Synthesis of Graphene Oxide/Corn Cob Composites and investigation of their adsorption performance of Dye

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Abstract: Corn cob and Graphene oxide were used to prepare and characterize corn cob/graphene oxide (GO/CC) composites. The adsorption performance of GO/CC on dye wastewater was studied, and the factors affecting the adsorption effect were investigated. The results showed that GO/CC had rich functional groups which could provide sufficient binding sites for Congo red. It could remove Congo red solution strongly, and the removal rate was as high as 80%. GO/SP was endothermic in the process of Congo red adsorption. The reaction was mainly based on chemical adsorption.

1. Introduction

With the development of the printing and dyeing industry, dyes had been used on a large scale, which had caused huge environmental pollution. Printing and dyeing wastewater was characterized by deep chroma, high concentration of organic pollutants, poor biodegradability and large emission. It was a refractory industrial wastewater which was difficult to treat effectively by conventional wastewater treatment technology [1,2]. At present, industrial wastewater treatment methods could be divided into physical method, chemical method, physical and chemical method and biological treatment method [3-5]. The adsorption method of the physical and chemical method could treat printing and dyeing wastewater efficiently because it had the advantages of simple operation and it was not easy to cause secondary pollution [3]. Graphene was a new type of single-atom-thick material composed of carbon atoms of the sp² structure. Its excellent electronic, mechanical and thermal properties had become the focus of research. However, there was a strong vander Waals force between the graphene sheets and it was easy to produce accumulation and agglomeration, so its application was limited to a certain extent [6]. Graphene oxide (GO) is an important derivative of graphene. It had a large number of oxygen-containing groups on the surface, such as hydroxyl, carboxyl, and epoxy groups [7,8]. These characteristics made graphene oxide receive widespread attention as an adsorbent in the treatment of printing and dyeing wastewater. However, graphene oxide was easily dispersed in water and difficult to separate, it has brought great difficulties to the treatment process after dye adsorption. Compounding graphene oxide with corn cob could be used as a composite material in effectively solve this problem while maintaining a good adsorption effect. The research results had important practical significance for solving the severe water pollution problem in China's dye industry.
2. Experimental Part
Preparation of corn cob. The corn cob was dried, then pulverized and passed through a 60-mesh sieve, then dried at 60°C to obtain a corn cob adsorbent (CC).

Preparation of Graphene Oxide. Graphene oxide was prepared by improving Hummers method [9]: 1g graphene was added to 25ml concentrated sulfuric acid for 1h, then 3.5g potassium permanganate was added in the beaker. After 8h of ultrasonic stripping, 46ml of deionization was slowly got in the beaker to stop the reaction. 140ml Deionized water and 15 ml 30% hydrogen peroxide was added to the reaction system. After washed to neutrality, the production was dried at 60°C to obtain graphene oxide (GO).

Preparation of Graphene Oxide/Biomass Composites. Weighted 1.084g graphene oxide and added 433.6ml deionized water. After the graphene oxide fully dissolving, slowly added 17.344g corn cob, and allowed it to react fully for 2h, then dried it at 60°C to prepare a graphene oxide composite (GO/CC).

Scanning Electron Microscope Analysis (SEM). An environmental scanning electron microscope (quanta 450, FEI, USA) was used to characterize the apparent morphology of the experimental samples.

Fourier Infrared Spectrometer Analysis (FT-IR). The functional group structure analysis was performed on the sample with an EQUINOX55 Fourier transform infrared spectrometer which was produced by the German company Bruker. The graphene oxide/biomass composite to be measured was mixed with potassium bromide powder at a ratio of 1:100 (GO/CC) and mixed in grinded in an agate mortar. The potassium bromide powder was dried in an infrared drying box in advance, and finally the translucent tablet was formed through the tablet pressing mechanism.

3. Results and Discussion

3.1 Scanning Electron Microscope Analysis Results.

![Fig 1 Electron microscopy of GO (a), CC (b) and GO/CC (c)](image)

As shown in Figure 1, the surface morphology of GO, CC, and GO/CC was characterized by using a scanning electron microscope. Figure 1 (a) had a clear layer structure, which indicated that GO had been successfully prepared. GO is a two-dimensional structured nanomaterial. And the sheet layer is larger, the surface has wrinkles, and has a larger specific surface area. Comparing Fig. 1 (b) and Fig. 1 (c), we could find that CC was embedded in GO. Because of the electrostatic force of graphene oxide, the CC molecules were in contact with GO. It was adsorbed by graphene oxide during the collision process, which indicated that the GO/CC composite was successful.
3.2 Analysis Results of Fourier Infrared Spectrometer.

![FTIR spectra of GO/CC, GO and CC](image)

In Figure 2, there were obvious absorption peaks at 3490, 1556, 1491, and 1004 cm\(^{-1}\) on the GO curve, and 3490 cm\(^{-1}\) was the stretching vibration peak\(^{[10]}\) of hydroxyl (-OH); 1556 cm\(^{-1}\) was the stretching vibration peak of C=C in the benzene-like ring structure of graphene oxide; 1491 cm\(^{-1}\) was the stretching vibration peak of C=O in the carboxyl group; at 1004 cm\(^{-1}\), the vibration peak of the phenolic hydroxyl group was represented\(^{[11]}\), and the above characteristic peaks were the characteristic vibration peaks of GO. There was no peak of GO at about 3490 cm\(^{-1}\); and there was an obvious absorption peak of CC at 3490 cm\(^{-1}\), which was caused by the stretching vibration of the hydroxyl peak (O-H), which came from the free hydroxyl, carboxyl, phenol and alcohol compounds\(^{[12]}\), but there was an obvious absorption peak of GO/CC at 3490 cm\(^{-1}\), which was due to the combination reaction of C=C in the benzene-like ring structure of GO and -OH in CC. By comparison, GO/CC had abundant functional groups, which can provide sufficient binding sites for Congo red, and had strong adsorption capacity for Congo red solution. Red shift occurred in the C=C bond CC in GO/CC. Due to the combination of GO and CC, the C=C bond in GO/CC moved towards the long wave direction, and the energy increased. Therefore, compared with the C=C bond in CC, the C=C bond in GO was more stable. At 830 cm\(^{-1}\) and 1250 cm\(^{-1}\), GO/CC was the stretching vibration of aromatic C-H, CO- and -OH. The hydroxyl peak (O-H) in the benzene ring of Congo red dye can provide the electron donor, form the bond with the conjugated (C-H, CO- and -OH) part of GO/CC, and combine with the electron donor-receptor interaction. As Congo red was an anionic dye, it can generate electrostatic attraction with GO/CC, thereby promoting adsorption\(^{[13]}\).

![Effect of dosage on adsorption performance](image)

![Effect of adsorption time on adsorption performance](image)
Effect of Dosage on Adsorption. As shown in Figure 3, when the amount of CC increased from 0.2 g/L to 1.4 g/L, the removal rate of Congo red increased from 16.38% to 69.43%; when the amount of GO/CC increased from 0.2 g/L to 1.4 g/L, the removal rate of Congo red increased from 25.30% to 86.78%, both of which increased with the amount of CC. This was because with the increase of GO/CC and CC dosage, and other conditions remained unchanged, the average effective adsorption or contact probability of Congo red molecules per GO/CC and CC increased, so the removal rate was higher. Through data comparison, when the dosage was constant, the removal rate of GO/CC for Congo red was higher than that for CC, because the hydroxyl peak (O-H) in the benzene ring of Congo red dye provided the electron donor, formed the bond with the conjugated (C-H, CO- and -OH) moieties in GO/CC, and combined the interaction of the electron donor and receptor, and the micro channels between the lamellar structures of GO/CC greatly facilitated adsorption of red, so GO/CC removal of Congo red was significantly enhanced. By comparing the increase of the dosage from 1.2 g/L to 1.4 g/L, the removal rate of Congo red by the two did not change much, so considering economic factors and subsequent treatment, 1.2 g/L was selected for subsequent experiments.

Effect of Adsorption time on Adsorption. As shown in Figure 4, after 60 min, the removal rate was basically balanced. The average removal rates of GO/CC and CC for Congo red were 85.23% and 56.5%, respectively. When the initial concentration of Congo red solution and the dosage of adsorbent remained unchanged, as the adsorption time increased, more contact time was provided between the absorbable sites of the Congo red molecules, which was conducive to the adsorption process. However, the adsorption site was fixed. After a certain period of time, the adsorption of Congo red by the adsorption site became saturated, and the mass of Congo red adsorbed by the unit mass GO/CC and CC did not change, so the adsorption gradually became balanced[14]. Therefore, 60 min was selected for subsequent experiments.

Effect of Temperature on Adsorption. As shown in Figure 5, the removal rate of Congo red by GO/CC and CC all increased with increasing temperature, and the removal rate reached the maximum at 30°C. Increasing the temperature was beneficial to the adsorption of Congo red by the two, which indicated that the adsorption process may be an endothermic reaction[15,16]. When the temperature was increased, the increased energy was beneficial to overcome the energy barrier between the adsorbate and the adsorbent. The intensification of DRC increased the diffusion and propagation speed of Congo red molecules into the voids of GO/CC and CC materials, and promoted the occurrence of adsorption reactions. The adsorption temperature decreased from 30-60 °C to the Congo red removal rate, which was because the temperature increased and the molecular irregular movement speed increased. Congo red molecules adsorbed by GO/CC and CC will be desorbed, so the removal rate will decrease. Considering the overall consideration, chose 30 °C as the optimal adsorption temperature.

Effect of Solution pH on Adsorption. According to Figure 6, when the initial pH of the Congo red solution was 3, both GO/CC and CC had the best adsorption effect. As the initial pH value
increased, the removal rates of GO/CC and CC decreased, respectively from 91.28% to 38.13%, from 80.21% to 21.17%. This was due to the fact that Congo Red [17, 18] would crystallize into a blue-black floc material under extremely acidic conditions [19], so the adsorption capacity became stronger. As the acidity weakened, the degree of Congo red crystals decreased, and the adsorption of GO/CC and CC also decreased. With the increased of pH, H+ decreased, the positively charged adsorption sites gradually decreased, and electronegativity began to appear. It started to repel Congo Red, and the electrostatic effect [20] weakened, so the adsorption amount gradually decreased.

As shown in Figure 7, the adsorption curves of CC and GO/CC both decreased with the increase of the initial concentration. Since the unit CC and the unit GO/CC were unchanged, the adsorption sites on the surface of CC and GO/CC were changed. Congo red ions were surrounded, and adsorption was close to saturation. As the initial concentration of the Congo red solution increased, Congo red molecules per unit volume in the solution increased, and the number of binding sites that can be bound decreased, so it showed a downward trend. According to data comparison, when the initial concentration was 40 mg/L, 50 mg/L, 60 mg/L, the effect on the removal rate of Congo red solution was not much different. For economic benefits and subsequent processing considerations, the initial concentration was chosen to be 40 mg/L.

4. Summary
Graphene oxide was first prepared by means of Hummers approach, and then underwent the reaction with corn cob to obtain the composite material of graphene oxide/corn cob, which structure and characterization were analyzed. The analysis showed that GO/CC had a rich functional group, being able to provide sufficient binding sites for Congo red, and having strong adsorptivity of Congo red solution.

Compared with CC, GO/CC had better Congo red adsorption effect. With the increase of dosing quantity, the removal rate of Congo red which concentration was 40 mg/L keep increasing. When the dosing quantity was 1.2g/L, slight changes occurred to the removal rate. The adsorption process of Congo red by GO/SP was an endothermic reaction, being primarily chemical and being so fast that an adsorption balance was reached in around sixty minutes.

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