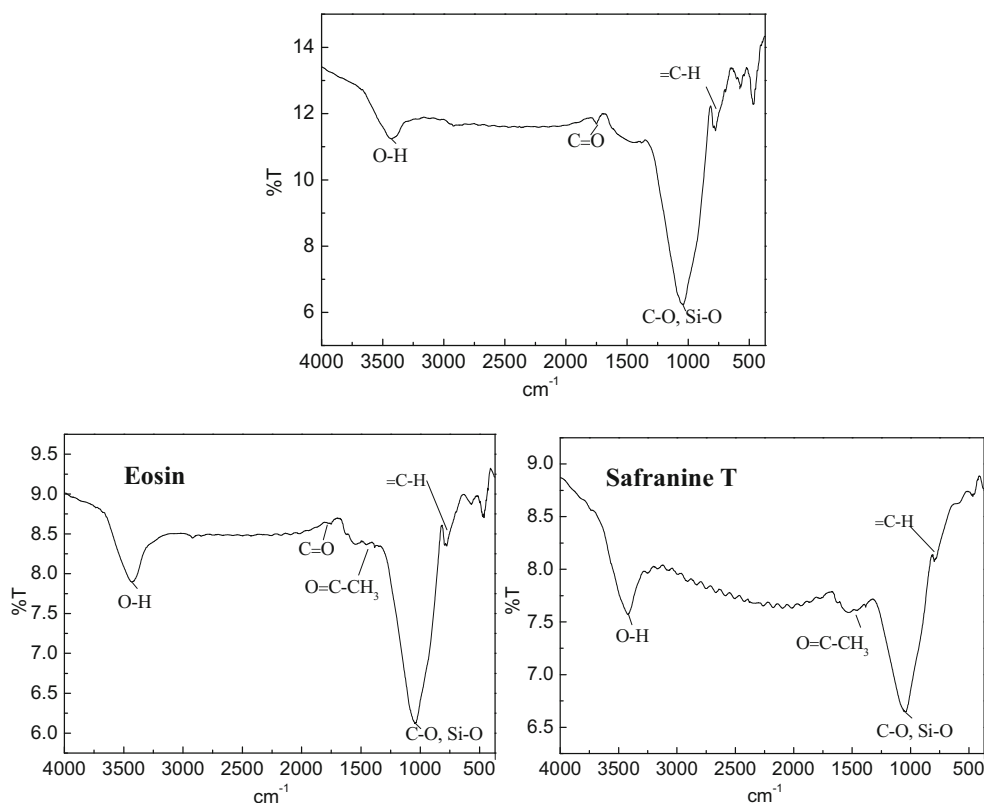
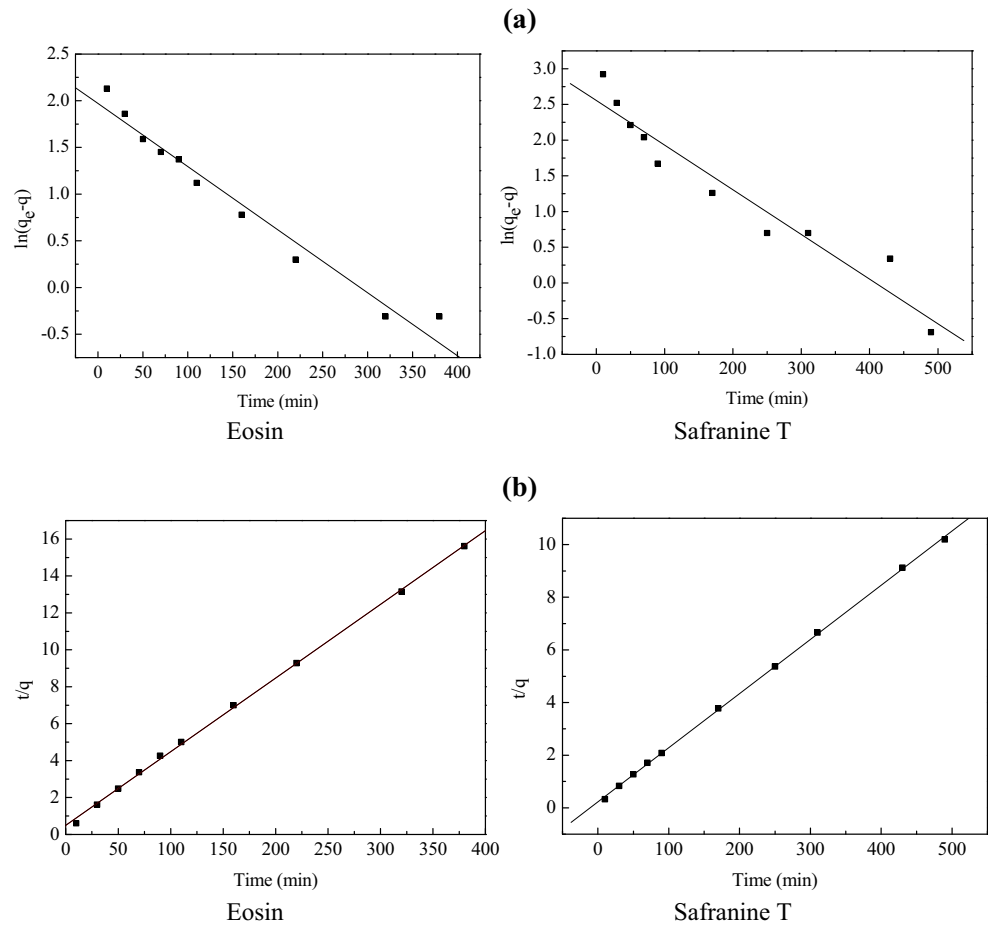


Fig. 8 Adsorption kinetics of eosin and safranin T onto the sludge-based adsorbent (AC-1). **a** Fittings to the first-order kinetic model. **b** Fittings to the second-order kinetic model



Salvadori et al. 2013):

$$\ln(q_e - q) = \ln q_e - k_1 t \tag{2}$$

where q_e (mg/g) is the calculated equilibrium amount of dyes on AC-1; q (mg/g) is the amount of dyes adsorbed on AC-1 at time t (min); k_1 (min⁻¹) is the rate constant of Lagergren first-order equation.

Lagergren second-order kinetics are expressed by Eq. (3):

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{3}$$

where q_e (mg/g) and q (mg/g) are uptake of dyes at time t and equilibrium, respectively; k_2 (g/(mg min)) is the rate constant of Lagergren second-order equation.

Table 3 Kinetic parameters for adsorption of dyes on AC-1

Sample	q_e (mg/g)	Lagergren first-order		Lagergren second-order	
		k_1	R^2	k_2	R^2
Eosin	25.063	0.0067	0.9674	0.00327	0.9992
Safranin T	48.544	0.0062	0.9356	0.00186	0.9997

The fitting curves of Lagergren first-order and Lagergren second-order models are shown in Fig. 8a, b, and corresponding kinetic parameters are presented in Table 3. From Fig. 8, it was seen that both the Lagergren first-order and Lagergren second-order models fitted the experimental data well, but the Lagergren second-order kinetics model fitted better which could be confirmed by the higher correlation coefficient in Table 3. This revealed that the limiting stage of adsorption process was more chemical sorption mechanism than the mass transfer from the solution to the adsorbent surface (Rozada et al. 2005).

Additionally, the adsorption isotherm experiments were also conducted in this study and the isothermal results are shown in Table 4. Langmuir and Freundlich models were used to fit these isotherm data. For the eosin adsorption, the

Table 4 Results from fitting to Langmuir and Freundlich models

Sample	Langmuir isotherm			Freundlich isotherm		
	b (L/mg)	q^0	R^2	n	k	R^2
Eosin	1.0116	38.3142	0.9833	4.2070	18.7068	0.9204
Safranin T	0.1100	149.2537	0.7984	1.4663	17.1672	0.8702

Langmuir adsorption isotherm provided better fitting in terms of R^2 (0.9833), suggesting the adsorption of eosin was mainly due to monolayer coverage of eosin molecules onto the surface of prepared carbon adsorbents. However, the adsorption of Safranin T followed the Freundlich isotherm better with a higher coefficient. The $1/n$ values in Freundlich model were below 1 indicating favorable adsorption of the two dyes on the prepared carbon adsorbents.

Conclusions

This study investigated the dual effects of biochar on industrial wastewater treatment and on raising pyrolysis temperature as adsorbents and microwave receptor, respectively. The S_{BET} and pore volume of prepared adsorbents (AC-1) reached $459 \text{ m}^2/\text{g}$ and $0.23 \text{ cm}^3/\text{g}$, respectively, which was better than those obtained by conventional pyrolysis/carbonization and physical activation methods. Multiple reuses of biochar adsorbents (AC-1 to AC-5) as microwave receptor was feasible during microwave pyrolysis, where the pyrolysis temperature increased sharply to $800 \text{ }^\circ\text{C}$ within 5 min. However, the total iodine value of each adsorbent decreased in the order of AC-1 > AC-2 > AC-3 > AC-4 > AC-5. AC-1 was the better one among all the adsorbents in terms of surface area, porous structure, heating characteristic, and iodine value. For adsorption performance, AC-1 presented the highest removal efficiency of 97.3 and 95.9% for eosin and safranin T respectively under the experimental condition. Further FTIR analysis found that the adsorption of acidic and basic dyes on the surface of AC-1 was the combined effect of physical adsorption and surface chemistry process. The adsorption kinetic could be better described by Lagergren second-order model, and favorable adsorption of eosin and Safranin T was fitted well by Langmuir and Freundlich isotherm, respectively.

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