Preparation of activated carbon from sludge by ‘double green activation’ and adsorption capacity for Congo red dye

Jun Chen a,b,c,*, Xiaowan Dong a,b, Sisi Cao a,b, Layun Zhu a,b, Zihui Song a,b, Jie Jin a,d, Hongxing Yang b

aSchool of Biology, Food and Environment, Hefei University, Hefei 230601, China, Tel. +86 551 62158405; Fax: +86 551 62158406; emails: chenjun@hfuu.edu.cn (J. Chen), 1823641450@qq.com (X. Dong), 214715398@qq.com (S. Cao), 2966705708@qq.com (L. Zhu), 2966705708@qq.com (Z. Song), Tel. +86 551 62158409; Fax: +86 551 62158406; email: 2378859912@qq.com (J. Jin)
bAnhui Key Laboratory of Sewage Purification and Eco-restoration Materials, Hefei 230088, China, Tel. +86 551 65326105; Fax: +86 551 62158406; email: 331279963@qq.com (H. Yang)
cAnhui Guoke Testing Technology Co., Ltd., Hefei 230041, China

Received 21 August 2021; Accepted 3 January 2022

ABSTRACT

The sludge was transformed into activated carbon (SAC) by the green activation method. Citric acid (C₆H₈O₇) and potassium ferrate (K₂FeO₄) were used as different activators, and four kinds of SAC (SACn, SACCA, SACPF, SACCA-PF) were prepared by different activator combinations. The SACCA-PF was produced with C₆H₈O₇ and K₂FeO₄ by the ‘double green activation’ method, it had the highest specific surface area (136 m² g⁻¹) and abundant functional groups (C=O, Si–C) attached to it. The adsorption capacity of SACCA-PF for Congo red (CR) was 98.61 mg g⁻¹, faster and more efficient than the other SAC. The adsorption process was well described by the Langmuir model and quasi-second-order kinetic model. The adsorption mechanism of SACCA-PF (available on the CR surface) was attributed to various interactions, such as hydrogen bonding and electrostatic attraction. Moreover, SACCA-PF could be regenerated by Fenton reaction, and the removal rate was still more than 80% after five cycles of used. The results indicated that the impregnation of C₆H₈O₇ and K₂FeO₄ can effectively improve the adsorption efficiency of SAC, prepared by the ‘double green activation’ method. This method can be applied for carbonized sludge and dye wastewater treatment in an environment-friendly way.

Keywords: SAC; Double green activation; Adsorption performance

1. Introduction

With the rapid increase in population, usage and the development of the sewage treatment industry have also increased. During the sewage treatment, a large number of surplus sludge is produced due to the separation and conversion of the wastewater. China produces about 65 million tons of sludge every year. Sludge contains a huge amount of organic matter, insoluble inorganic substances, etc. In this process, different types of microbe micelle form a variety of microbes. Hence, untreated sludge poses a great threat to human lives [1–3].

With the development of different materials, there have been many studies on biomass materials as raw materials of activated carbon to achieve the regeneration of resources [4]. The amount of harmful wastes has increased in the sludge. Hence, sludge treatment and disposal have become very important. Sludge has high water content and complex
composition. It is a mixture of organic matters (maximum), inorganic matters, heavy metals, and microorganisms in the dissolved or suspended state, which is easy to decay. At present, the commonly used sludge disposal methods mainly include anaerobic digestion, incineration and landfill, compost making, land usage, and so on [5–7]. However, these methods are inefficient in separating different elements of the wastes; for example, sludge landfill, which is one of the disposal methods, may cause toxic leaching of heavy metals and occupy a large amount of land area, which may cause further environmental pollution [1,8].

Due to the difficulty of subsequent sludge disposal, it is a good idea to utilize the resources of sludge and make renewable materials, like sludge-based activated carbon (SAC) [9,10]. It not only solves the problem of environmental pollution caused by traditional sludge disposal but also reduces the high cost of raw materials used for producing activated carbon. Thus, the goal of ‘killing two birds with one stone’ can be achieved. At present, a large amount of research has been carried out on research on the adsorption of dyes on activated carbon, such as powdered activated carbon, green activated carbon made of an orange tree wood, and tin sulfide nanoparticles loaded on activated carbon [11–15].

Several studies observed that the SAC could be used as a carbonized material, such as adsorbent, catalyst, lubricant, amendment, and electrode material, etc. The sludge-based adsorbents could be used to remove contaminants such as heavy metals, dyes, organic pollutants, phosphates, phenolic compounds, and other compounds from the environment [10,16–19]. However, the direct adsorption performance of SAC is poor due to its small specific surface area and pore volume, and large ash content. In recent years, many researchers have been trying to increase the performance of SAC, especially the specific surface area. For example, alkaline reagents and activators [20] can modify the activated sludge to produce derivative adsorbents. Some studies have shown that the mechanical strength of sludge can be improved by modifying the sludge with alkali and then using a cross-linking agent. Activation, which is divided into physical activation and chemical activation, is usually used to improve the specific surface area and adsorption capacity of the sludge carbon [21]. Physical and chemical techniques can be used to obtain activated carbon from bituminous coal and study the adsorption performance of textile dye basic blue 41 [22]. The specific surface area of the activated carbon prepared by modifying the organic waste with carbon dioxide is much larger than that of the water vapor-modified activated carbon [23]. Chemical activation refers to the addition of chemical agents for sludge impregnation and then adding inert gas as a protective gas for high-temperature carbonization. Compared with physical activation, it has the advantages of simple operation, low activation temperature, relatively short activation time, low energy consumption, and the generation of many functional groups on the surface of the composite materials. However, it may corrode the equipment. At present, the chemical reagents used in the laboratory generally include KOH, NaOH, ZnCl2, FeCl3, H2SO4, H3PO4, uric acid and others. Yang et al. reported that Fe3(SO4)2 efficiently activated the sludge-based carbon to adsorb tetracycline [24]. Used Fe3O4 modified sludge-based biochar was used to adsorb phosphate, and the effect was satisfactory. After impregnation with FeCl3, the maximum adsorption capacity reached up to 11.0 mg g–1 [25].

In general, the chemical activation method can improve the specific surface area of the activated carbon, but the energy consumption is still relatively high in this process. In recent years, numerous studies have been reported on the usage of chemical activation at low temperatures (400°C–600°C). However, most of the activators are harmful to human health. For example, the strong alkali and the metallic zinc in zinc chloride (used in the activation process) must be treated to prevent secondary pollution. Therefore, future research should seek a new chemical agent.

In this paper, based on the resources of sludge, a chemical activation method is adopted, and environment-friendly activators such as citric acid (C6H8O7) and K2FeO4 are selected to carry out the green carbonization of sludge. SAC with low cost and high efficiency was obtained. The effect of chemical substances on the modification of structural properties of SAC was studied, including microstructure, pore structure, elemental composition, and functional groups. The adsorption performance and mechanism of the prepared SAC for dye of Congo red (CR) were evaluated, and the application prospect of the SAC for dye of CR was also explored.

2. Materials and methods

2.1. Materials

The sludge used in the experiment was taken from the sewage treatment plant of the Hefei Economic Development Zone. K2FeO4, C6H5O7, HCl (36.5%), NaOH, FeSO4·7H2O, H2O2, CR, Methylene blue (MB), Rhodamine B (RB) were purchased from Sinopharm Chemical Reagent Co, Ltd. All chemicals were used without further purification, and the solutions were prepared by deionized water.

2.2. Preparation of SAC

To minimize impurity, the sludge was dried, crushed, and screened (80 mesh). The screened sludge samples were heated up to 500°C in the ceramic ark of a vertical tubular furnace at a rate of 5°C/min with a flow rate of 100 mL min–1. The carbonization process was held for 2 h under the nitrogen ambiance. The samples were taken out after the furnace temperature dropped to 100°C and then kept in a dryer at room temperature. The obtained sample was soaked in 0.5 mol L–1 HCl for 2 h, filtered and washed with distilled water until it was neutral. Then the sludge carbon into powder was ground and passed through 200 mesh sieves. The SAC sample prepared without any activator was named SAC0.

A certain mass of the sludge sample and a certain mass of C6H5O7 or K2FeO4 solution was mixed at 40°C for 6 h (5 g sludge, 100 mL of 10 wt.% C6H5O7 solutions; 5 g sludge, 100 mL 0.1 mol L–1 K2FeO4 mixed solutions; 5 g
sludge, 100 mL mixed solution containing 10 wt.% C₆H₈O₇ and 0.1 mol L⁻¹ K₂FeO₄ and dried at 105°C to carbonize the obtained sample according to the carbonization method of SACₚ. The obtained sample was soaked and pickled with 0.5 mol L⁻¹ HCl for 2 h, then filtered and washed with distilled water until neutral, then dried at 105°C and passed through 200 mesh sieve for retention spare. The SAC samples prepared with C₆H₈O₇, K₂FeO₄ and a mixture of C₆H₈O₇ and K₂FeO₄ were named SACₚᵥ, SACₚᵣ and SACₚᵥᵣ, respectively.

2.3. Batch adsorption study

2.3.1. Determination of adsorption properties of SAC

Four kinds of SAC (0.2 g) (SACₚᵥ, SACₚᵣ, SACₚᵣᵥ, SACₚᵣᵣ) were added into 100 mL of CR solution with an initial concentration of 200 mg L⁻¹, respectively, and placed in a water bath with an oscillating chamber at 25°C at a speed of 100 rpm. During the oscillation process, samples were taken out after 4, 8, 16, 30, 60, 90, 120, 240, 480, 600, and 720 min and filtered using a filter membrane (0.45 µm). The absorbance was measured at 498 nm using a V5000 visible spectrophotometer, the results were mean values from duplicate experiments. The adsorption capacity and removal efficiency of different samples were calculated using Eqs. (1) and (2).

Adsorption capacity:

\[
q = \frac{V(C_0 - C_t)}{m} \tag{1}
\]

Removal efficiency:

\[
R(\%) = \left( \frac{C_0 - C_t}{C_0} \right) \times 100 \tag{2}
\]

where \( q \) (mg g⁻¹) is the adsorption capacity at the time, \( V \) (L) is the volume of adsorbent solution, \( C_0 \) (mg L⁻¹) is the initial mass concentration of adsorbent solution, \( C_t \) is the mass concentration of adsorbent in solution at the reaction time, \( m \) (g) is the mass of adsorbent, and \( R \) is the removal efficiency of the adsorbent solution.

2.3.2. Research methods of adsorption kinetics

The CR stock solution was diluted to 200 mg L⁻¹ and 100 mL aqueous dye solution was put into a conical flask (150 mL). The pH of the solution was considered as the initial pH. The prepared four kinds of SAC were added to the solution (0.2 g of SAC carbonized at 500°C, which was vibrated in a water bath oscillator at 25°C and 100 rpm). The solution was taken out at different intervals, like 4, 8, 16, 30, 60, 90, 120, 240, 480, 600, and 720 min, respectively, filtered with 0.45 µm of the filter membrane. The absorbance of each sample was measured at 498 nm, and the adsorption capacity was calculated.

2.3.3. Process to obtain adsorption isotherm

The CR stock solution was diluted to 100, 200, 300, 400 and 500 mg L⁻¹ respectively. Solution of 50 mL was put inside a 150 mL conical flask, 0.1 g of SAC was added into the flask, and then it was shaken at a constant temperature water bath oscillator at 25°C, 100 rpm for 12 h. After shaking, it was taken out, filtered with 0.45 µm of the filter membrane, and its absorbance was measured at 498 nm.

2.4. Analytical methods

The gold-plated samples were observed by scanning electron microscopy (SEM) using SU8010 cold-field emission scanning electron microscope (Hitachi Company, Japan). TD-3500 X-ray diffractometer (Dandong Tongda) was used to obtain X-ray diffraction (XRD) patterns of the samples. The X-ray photoelectron spectroscopic (XPS) spectra were obtained using the Thermo Fisher Kα XPS instrument (Thermo Field). The samples were scanned by the Nicolet IS 50+ Continuum Fourier-Transform Infrared Spectrometer (FTIR) (Thermo Fisher, USA). Raman spectra were obtained by the DXR laser confocal micro-Raman spectrometer (Thermo Fisher, USA). The pore size of the sample was determined by the nitrogen adsorption/desorption curves using a fully automated surface and porosity tester (Quantachrome, USA) and Brunauer–Emmett–Teller (BET) analysis. The zeta potential was measured by a particle size and zeta analyzer (Zetasizer Nano-ZS 90, Malvern, USA).

3. Results and discussion

3.1. Characterization of SAC adsorbent

Fine pores are seen on the surface of the pure SACₚ sample (Fig. 1a), while Fig. 1b and c show some rough flaked pores on the surface of the SACₚᵥ, SACₚᵣ, SACₚᵣᵥ samples (obtained by impregnation with C₆H₈O₇ and K₂FeO₄, respectively). The reason is that C₆H₈O₇ and K₂FeO₄ can cover the surface pores as well as react with the surface carbon to form rough pores. In Fig. 1d more circular apertures appear on the surface. It was mainly due to the fact that these two materials can decompose through the coupling action at high temperatures and generate gas, which may form mesopores on the surface. This also confirmed the successful synthesis of SAC.

XRD peaks of the samples are shown in Fig. 2a. The reflections at 2θ = 26.603°, 43.450°, 46.333°, 54.793°, 56.667° corresponded to quartz (JCPDS Card No: 26-1079). The results indicated that the SACₚᵥᵣ was graphitized. Three major peaks with the binding energy of 284.2 (±0.3 eV), 285.1 (±0.3 eV), and 288.7 (±0.3 eV) can be identified as C–C (C=C), C=O, and O–C=O, which were obtained by dividing the C1s spectra. The result was consistent with the literature data [27].

The FTIR spectra of SAC (Fig. 3a) indicate the presence of a large number of carbon and oxygen-containing functional groups in the material. The peak value around 777 cm⁻¹ was considered to be the stretching vibration mode of Si–C. The peak value of 827 cm⁻¹ was the symmetric stretching peak of Si–O–Si. The peak at 1,000 cm⁻¹ was the C–O peak of the P–O–C anti-symmetric stretching vibration. The peak values at 1,500 and 1,588 cm⁻¹ were the C=C stretching vibration peaks. In the infrared spectrum of SAC, in addition to the above peaks, there were also some characteristic absorption peaks. The peak of 2,000 cm⁻¹ was the stretching vibration peak of metal carbonyl (C=O).
Fig. 1. SEM images of (a) SAC$_N$, (b) SAC$_{CA}$, (c) SAC$_{PF}$, and (d) SAC$_{CA-PF}$.

Fig. 2. (a) XRD and (b) XPS patterns of SAC$_N$, SAC$_{CA}$, SAC$_{PF}$, and SAC$_{CA-PF}$. 
The peak at 2,158 cm⁻¹ was the vibration peak of C≡N of the metal thiocyanate salt M–S–C≡N. The 3,693 cm⁻¹ peak corresponded to the O–H stretching vibration band of C₆H₈O₇. The existence of this hydrophilic functional group enhanced the hydrophilicity of the SAC, which was conducive to the removal of dyes. The results showed that SACCA-PF was successfully prepared by the coupling reaction of C₆H₈O₇ and K₂FeO₄ [28,29].

The symmetric stretching motion of O–C=O of carboxylate occurs at the peak value of 1,379 cm⁻¹, which was related to the type and coordination mode of metal ions, as shown in Fig. 3b. Therefore, it can be concluded that Fe ions and carboxylate form a monodentate coordination compound. The peak at 1,599 cm⁻¹ corresponds to the stretching vibration of C=C (Fig. 3a). At 2,620 and 2,980 cm⁻¹, the first frequency doubling peaks appeared which resonate with the anti-symmetric stretching vibration peaks of CO₃. This confirmed that C₆H₈O₇ and K₂FeO₄ cover the surface of SAC [30].

Fig. 4 shows the BET and Barrett–Joyner–Halenda (BJH) results of SACCA-PF. The presence of unclosed hysteresis loops and mesoporous structures was observed in the samples, which was mainly attributed to the instability of component condensation in the pores. Fig. 4a shows that SACCA-PF sample had the strongest hysteresis loop effect, and the hysteresis loop was the H₄ type, which was a slit pore that often appears on the activated carbon adsorbent mixed with micropores and mesopores. Similarly, the type-I isotherm characteristics also indicated micropores which proved that SACCA-PF had a strong adsorption capacity [31]. This result was consistent with the BJH pore size distribution. As shown in Fig. 4b, the pore size distribution peaks of the samples are all between 0 and 5 nm, indicating that SACCA-PF forms micropores and small mesopores [29,32].

Table 1 compares and analyzes the specific surface area parameters of the four types of SAC. It was found that the specific surface area of the directly carbonized SAC was about 35.698 m² g⁻¹, and the total pore volume was
The specific surface area increased slightly because the surface was covered by \( C_6H_8O_7 \) and \( K_2FeO_4 \). The specific surface area of SAC CA-PF was greatly increased up to 136.339 m\(^2\) g\(^{-1}\), which was larger than that of SACN, SACCA and SACPF. The pore size and total pore volume were 12.3092 nm and 0.1205 cm\(^3\) g\(^{-1}\) [33].

### 3.2. Effect of different adsorbents by SAC

The adsorption capacity of different SAC was displayed in Fig. 5.

From the adsorption performance of the four types of SAC (Fig. 5), it was found that the adsorption effect of SACCA-PF was significantly higher than that of the other three SAC, and it could reach the adsorption equilibrium in about 120 min, with the adsorption capacity up to 98.61 mg g\(^{-1}\), 1.6 times than the SACN. The results indicated that the specific surface area and pore volume of SAC can be significantly increased by the coupling reaction of \( K_2FeO_4 \) and \( C_6H_8O_7 \). \( K_2FeO_4 \) was a strong oxidant, and \( C_6H_8O_7 \) can decompose and generate carbon dioxide gas at high temperatures and can also generate a certain pore structure on the surface of the SAC [34].

### 3.3. Effect of pH and temperature on adsorbents of SAC

The effects of pH and temperature on adsorption efficiency were evaluated, and the results are shown in Fig. 6a and b. In order to investigate the influence of the initial pH value of the solution on the adsorption performance of ionic dyes, it was very important to measure the zeta potential of adsorbent and get the point of zero charge (pH\(_{pzc}\)) value of adsorbent. The pH\(_{pzc}\) values of the four SAC are shown in Fig. 6a (insert).

It can be seen that the zeta potential values of the four adsorbents were positive when pH was 2, and negative when pH was 4–10. The pH\(_{pzc}\) values of the four materials were all low (2.0–4.0), which was due to the fact that CA and \( K_2FeO_4 \) contain acidic groups on their surfaces to provide negative charge, thus attracting more H\(^+\) and generating positive potential. Therefore, the zeta values of the four SAC were positive at lower pH [35]. Meanwhile, SACCA-PF had the best adsorption effect, with adsorption capacity up to 99.63 mg g\(^{-1}\). In addition, at any pH, the CR removal rate of SACCA-PF was higher than that of the other three SAC, indicated that the CR removal rate of SACCA-PF was significantly improved due to the coupling effect of the two reagents. With the increased of pH, the adsorption capacity of SAC decreased gradually, indicated that the adsorption performance of SAC was better in low pH environment. Due to the low pH value, the carboxyl and hydroxyl groups on the surface of SAC were positively charged. After protonation of CR, the anionic dye sulfonate group was decomposed into sulfonate anions, which increased electrostatic attraction and corresponded to the increase of zeta potential [36]. On the contrary, when the pH value was high, the adsorbent had a negative charge and generated electrostatic repulsion with the anionic dye, thus reducing the adsorption capacity. This was consistent with the analysis of potential value [30].

This phenomenon had also been explained in other studies, suggesting that the surface charge distribution and properties of SAC were affected by strong acids and bases. Thus, the electrostatic interaction between SAC and CR dye was changed [37]. The initial pH of the solution was 6. It can be seen that when the pH was lower than 6, there was little difference in the adsorption performance of different types of SAC. When pH was 6, the effect of SAC was better than that of pH 4, and the effect gradually decreased [38]. For finding the influence of temperature on the adsorption of dye by SAC, three temperature gradients were selected in this study. It can be clearly seen that the lower temperature was not conducive to the adsorption, which may be due to the fact that at the lower temperature, the kinetic energy of CR molecules was less, which results in less contact between the SAC and CR molecule. However, when the temperature increased, the degree of activation of ions in the solution also increased.

### Table 1

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Average pore diameter (nm)</th>
<th>Total pore volume (cm(^3) g(^{-1}))</th>
<th>Specific surface area (m(^2) g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAC(_N)</td>
<td>9.9501</td>
<td>0.1259</td>
<td>35.698</td>
</tr>
<tr>
<td>SAC(_{CA})</td>
<td>48.0248</td>
<td>0.1163</td>
<td>37.585</td>
</tr>
<tr>
<td>SAC(_{PF})</td>
<td>45.3295</td>
<td>0.1569</td>
<td>69.571</td>
</tr>
<tr>
<td>SAC(_{CA-PF})</td>
<td>12.3092</td>
<td>0.1205</td>
<td>136.339</td>
</tr>
</tbody>
</table>

Fig. 5. Comparison of adsorption capacity of four different SAC (CR: 200 mg L\(^{-1}\); T: 25°C; pH: 6; dose of SAC: 0.2 g).
However, when the temperature reached a certain level, the adsorption capacity attained a steady state.

### 3.4. Adsorption kinetics

For understanding the adsorption and diffusion process of SAC, the kinetic data were fitted to the pseudo-first-order and pseudo-second-order kinetic models and intraparticle diffusion models. Lagergren equation [Eq. (3)], pseudo-second-order equation [Eq. (4)] and Weber-Morris intraparticle diffusion equation [Eq. (5)] are respectively expressed as [40]:

\[
\log(q_t - q_e) = \log q_e - k_1 t
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}
\]

\[
q_t = k_3 t^{0.5} + b
\]

where \( q_e \) (mg g\(^{-1}\)) is the adsorption capacity at equilibrium time, \( q_t \) (mg g\(^{-1}\)) is the adsorption capacity at \( t \) time; \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)) are the first-order and second-order adsorption rate constants, respectively, and \( t \) (min) is the time. \( k \) (mg g\(^{-1}\) min\(^{-0.5}\)) is the internal diffusion rate constant, and intercept \( b \) reflects the boundary layer effect. The results are shown in Figs. 7 & 8 and Table 2.

By comparing Fig. 7a and b, it can be seen that the simulation effect of the second-order adsorption kinetic model on the CR adsorption behavior of the four kinds of

---

**Fig. 6.** The effects of (a) pH (inset: zeta potential of SAC at different pH) and (b) temperature on the adsorption of CR by four different SAC (CR: 200 mg L\(^{-1}\); dose of SAC: 0.2 g; time: 720 min).

**Fig. 7.** (a) Pseudo-first-order kinetic model and (b) pseudo-second-order kinetic model of CR adsorption by four SAC (CR: 200 mg L\(^{-1}\); T: 25°C; pH: 6; dose of SAC: 0.2 g; time: 720 min).
SAC was more consistent than that of the first-order kinetic model. Similar kinetic model results were observed for the different adsorbent-dye systems in the literature [41,42]. However, the two kinetic models showed a higher efficiency in simulating the adsorption behavior of SAC than the other three kinds of SAC. In Table 2 all the values of correlation coefficient \( R^2 \), obtained after second-order dynamic simulation, were greater than 0.99, and the correlation coefficient \( R^2 \) of SAC reached up to 0.99. Besides, the calculated value of equilibrium adsorption \( q_e \) of SAC, simulated by the second-order kinetics, was about 91.075, which was significantly different from the experimental value (87.99). The other three calculated values of equilibrium adsorption look almost the same as that of the experimental values (including the experimental errors). Therefore, according to the above analysis, the values of CR dye adsorption behavior of SAC simulated by the second-order kinetic model look more consistent. The observed results look more consistent with the chemical adsorption phenomenon, and electrostatic attraction might be the main driving force for the adsorption [43]. Comparison of the \( R^2 \) values obtained from the first-order kinetic model and the intraparticle diffusion model (Table 2 and Fig. 7) shows that physical adsorption and intraparticle diffusion contribute to the adsorption of CR by SAC [6]. The whole adsorption process can be classified into two parts. The intercept of the former stage is lower than that of the second stage, so the former stage was mainly affected by intraparticle diffusion and membrane diffusion. From the perspective of \( K_{p1} \), the diffusion constant of SAC was the smallest while the value of SAC was the largest. In addition, the line shown in Fig. 8 does not pass through the origin, which indicates the existence of boundary layer adsorption, which was consistent with the previous dynamic simulation.

3.5. Adsorption isotherms

Adsorption isotherm refers to the relationship between the adsorbate in the liquid phase and the adsorbate adsorbed on the surface of the adsorbent at equilibrium at a certain temperature. By fitting the adsorption isotherm with the adsorption model, the maximum adsorption capacity of the adsorbents can be calculated. Commonly used adsorption isotherm fitting models include Langmuir and Freundlich adsorption models. Freundlich isotherm model was often used to describe the multilayer adsorption of the adsorption solution by the adsorbents [44]. Langmuir isothermal model [Eq. (6)] and Freundlich isothermal model [Eq. (7)] are expressed below:

\[
\frac{1}{q_e} = \frac{1}{Q_m} + \frac{1}{K_L C_e} \\
\log q_e = \log K_f + \frac{1}{n} \log C_e
\]

where \( q_e \) (mg g\(^{-1}\)) is the amount of adsorption at the equilibrium of the adsorbent, \( Q_m \) (mg g\(^{-1}\)) is the Langmuir saturated amount of adsorption, \( C_e \) is the equilibrium concentration of adsorbate in solution (mg L\(^{-1}\)), \( K_f \) is the Langmuir adsorption constant, \( Q_m \) reflects the adsorption capacity of adsorbates by the adsorbents. The higher the \( Q_m \) value, the stronger

![Fig. 8. Intraparticle diffusion model of CR adsorption by four SAC (CR: 200 mg L\(^{-1}\); T: 25°C; pH: 6; dose of SAC: 0.2 g; time: 720 min).](image)

### Table 2

The kinetic parameters and intraparticle diffusion parameters of SAC

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>First-order kinetic model</th>
<th>Second-order kinetic model</th>
<th>Intraparticle diffusion parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_e ) (mg g(^{-1}))</td>
<td>( k_1 ) (min(^{-1}))</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>SAC(_N)</td>
<td>149</td>
<td>0.015</td>
<td>0.646</td>
</tr>
<tr>
<td>SAC(_CA)</td>
<td>35.313</td>
<td>0.005</td>
<td>0.920</td>
</tr>
<tr>
<td>SAC(_PF)</td>
<td>96.022</td>
<td>0.018</td>
<td>0.698</td>
</tr>
<tr>
<td>SAC(_CA-PF)</td>
<td>49.041</td>
<td>0.056</td>
<td>0.946</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
is the adsorption capacity. $K_L$ reflects the binding ability of the adsorbent to the adsorbent site. $1/n$ is the constant related to the maximum adsorption capacity and adsorption energy, $K_f$ is the Freundlich adsorption constant.

Fig. 9a and b shown the Langmuir adsorption isotherm and the Freundlich adsorption isotherm, respectively. The simulation efficiency of the Langmuir adsorption isotherm looked better than that of the Freundlich isotherm, and its correlation coefficients $R^2$ were all greater than that of the Freundlich isotherm, which showed that the adsorption process was mainly of monolithic nature. The obtained isotherm results were in agreement with the previous studies [45–47].

However, all $n$ values (Table 3) obtained from the Freundlich isotherm were greater than 1, which proves that it is favorable for adsorption. Besides SACN, all the correlation coefficient values ($R^2$) of the other three types of SAC are greater than 0.99. Therefore, the adsorption of CR by SAC conformed to the Langmuir thermodynamic model, where the adsorption heat was independent of the surface coverage rate [38].

### 3.6. Adsorption mechanism

In this study, the used activators C$_6$H$_8$O$_7$ and K$_2$FeO$_4$ both formed pores. Compared with the sludge charcoal, which was directly carbonized, the specific surface area of SAC samples prepared using the activators was improved. In the process of C$_6$H$_8$O$_7$ pyrolysis, carbon dioxide was evolved, and large pores were generated during the process of sludge carbonization. However, when K$_2$FeO$_4$ was heated, it decomposed and produced oxygen under the acidic condition, forming mesopores and micropores. The SAC prepared by coupling the C$_6$H$_8$O$_7$ and K$_2$FeO$_4$ had a special pore structure, and mesopores and micropores were generated in the macropores. The C$_6$H$_8$O$_7$ and K$_2$FeO$_4$ used in the study are both green chemical agents and the double coupling effect of the two changes the characteristics of the SAC. In addition, neither of them causes secondary pollution. It had opened up the field of sludge resource utilization, implemented effective treatment and disposal of residual sludge, and also realized the purpose of treating waste by waste, and achieved remarkable results.

The Fig. 10 showed the chemical structure of the SAC adsorbent and its binding mechanism with the CR dye, which can be attributed to various types of interactions. K$_2$FeO$_4$ can be reduced to ferric iron at high temperatures under acidic conditions, so iron-rich adsorbents can electrostatically bind the anionic reactive dyes. Some adsorbents that adsorb dye molecules of opposite charges through the charged groups present on the surface, such as sludge adsorbents modified by KOH, had hydroxyl groups on the surface, hydrogen bonds between the nitrogen atoms in the dye molecules, and electrostatic attraction and van der Waals forces to bind the reactive dyes containing amino groups [30,36,48]. Therefore, the SAC produced in this study can be used to electrostatically bind the reactive anionic dyes.

### 3.7. Color retention of adsorbent and adsorbent regeneration

#### 3.7.1. Color retention capacity of the SAC

The SAC samples were removed from the non-woven fabric and cleaned until no more dye was coming out of it. Then, the weights of the samples were recorded, and the weights were measured again after the samples were centrifuged (at 1,000, 2,000, 3,000 rpm) for 10 min. The color retention capacity of the SAC was calculated by the change in the CR solution and adsorbent mass.
Color retention capacity(%) = \( \frac{W'_W}{W_t} \)  \( (11) \)

where \( W'_W \) is the weight of each SAC sample after centrifuging for 10 min.

As shown in Fig. 11, the color retention capacity of SACCA-PF dose not decreased with the increased in eccentricity after the adsorption of dyes. Possibly, SAC CA-PF closely binds with the functional groups present in CR rather than adsorbing. This result demonstrated that the adsorption data could be well simulated using the quasi-second-order adsorption kinetics model (Fig. 7 and Table 2). These results suggested that SACCA-PF had a good retention performance and has a broad prospect in practical application.

3.7.2. Adsorbent regeneration of SAC

The Fenton oxidation method was used to regenerate the SACCA-PF after it had been used to adsorb the dyes (the Fenton's reagent was composed of FeSO\(_4\)·7H\(_2\)O and H\(_2\)O\(_2\)). When the SACCA-PF adsorbed the CR after 720 min, the SAC was treated by Fenton's reagent before reusing it. The results of SACCA-PF regeneration for five times (for a different time) are shown in Fig. 12.

The multiple utilization of adsorbents was a basic criterion for assessing their potential for practical application.

3.8. Practical application tests of the SAC

The developed SAC adsorbent was mainly used for environmental protection, such as wastewater treatment in the dye industry, etc. Different concentrations and different types of dyes were tested with SACCA-PF. In addition, adsorbent products were designed and tested in the laboratory.

Table 3
Freundlich and Langmuir adsorption isotherm simulation parameters

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>( Q_m ) (mg g(^{-1}))</th>
<th>( K_L ) (L mg(^{-1}))</th>
<th>( R^2 )</th>
<th>( n )</th>
<th>( K_f ) (mg/g (mg/L))(^{1/n} )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAC(_N)</td>
<td>125.313</td>
<td>0.203</td>
<td>0.710</td>
<td></td>
<td></td>
<td>6.298</td>
</tr>
<tr>
<td>SAC(_CA)</td>
<td>104.384</td>
<td>0.287</td>
<td>0.990</td>
<td></td>
<td></td>
<td>6.314</td>
</tr>
<tr>
<td>SAC(_PF)</td>
<td>196.464</td>
<td>0.096</td>
<td>0.992</td>
<td></td>
<td></td>
<td>3.219</td>
</tr>
<tr>
<td>SACCA-PF</td>
<td>186.220</td>
<td>0.353</td>
<td>0.999</td>
<td></td>
<td></td>
<td>4.037</td>
</tr>
</tbody>
</table>

Fig. 10. Possible mechanism of CR dye adsorption on SACCA-PF.
3.8.1. Adsorption efficiency of SAC for different concentrations of dye

As shown in Fig. 13, the amount of adsorption increased with an increase in the concentration (when the same amount of SACCA-PF was added). When the initial concentration was increased from 100 to 200 mg L\(^{-1}\)\), the adsorption amount increased significantly. When the concentration exceeded 300 mg L\(^{-1}\)\), the adsorption amount increased very slowly. This may be because, at a high concentration, the adsorption performance by SACCA-PF got saturated along with a reduction in the adsorption sites. However, it was seen that SACCA-PF could also be well applied in the treatment of highly concentrated wastewater, such as wastewater containing industrial dye, and showed a great prospect for certain applications in the future.

3.8.2. Adsorption applications of SAC for three different dyes

By comparing the three different dyes in Fig. 14, it is found that SACCA-PF had a better adsorption effect on CR and RB, and the adsorption efficiency was almost equal in both cases. In comparison, the adsorption efficacy of SAC with respect to MB was obviously poor, and the adsorption amount does not change much with time. This may be because the surface of the adsorbent was positively charged, so the adsorption of anionic and neutral dyes was better, but the positive charge of the cationic dyes and the surface of the adsorbent exerted repulsion to each other [30]. At the same time, it was observed that under a certain concentration and dosage of adsorbent, the rate of adsorption gradually becomes flat with further adsorption, which indicated the saturation of active sites on the surface of the adsorbent [50].

4. Conclusions

The SACCA-PF was successfully prepared by the ‘double green activation’ method with the mixture of C\(_6\)H\(_8\)O\(_7\) and \(\text{K}_2\text{FeO}_4\) activators. Compared with the other three kinds...
of SAC, the SAC\textsubscript{CA-PF} had the highest specific surface area (136 m\textsuperscript{2} g\textsuperscript{-1}) and abundant functional groups attached to the surface. The adsorption capacity of SAC\textsubscript{CA-PF} for CR was the highest (98.61 mg g\textsuperscript{-1}) in the SAC, the adsorption was mainly affected by the chemical adsorption and monolayer adsorption process. The adsorption mechanism of CR by SAC\textsubscript{CA-PF} involved hydrogen bonding, electrostatic attraction, and ion interaction. The study could provide technical support for carbonized sludge and dye wastewater treatment in an environment-friendly way.

Acknowledgements

This research was supported by the National Key R&D Program of China (2020YFC1908601, 2020YFC1908602). Science Development Fund Project of Hefei University (22040521004).

References


[33] L. Yang, Y. Zhan, Y. Gong, E. Ren, Development of eco-friendly CO\textsubscript{2}-responsive cellulose nanocelluloses as “green”...


[43] X. Guo, B. Du, W. Qin, J. Yang, Synthesis of amino functionalized magnetic graphenes composite material and its application to remove Cr(VI), Pb(II), Hg(II), Cd(II) and Ni(II) from contaminated water, J. Hazard. Mater., 278 (2014) 211–220.