

Article Adsorption of Methylene Blue by Coal-Based Activated Carbon in High-Salt Wastewater

Jinlong Wang¹, Jingqian Ma² and Yongjun Sun^{2,*}

- ¹ College of Environmental Science and Engineering, Nanjing Tech University, Nanjing 211816, China
- ² College of Urban Construction, Nanjing Tech University, Nanjing 211800, China

* Correspondence: sunyongjun@njtech.edu.cn

Abstract: High-salt printing and dyeing wastewater is a difficult industrial wastewater to treat. Coal-based activated carbon (CBAC) can be used as an adsorbent to treat high-salt printing and dyeing wastewater and realize the resource utilization of CBAC. In this study, simulated wastewater that contained methylene blue (MB) was used as the research object, and CBAC was used as the adsorbent. The effects of CBAC dosage, NaCl concentration, coexisting ions, adsorption time, MB concentration, humic acid concentration, and solution pH on the adsorption performance of CBAC with MB were discussed. The results showed that when the CBAC dosage was 0.6 g/L, the solution pH was greater than 6, the adsorption time was 8 h, the adsorption temperature was 308 K, and the MB concentration was 10 mg/L. Thus, the maximum adsorption capacity of CBAC with MB was obtained. The maximum adsorption capacity and removal rate were 15.5 mg/L and 90%, respectively. High-salt wastewater can inhibit the adsorption capacity of coal-based activated carbon. In addition, 20 g/L of NaCl reduced the adsorption capacity of coal-based activated carbon by 1.8 mg/g. Compared to the other coexisting ions, the influence of the presence of Cu²⁺ and Fe³⁺ on the removal of methylene blue was greater. However, when Cu²⁺, Fe³⁺ and high-salt wastewater coexist, the inhibition effect decreases.

Keywords: coal-based activated carbon; high-salt wastewater; coexisting ions; methylene blue; adsorption

1. Introduction

High-salt printing and dyeing wastewater is a difficult industrial wastewater to treat because it has large chroma, many refractory biodegradable substances, and contains a large amount of inorganic salts [1]. The printing and dyeing process generally requires a large amount of inorganic salts, mainly NaCl and KCl and other metal salts, to adjust the pH and ionic strength. According to the statistics, the salt content of high-salt water can reach 60 g/L [1–4]. Therefore, high-salt wastewater causes great harm to the environment [5–7]. The direct discharge of wastewater without treatment will not only pollute water resources, but also cause land salinization [8]. In addition, different dyes and heavy metals coexist in printing and dyeing wastewater [9,10]. Studies have shown that cationic dyes, acid dyes, direct dyes, and disperse dyes can lead to the formation of tumors, dermatitis, rhinitis, and other diseases [11].

At present, the treatment methods of high-salt wastewater mainly include a biological method, physical method, chemical method, and a combination of these three methods [4,7,12–22]. Among them, the research on the biological method mainly focuses on the following two aspects: first, the cultivation and domestication of halophilic bacteria; second, the development of new biological treatment processes. The researchers isolated the moderately halophilic bacterium Halomonas sp.KHS3 from the polluted seawater of Puerto de Mar del Pula, demonstrating that it can grow in saline environments, using different monoaromatic and polyaromatic compounds as carbon and energy sources [20].



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Biological methods have been applied in organic wastewater treatment on a large scale, and various biological treatment processes have been developed. However, biological methods have certain limitations in the treatment of high-salt wastewater, such as complex preparatory work and long durations. Physical and chemical methods include electrochemical methods, ion exchange methods, membrane separation methods, reverse osmosis, and adsorption methods. Methods such as coagulation and advanced oxidation have complicated operation procedures, high costs, and secondary pollution. The adsorption method is widely used in the treatment of wastewater because of its low cost, simple operation, and greenness [21–23]. However, no clear experimental results have been obtained on the adverse effects of inorganic salts in wastewater on the adsorption of methylene blue (MB).

The focus of research on adsorption technology is the selection of suitable adsorbents. At present, the most commonly used adsorbents include molecular sieves, silica gel, and resins [24–26]. However, their high price limits their wide application. Thus, finding adsorbents that are widely available, with low costs, and good removal effects is urgent [27]. Therefore, the development of efficient and inexpensive adsorption materials is the key to practical applications. In previous studies, the adsorption efficiency of some commonly used adsorbents (e.g., mesoporous carbonaceous materials, chitosan, siliceous materials, mineral materials, and biological materials) with MB was investigated. Among them, powdered activated carbon (PAC) has the advantages of strong adsorption performance, mild reaction conditions, and no by-products, and is considered a reliable adsorbent for MB removal [28,29]. Almost any natural or synthetic carbonaceous material can be used to produce activated carbon. Commercial raw materials include biomass raw materials (e.g., wood, fruit stone and husk), degraded or coalified plants (e.g., peat), coal of all different degrees of deterioration and synthetic polymer materials [30-37]. Compared with other raw materials, coal-based activated carbon (CBAC) has a wide range of sources and low prices, and it has high mechanical strength and chemical stability. Therefore, from the comprehensive consideration of the raw material source, cost, and product performance, coal has become the main raw material for the preparation of activated carbon [38–40].

At present, most of the research focuses on the effect of modified activated carbon on the adsorption of MB. Studies on the adsorption of MB by CBAC are limited. To expand the research on the removal of MB from wastewater by adsorption, this paper uses unmodified CBAC to treat high-salt MB wastewater and investigates the adsorption efficiency of CBAC with MB wastewater. The removal effect and influencing factors provide a theoretical basis for revealing the physicochemical characteristics that affect the adsorption of MB.

The main objective of this work includes the following aspects. The surface morphology and functional groups of CBAC before and after the adsorption of MB were analyzed by using characterization methods, such as scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). The influence of various factors, including the dosage of the adsorbent, pH, initial concentration of MB, salinity, and coexisting ions, on the adsorption effect were studied, and the kinetic characteristics of the adsorption process and mechanism were discussed [41].

2. Materials and Methods

2.1. Materials

The CBAC was made in the laboratory. Prior to use, the CBAC passed through a 60-mesh sieve. MB was purchased from Shandong Yousuo Chemical Technology Co., Ltd. Copper sulfate, anhydrous sodium sulfate, sodium chloride, and sodium nitrite were purchased from Nanjing Chemical Reagent Co., Ltd. Ferric sulfate was purchased from Xilong Science Co., Ltd. Potassium sulfate, ferrous sulfate heptahydrate, hydrochloric acid, and sodium hydroxide were purchased from Sinopharm Chemical Reagent Co., Ltd. Humic acid (HA) was purchased from Shanghai McLean Biochemical Technology Co., Ltd.

2.2. Characterization Method

The morphologies of the adsorbents were characterized by SEM. The functional groups present in each sample were analyzed by FTIR. The zeta potential of the samples was measured using a zeta potential tester at different pH of the solution. The surface adsorption properties of coal-based activated carbon were determined by N₂ isothermal adsorption desorption (BET), the surface area of the sample was determined by the BET equation, and the pore volume and average pore size of the sample were calculated by the BJH formula.

2.3. Preparation of Activated Carbon

Forty grams of pulverized coal was weighed and placed into a tubular furnace for hightemperature pyrolysis under the protection of N₂. The heating rate was set to 5 °C/min. After heating to 450 h for 70 min, the carbonized material and activator KOH were mixed evenly according to the mass ratio of 2:1, impregnated at room temperature for 24 h, and placed in a 105 r constant temperature oven for 24 h [42].

2.4. Adsorption Experiments

A 10 mg/L MB solution was prepared in a 250 mL conical flask, a certain dose of adsorbent was added, and then a blank sample was designed to correct uncertain effects in a constant temperature shaker at a temperature of 303 K. By adding different qualities of CBAC, the effect of adsorbent dosage on adsorption performance was investigated. The initial pH (2, 4, 6, 8, 10) of the solution was adjusted with hydrochloric acid and sodium hydroxide, and the effect of different initial pH on the adsorption performance was investigated. Different concentrations of NaCl (0, 5, 10, 15 and 20 g/L) were added to explore the effect of salinity on the adsorption performance. In addition, 200 mg/L of coexisting ions (Cu²⁺, Fe³⁺, K⁺, Cl⁻, SO₄²⁻ and NO²⁻) and an NaCl concentration of 10 g/L were prepared to explore the effect of coexisting ions on the adsorption of CBAC. After shaking at 303 K for 8 h, samples were extracted from the vials, filtered through a 0.45 um filter, and analyzed by a UV spectrophotometer at $\lambda = 664$ nm.

The adsorption kinetics experiments were carried out by mixing 0.6 g/L of adsorbent with 200 mL of MB solutions of different initial concentrations (10, 20, 30, 40 and 50 mg/L) and shaking at 303 K for specified time intervals (from 2 min to 1440 min) to sample and measure the concentration of the adsorbate in the solution. The intra-particle diffusion model, pseudo-first-order model, and pseudo-second-order model were analyzed to enrich the mechanism of CBAC adsorption of MB. In addition, HA was applied to explore the effect of organic matter on the adsorption of MB by CBAC. In order to ensure the reliability of the experimental results, the experiments were conducted three times and the relative standard deviation (RSD) was calculated.

3. Results

3.1. Characterization of CBAC

3.1.1. Pore Structure Characterization

Figure 1 shows that the surface of CBAC without the adsorption of MB is rough with many pores and has a large number of fragments. The surface of CBAC after the adsorption of MB is smoother than the initial state, and the debris is reduced. However, the structure did not change significantly before and after adsorption. As shown in Figure 2, the nitrogen adsorption and desorption isotherms of coal-based activated carbon without methylene blue adsorption have obvious H₃ hysteresis rings, which belong to typical type IV isotherms. Table 1 shows that the specific surface area and average pore size of CBAC are $4.0697 \text{ m}^2/\text{g}$ and 13.388 nm, respectively.

Figure 1 also demonstrates that the process of removing MB from CBAC does not involve surface precipitation. The dyes can bind to the active sites of the sorbent through electrostatic attraction or hydrogen bonding. Therefore, the removal of dyes by activated carbon is mainly through physical adsorption, and the contribution of chemical adsorption is small. The type IV isotherm in Figure 2 and Table 1 show that coal-based activated carbon mainly has a mesoporous structure [43].



Figure 1. SEM images of CBAC: (a) without MB; (b) with MB.



Figure 2. Pore structure analysis of coal-based activated carbon: (**a**) pore size distribution of BJH; (**b**) nitrogen adsorption and desorption isotherms.

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	Sample	S _{BET} (m²/g)	V _{Total} ¹ (cm ³ /g)	V _{micro} (cm ³ /g)	V _{meso} (cm ³ /g)	Average Pore Size (nm)
	CBAC	165.815	0.014	0.006	0.008	13.388

Table 1. Porosity characteristics of CBAC.

 $\overline{1}$ Total pore volume (V_{Total} = V_{micro} + V_{meso}).

3.1.2. FTIR

Figure 3 shows the FTIR analysis of high-salt wastewater and the adsorption of MB by CBAC, the effect of coexisting ions on the adsorption of MB by CBAC, and the effect of organic matter on the adsorption of MB by CBAC. The characteristic peaks of CBAC at 3436.00, 2923.94, and 1604.53 cm⁻¹ correspond to –OH, –CH₃, and C=C/C=O, respectively; meanwhile, the characteristic peaks at 1034.21 and 914.56, and 796.40 cm⁻¹ correspond to C–O–C and C–H, respectively [44,45]. The FTIR of CBAC was not significantly different after the adsorption of MB in its normal state, or for the coexisting ions (except Fe³⁺), and high-salt wastewater. However, the characteristic peaks of CBAC at 3436.00 cm⁻¹ and 2923.94 cm⁻¹ changed greatly after the adsorption of Fe³⁺ and HA, respectively.

Figure 3 shows that CBAC has abundant functional groups, including –OH, –CH₃, C=C/C=O, C-O-C, and C-H. In addition, the functional groups of CBACs with and without MB adsorption were not significantly different, indicating that the proportion of chemisorption in the adsorption between MB and CBACs was very small. In addition, the FTIR of methylene blue adsorbed by coal-based activated carbon in high-saline water was not very different from the FTIR under normal conditions. It indicates that the type of adsorption of methylene blue by coal-based activated carbon is physical adsorption even in high-salt wastewater. However, the positions of functional groups in the CBAC after the adsorption of MB shifted. For instance, 3694.32 cm⁻¹ transferred to 3494.52 cm⁻¹, 3618.35 cm⁻¹ transferred to 3618.85 cm⁻¹, 3436.00 cm⁻¹ transferred to 3433.71 cm⁻¹, 2923.94 cm⁻¹ was transferred to 2923.63 cm⁻¹, 1604.53 cm⁻¹ was transferred to 1596.81 cm⁻¹, 1034.21 cm⁻¹ was transferred to 1034.13 cm⁻¹, and 914.65 cm⁻¹ was transferred to 913.35 cm⁻¹. This result indicates that some functional groups are involved in the adsorption of MB. When Fe³⁺ and HA are present, the FTIR of coal-based activated carbon adsorption of methylene blue is significantly different from that in the initial state, indicating that when Fe³⁺ and HA are present, chemisorption may exist in the adsorption process of coal-based activated carbon [46].



Figure 3. Cont.



Figure 3. FTIR spectra of CBAC: (a) high-salt wastewater; (b) coexisting ions; (c) organic matter.

3.2. Effect of Adsorbent Dosage on MB Adsorption

Figure 4 shows the effect of the adsorbent dosage on the adsorption of MB by CBAC. With the addition of CBAC, the removal rate of MB began to increase sharply. When the dosage of CBAC was 1.0 g/L, the removal rate of MB reached a maximum of 97.29% and reached a stable level when the dosage of CBAC was 0.6 g/L and the removal rate of MB was 90.0%. The adsorption capacity of MB decreased rapidly with the increase in CBAC dosage and then reached a stable level. When the CBAC dosage was 1.0 g/L, the adsorption capacity was 9.7 mg/g. When the CBAC dosage was 0.6 g/L, the adsorption capacity was 15.0 mg/g. In addition, the RSD of the experimental results was less than 2%.



Figure 4. Effect of adsorbent dosage on MB adsorption.

Studies have shown that higher doses of adsorbents have more adsorption sites, but when the content reaches a certain point, it will not continue to promote adsorption, and the active sites may also be limited at a certain concentration, meaning that the adsorption effect tends to be flat [47]. Therefore, when the MB concentration in the solution is constant, the adsorbent will not fully utilize the adsorption sites. Following comprehensive consideration, 0.6 g/L of CBAC was added.

3.3. Effect of Solution pH on MB Adsorption

Figure 4 shows that the initial pH of the solution has a great influence on the adsorption of MB by activated carbon. The RSD of the experimental results is less than 2%. The removal rate can reach a maximum of 96.4% with the increase in the pH of the solution and reaches a stable level when the pH reaches 6. As the pH continued to increase, the removal rate did not change significantly. The change trend of the adsorption capacity is similar to that of the removal rate. The maximum can reach 13.3 mg/g, and it is stable when pH reaches 6. Figure 4 also shows that the pH of the zero point charge of CBAC is between 2 and 4. When pH < pH_{PZC}, CBAC is positively charged, and when pH > pH_{PZC}, CBAC is negatively charged [48]. In addition, the pH_{PZC} of the CBAC that adsorbed MB was slightly larger than that of the CBAC that had not adsorbed MB.

It can be observed from Figure 5 that in a wide pH range, coal-based activated carbon has stable adsorption performance for methylene blue. This is similar to the research results of Noppon Somsesta and F.Arrackchi et al., but the adsorption performance of activated carbon in the experiment of Noppon Somsesta and F.Arrackchi et al. is far better than the results of this experiment [49,50]. This may be because the activated carbon in this experiment was not impregnated or further activated to improve the performance. When the pH is lower than pH_{PZC} , the electrostatic repulsion between CBAC and MB decreases with the increase in pH, which is favorable for adsorption. When the pH is greater than pH_{PZC} , the electrostatic repulsion between CBAC and MB increases with the pH, but at a higher pH, the MB removal rate is not greatly affected [51]. Therefore, in the adsorption system of CBAC and MB, the effect of electrostatic adsorption is very minimal [43].



Figure 5. Effect of solution pH on MB adsorption: (**a**) effect of different initial pH on adsorption of MB by CBAC; (**b**) zeta potential of CBAC at different pH.

3.4. Effect of NaCl Concentration on MB Adsorption

Figure 6 shows that with the increase in NaCl dosage, the removal rate and adsorption capacity of MB gradually decreased. Without adding NaCl, the removal rate of MB was 79.0%, and the adsorption capacity of CBAC was 13.4 mg/g. When the dosage of NaCl was 20 g/L, the removal rate of MB was 68.0%, and the adsorption capacity of CBAC was 11.6 mg/g. The removal rate of MB decreased by 13.9%, and the adsorption capacity of CBAC decreased by 1.8 mg/g. In addition, the RSD of the experimental results is less than 2%.

Figure 6 also shows that the increase in NaCl concentration has an adverse effect on the adsorption of MB by CBAC. Because the increase in inorganic salt concentration will shield the charged site of the adsorbent, resulting in the inhibition of electrostatic interaction (reduction in electrostatic attraction and electrostatic repulsion), this will affect the change in dye adsorption amount [52]. In general, with the increase in ionic strength, the adsorption capacity will rise slightly. However, the adsorption capacity of MB decreases with the increase in ionic strength, so it is believed that the electrostatic attraction between MB and coal-based activated carbon will decrease, resulting in the reduction in the adsorption capacity of coal-based activated carbon for methylene blue. CBAC has poor adaptability to complex aquatic environments, so CBAC does not have superior adsorption performance in high-salt wastewater [53].



Figure 6. Effect of NaCl concentration on MB adsorption.

3.5. Effect of Time on MB Adsorption and Adsorption Kinetics

Figures 7 and 8 show that the adsorption of MB by CBAC is a time-dependent process. The concentration of MB in the solution decreased with time, and Q_e increased with time. In the initial stage of adsorption (0–2 h), the adsorption rate of activated carbon to MB in the solution was very fast, and with the progress of the adsorption reaction, the adsorption rate decreased in the middle and late stages (2–24 h). After about 8 h, the CBAC effectively reached the adsorption equilibrium. With the prolongation of adsorption time, the results of Q_e with the addition of NaCl and in the absence of NaCl at the same MB concentration were different. The overall result shows that under the same MB concentration and the same adsorption time, the Q_e with NaCl is smaller than that without NaCl.

Figures 7 and 8 show that with the extension of time, the adsorption sites on the CBAC decrease, and the adsorption amount gradually increases. To evaluate the adsorption kinetic behavior of CBAC with MB, the pseudo-first-order model and pseudo-second-order model were used to fit the experimental data, and the experimental data in Tables 2 and 3 were obtained [54]. The relative standard deviation of Q_e in Tables 2 and 4 is 0.20~0.93%. At different initial concentrations, the R^2 of the pseudo-second-order model is always larger than that of the pseudo-first-order model, indicating that the pseudo-second-order model is always closer to the experimental data points than the pseudo-first-order model [55]. Therefore, the pseudo-second-order model can describe the adsorption kinetics of CBAC for the adsorption of MB better. To understand the potential control rate and diffusion mechanism of the adsorption process better, the data were processed using an intra-particle diffusion model, and the results showed that the adsorption of MB by CBAC was linked through multiple steps. Good correlation coefficients and all Ci values are given in Tables 4 and 5, indicating that intraparticle diffusion occurs during the adsorption process, but this is not the only rate-limiting step. The slope at the beginning is very obvious, indicating that MB flows rapidly on the surface of CBAC. The second stage is progressive, and the speed limiting step in this stage is intra-particle diffusion. The slope gradually increases at the later phase of this stage, indicating that the adsorption reaches equilibrium [56]. In addition, at different initial concentrations, K_1 with added NaCl was smaller than K_1 without NaCl, indicating that the CBAC without NaCl added at the initial stage adsorbed MB faster than the CBAC with NaCl added.



Figure 7. Adsorption kinetics of MB by CBAC: (a) effect of time; (b) intra-particle diffusion model.



Figure 8. Cont.



Figure 8. Adsorption kinetics of MB by CBAC in high-salt wastewater: (**a**) effect of time; (**b**) intraparticle diffusion model.

Table 2. Pseudo-first-order model and pseudo-second-order model parameters for adsorption of MB by CBAC.

C _O (mg/L)	Q _e (mg/L)	RSD (%)	Pseudo-First-Order Model	Pseudo-Second-Order Model
			R ²	R ²
10	15.67	0.43	0.9256	0.9837
20	24.48	0.23	0.9519	0.9780
30	27.37	0.20	0.7997	0.9727
40	31.92	0.75	0.9632	0.9918
50	34.48	0.65	0.9574	0.9865

Table 3. Pseudo-first-order model and pseudo-second-order model parameters for adsorption of MB by CBAC in high-salt wastewater.

C _O (mg/L)	Q _e (mg/L)	RSD (%)	Pseudo-First-Order Model	Pseudo-Second-Order Model		
			R ²	R ²		
10	13.10	0.88	0.8907	0.9740		
20	20.40	0.88	0.9475	0.9667		
30	23.90	0.57	0.9590	0.9918		
40	28.17	0.55	0.9348	0.9765		
50	30.48	0.93	0.9203	0.9710		

Table 4. Parameters of intra-particle diffusion model for adsorption of MB by CBAC.

C _O (mg/L)	K ₁	C ₁	R ²	K ₂	C ₂	R ²
10	1.042	4.649	0.9267	0.087	12.807	0.5466
20	1.491	6.922	0.9625	0.192	17.892	0.7132
30	1.398	8.083	0.9758	0.242	18.828	0.8102
40	2.570	2.832	0.9517	0.294	21.310	0.9058
50	2.556	5.424	0.9419	0.286	24.207	0.8892

C _O (mg/L)	K ₁	C ₁	R ²	K ₂	C ₂	R ²
10	0.345	6.664	0.5705	0.064	10.942	0.6212
20	0.390	9.668	0.3335	0.170	14.539	0.7404
30	1.157	7.669	0.9069	0.166	18.291	0.6584
40	0.635	13.933	0.5714	0.222	20.283	0.8551
50	1.093	14.256	0.8795	0.210	22.812	0.9389

 Table 5. Intra-particle diffusion model parameters of CBAC for adsorption of MB in high-salt wastewater.

3.6. Effects of Coexisting Ions on MB Adsorption

Figure 9 shows that when the MB concentration is 10 mg/L, no coexisting ions are added, the NaCl concentration is 10 g/L, and the removal rate of MB is 67.4%. The removal rate increased to 76.1% and 70.8%. When the concentration of MB was 30 mg/L, no coexisting ions were added, the concentration of NaCl was 10 g/L, and the removal rate of MB was 47.7%. When NO^{2–} was added to the solution, the removal rate of MB increased to 47.8%. In the presence of Fe³⁺, the removal rates of MB (MB = 10 mg/L, 30 mg/L and 50 mg/L) in high-salt wastewater and under normal conditions were 63.7%, 45.1%, 40.3%, 24.5%, 29.6%, and 17.1%, respectively, which were lower than the removal rates of MB (MB = 10 mg/L, 30 mg/L and 50 mg/L) in high-salt wastewater and under normal conditions were 64.3%, 47.9%, 39.8%, 31.2%, 29.7%, and 14.7%, respectively, which are lower than the removal rates without coexisting ions and without coexisting ions and without coexisting ions and without coexisting ions and NI. So mg/L and 50 mg/L and 14.7%, respectively, which are lower than the removal rates without coexisting ions and without coexisting ions and without coexisting ions and NI.

Figure 9 shows that adding a small amount of Cl^- , NO^{2-} , SO_4^{2-} , and K^+ has a minimal effect on the adsorption capacity of CBAC and even increases the adsorption capacity of activated carbon slightly. This phenomenon may be due to the slight increase in the adsorption capacity of activated carbon after adding a small amount of NaCl. This may also be due to the existence of ionic dipoles, dipole–dipole interactions, and van der Waals forces between dye molecules, which increases the dimerization of MB in the solution [57]. According to the experiments of Rahim Shahrokhi-Shahraki et al., activated carbon also has adsorption properties when added to Fe^{3+} and Cu^{2+} . Thus, we can speculate that the presence of Fe^{3+} and Cu^{2+} has a great influence on the removal of methylene blue by adsorption by CBAC [58]. According to the experiment of Oueiroz et al., the adsorption performance of activated carbon with various pore sizes and a large specific surface area will be better. However, this may not be the case, as small pores do not trap large ions, and large pores may not be able to capture small ions [42]. In addition, activated carbon adsorption capacity will also be affected by temperature, raw materials, coexisting ions and other factors. It depends on the situation [35,45]. According to the experimental results, we can observe that the removal rate of methylene blue by coal-based activated carbon decreased significantly when Fe^{3+} and Cu^{2+} were present. As shown in Tables 6 and 7, when there is no NaCl present in the solution and the methylene blue concentration is 10 mg/L, the methylene blue removal rate is 82.4%. The removal rates of methylene blue decreased to 47.9% and 45.6% when Cu and Fe ions were added. This situation is consistent with the methylene blue concentration of 30 mg/L and 50 mg/L. In addition, coal-based activated carbon adsorption of copper and iron ions mainly depends on physical adsorption and electrostatic interaction, so when the NaCl concentration is high, electrostatic shielding, as described in Section 3.4, will also affect Fe³⁺ and Cu²⁺, so that methylene blue can obtain adsorption sites and pores. Therefore, it is speculated that when Fe^{3+} and Cu^{2+} and methylene blue coexist in high-salt wastewater, the adsorption performance of coal-based activated carbon is improved, compared with that of only Cu^{2+} and Fe^{3+} .







Figure 9. Effects of coexisting ions on MB adsorption: (**a**) MB = 10 mg/L; (**b**) MB = 30 mg/L; (**c**) MB = 50 mg/L.

C	Removal Efficiency (%)													
(mg/L)	N ¹	RSD (%)	Cl-	RSD (%)	NO ² -	RSD (%)	SO_4^{2-}	RSD (%)	Fe ³⁺	RSD (%)	K ⁺	RSD (%)	Cu ²⁺	RSD (%)
10	82.4	1.3	75.6	1.3	77.5	0.9	77.9	0.6	45.6	1.1	72.4	1.0	47.9	0.6
30	44.2	0.6	41.1	1.1	45.5	0.59	41.9	0.91	24.5	0.6	43.2	0.6	31.2	0.9
50	28.4	0.3	29.9	0.3	31.9	0.5	28.9	0.3	17.1	0.6	26.9	0.5	17.77	0.6

Table 6. Removal efficiency of MB by CBAC.

¹ N means none.

Table 7. Removal efficiency of MB by CBAC in high-salt wastewater.

6	Removal Efficiency (%)											
(mg/L)	Cl-	RSD (%)	NO ²⁻	RSD (%)	SO_4^{2-}	RSD (%)	Fe ³⁺	RSD (%)	\mathbf{K}^{+}	RSD (%)	Cu ²⁺	RSD (%)
10	67.4	0.7	76.1	0.8	70.8	0.7	63.8	0.8	71.1	0.9	64.3	1.3
30	47.7	0.9	47.8	0.9	42.8	0.8	40.3	0.4	45.1	1.4	39.8	1.0
50	30.9	0.2	29.3	0.5	30.1	0.7	25.6	0.6	27.8	0.2	25.7	0.3

3.7. Effects of Organic Matter on MB Adsorption

Figure 10 demonstrates that in the absence of NaCl, the removal efficiency of MB gradually decreases with the increase in HA concentration in the solution. When the HA concentration was 0 mg/L, the removal efficiency of MB was 82.3%. When the HA concentration was 40 mg/L, the removal efficiency of MB was 51.6%. The removal efficiency of MB decreased significantly. When 10 mg/L of NaCl was present in the solution, the removal of MB first increased and then decreased with the increment in HA concentration. When the HA concentration was 0 mg/L, the removal efficiency of MB was 70.5%. When the HA concentration was 10 mg/L, the removal efficiency of MB was 61.6%. The RSD of the experimental results is less than 2%.



Figure 10. Effects of organic matter on MB adsorption.

Figure 10 suggests that in the absence of NaCl, HA competes with MB for adsorption and will block the pores of the activated carbon. Therefore, with the increase in HA concentration, the efficiency of CBAC in the removal of MB decreases. In the presence of NaCl, the removal efficiency of MB was slightly increased compared with the same concentration of HA, which may be due to the interaction among the surface of activated carbon, HA, and MB. HA contains carboxyl and phenolic functional groups, and MB dye may interact with these functional groups that interacted with and were adsorbed by HA. However, this does not mean that there is no competition for adsorption sites and pore blockage, but the system is too complex to determine the degree of competition [59].

4. Conclusions

In this paper, the adsorption capacity and factors that influence methylene blue adsorption by CBAC at high-salt concentrations were studied. When the MB concentration is 10 mg/L, the dosage of CBAC is 0.6 g/L, the pH of the solution is greater than 6, the adsorption time is greater than 8 h, and the adsorption temperature is maintained at 308 K, which has a positive effect on the adsorption effect. Coexisting ions, organic matter, and high-salt water will all inhibit the adsorption of MB by CBAC. FTIR and SEM characterization showed that the adsorption of MB by CBAC belongs to physical adsorption, which does not change the structural characteristics of CBAC. When the dosage of CBAC is 0.6 g/L, the solution pH is greater than 6, the adsorption time is 8 h, the adsorption temperature is 308 K, and the MB concentration is 10 mg/L, and the maximum adsorption capacity and maximum removal rate of MB by CBAC were 15.0 mg/g and 90.0%, respectively. The adsorption mechanism of methylene blue absorbed by coal-based activated carbon is mainly affected by the interaction of pore filling and electrostatic repulsion. Small amounts of Cl⁻, NO^{2-} , SO_4^{2-} and K⁺ have little effect on the adsorption capacity of coal-based activated carbon. The high-salt wastewater has a great inhibitory effect on the adsorption of methylene blue by coal-based activated carbon, which is speculated to be because the increase in inorganic salt concentration will shield the adsorption sites on coal-based activated carbon, so that the electrostatic attraction between MB and coal-based activated carbon decreases accordingly. Alkaline solution pH is conducive to the removal of methylene blue from coal-based activated carbon, but a too high pH value is not economic and does not help the removal rate, because in the adsorption system of coal-based activated carbon and methylene blue, electrostatic adsorption plays a small role. In the presence of HA or Fe³⁺ in the solution, the adsorption efficiency of CBAC for MB will be reduced significantly.

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