Advances in preparation of modified activated carbon and its applications in the removal of chromium (VI) from aqueous solutions

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Abstract. The wastewater in which Cr(VI) is not fully treated has drawn environment researchers’ attention increasingly, due to its environmental pollution and harms to human health. Thus a high efficiency of modified activated carbon (MAC) to remove Cr(VI) has become one of the hot topics among environmental material research. This paper introduces the modification methods from the physical structure features and chemical properties of the activated carbon (AC) surface. At the same time, it briefly analyses the chemical characteristics of Cr(VI) in aqueous solutions, and on the basis of the aforementioned introduces the modification methods of the surface chemical characteristics of AC, such as: oxidation modification, reduction modification, loaded metal modification, and microwave modification. Combining studies on removing Cr(VI) from aqueous solutions by MAC in recent years, this paper anticipates the new trends of preparing MAC and the points in absorption research, offering some suggestions for future studies.

1. Introduction
Along with industrial development, the contaminants arising from human activities also increased significantly. Serious environmental problems, caused by heavy metals, have drawn extensive attention from environmental researchers [1], especially some heavy metals with high toxicity, which can cause serious problems to the ecosystem even at low concentrations [2]. Chromium is one of the most toxic heavy metals, coming from the milling machine and sheet metal, paint, tannery, and fertilizer industries [3]. Usually, Cr has two major oxidation states in water, Cr(VI) and Cr(III) [4]. However, due to its carcinogenicity, high toxicity and high aqueous solubility [5], Cr(VI) is 300 times more toxic than Cr(III) [6]. Most of the present domestic and foreign studies about treating wastewater containing Cr(VI), focus on ion exchange [7], electrolysis reduction [8], chemical precipitation [9] and adsorption [10]. At present, adsorption receives increasing attention from people because of its advantages such as high efficiency, simple operation, and low costs.

With great adsorption capacity, fast adsorption, and renewability after saturation, activated carbon (AC) is widely used in processing wastewater containing Cr(VI) [11,12,13]. For instance, Shashikant et al. [14] used CaCl\textsubscript{2} and NaCl solution to activate mango skin. Ramakrishna et al. [15] used ZnCl\textsubscript{2} to activate orange skin to prepare AC to remove Cr(VI) from solution; oth of them received good effects. However, traditional AC, with many ashes, performed poorer in adsorptive selectivity, and was limited
in removing pollutants in water. Therefore, in order to further improve adsorption and removal efficiency of AC towards Cr(VI), many researchers at home, and abroad, manage to apply some modification methods. Modified activated carbon (MAC) for absorbing and removing Cr(VI) in solution efficiently has become one of the hot research topics at present. This paper reviewed several kinds of preparations for MAC and their performances of removing Cr(VI) from the water, so as to offer some references for future studies on MAC to remove Cr(VI).

2. Chemical characteristics of Cr(VI) in water
Generally, Cr(VI) exists water in the following four forms: $H_2CrO_4$, $HCrO_4^-$, $CrO_4^{2-}$ and $Cr_2O_7^{2-}$. The proportion of four kinds of ions in aqueous solutions is determined by its concentration and pH value (namely, the $H^+$ concentration) [16]. Research shows that when the mass concentration of Cr(VI) is greater than 1g L$^{-1}$, the pH value of the solution influences the major forms of Cr(VI) as table 1 demonstrated [16].

| pH value in aqueous | Major forms of Cr (VI) |
|---------------------|------------------------|
| pH<1                | $H_2CrO_4$             |
| 1<pH<7              | $HCrO_4^-$ $Cr_2O_7^{2-}$ |
| pH>7                | $CrO_4^{2-}$            |

Equilibrium equations among all the forms of Cr(VI) are as follows.

$$H_2CrO_4 + H_2O \leftrightarrow H_3O^+ + HCrO_4^- \quad \text{lg}K_1=0.2 \quad (1)$$

$$HCrO_4^- + H_2O \leftrightarrow H_3O^+ + CrO_4^{2-} \quad \text{lg}K_2=-5.9 \quad (2)$$

$$2HCrO_4^- \leftrightarrow Cr_2O_7^{2-} + H_2O \quad \text{lg}K_3=1.53 \quad (3)$$

Cr(VI) has a strong oxidability. The oxidation of Cr(VI) is related to its concentration and pH value (namely, the concentration of $H^+$). The higher the Cr(VI) concentration, the lower the pH value (the higher the concentration of $H^+$), the greater the redox potential, and then the stronger the oxidation of Cr (VI). When reacting with a reducing agent, Cr(VI) will be reduced to Cr$^{3+}$ ions [17]. Under acid condition, the electrode reaction equation of Cr(VI) reacting with reducing agents in redox reaction can be expressed by equation (4).

$$Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O \quad (4)$$

3. Preparation of modified activated carbon
Activated carbon (AC) is a kind of absorption material with well-developed pore structure and huge specific surface area, thus it enjoys a stronger adsorptive performance. Because the adsorptive performance of AC is mainly determined by its surface physical structures and chemical properties, it is necessary to modify the physical structure and chemical properties of AC to a certain degree for improving its performance in adsorbing and removing specific pollutants.

3.1. Modification methods towards the surface physical structure of the activated carbon
The modification of surface physical structure of AC refers to utilizing physical or chemical methods to increase the specific surface area and changing the pore size (larger or smaller) or pore size distribution, in order to change the physical absorption performance of AC during its preparation, and to change the adsorptive structure of AC’s surface.

The modification of the surface physical structure of AC generally falls into two steps, a) carbonizing AC to remove volatile components, b) and using some oxidative gas to enrich the pore structure of AC. This can develop the pore structure of AC, and uniform the pore size distribution, through a good control of some carbonization conditions, such as: the carbonized time, carbonized temperature, activator types, and the activation time during activation, and addition of some oxidants [18]. Generally, the pore size
can be reduced by adopting the thermal shrinkage method, gas phase pyrolysis for blocked pores, and impregnation and covering method [19].

3.2. Modification of surface chemical properties of activated carbon and research on its performance for removing Cr(VI) from water
The modification of surface chemical properties of MAC refers to using physical or chemical methods to change the surface functional groups on AC and the ions and compounds loaded on the surface, making it the active point in specific adsorption, to control the hydrophilic/hydrophobic properties of AC and enhance its binding capacity with metal (or metal oxide). The modification methods of activated carbon’s surface chemical properties usually include: surface oxidation method, surface reduction method, load material modification method, microwave processing modification method, and alkali method [20]. According to the available reports, the modification methods to prepare AC which can remove Cr(VI) from water efficiently mainly include: oxidation modification, reduction modification, loaded metal modification and microwave processing modification.

3.2.1. Activated carbon modified by oxidation. After treating the surface of activated carbon by strong oxidant, under certain experimental conditions, the acidic groups are increased and the adsorption ability of activated carbon towards polar material is also improved. The types and quantities of groups on the surface of activated carbon, modified by different oxidants are also different. In general, the stronger oxidability of oxidant leads to a greater quantity of the oxygen-containing functional groups on the surface of the AC. At present, commonly used oxidants are nitric acid, potassium permanganate, sulfuric acid, and phosphoric acid [21].

Using sulfuric acid, phosphoric acid, nitric acid, Yao et al. [22] held a modified experiment on granular activated carbon after it was sieved by 10 to 16 mesh screens. The results showed that, under the optimum adsorption conditions, the highest removal rates for Cr(VI) of three kinds of acid-modified activated carbons were 95.79%, 97.50% and 99.2% respectively, and were increased by more than 30% compared with the virgin ones. Ryszard et al. [23] applied HNO$_3$ to the modification, and adopted argon gas to protect it under 1100 °C for degassing and modifying activated carbon. Making a comparison of the adsorptive performance for Cr(VI) of these two kinds of modified activated carbons, the results showed that when pH was 5, temperature was 25 °C, adsorption time was 3 hours. The maximum adsorption capacity for Cr(VI) of HNO$_3$ modified activated carbon was 6.92 mg/g, while degassing modified activated carbon was 2.07 mg/g, and the virgin activated carbon (before modification) was only 1.28 mg/g. This proved that the NO$_3^-$ and Cl$^-$ can reduce the adsorption performance of degassing modified activated carbon, while HNO$_3$ modified activated carbon was not affected by them. This further proved that the HNO$_3$ modified activated carbon demonstrated a better removal performance for Cr(VI). Jin et al. [24] used potassium permanganate to modify activated carbon, and the results showed that the optimum preparation condition was when potassium permanganate concentration was 0.01 mol/L, the solution pH was 3, the modification time was 5 hours, and the temperature of the solution was 35 °C. At the moment, the adsorption capacity of modified activated carbon for Cr(VI) in water reached 0.489 mg/g. Compared with the virgin activated carbon, adsorption capacity of modified activated carbon for Cr(VI) was increased by 85.89%. Ma et al. [25] used phosphoric acid modified activated carbon as raw material, modified it by nitric acid with 10% concentration for 4 hours under 40 °C, and obtained nitric acid modified activated carbon. At room temperature, 0.2 g of such MAC was used to treat 50 mL Cr(VI) solution with a concentration of 100 mg/L, and the adsorption rate of Cr(VI) was increased from 49.58% to 79.21%. The above studies showed that adsorption capacity for Cr(VI) of oxidation modified activated carbon was improved greatly.

3.2.2. Reduction-modified activated carbon. Surface reduction modification mainly refers to, under proper temperature, when suitable reducing agents are used to reduce the functional groups on the surface of the AC, increase the number of oxygenous alkaline groups on the surface of AC, enhance its surface nonpolar property, and enable a stronger adsorption capacity for nonpolar substances [26].
Common reducing agents are H\textsubscript{2}, N\textsubscript{2}, NaOH, KOH and ammonia. In the process of water treatment, the number of the surface oxygenous alkaline groups on AC after reduction treatment increased significantly. This helps AC to absorb some pollutants (particularly organic pollutants) [27]. Under acid condition, through the electrode equation of the redox reaction between Cr(VI) and reducing matters, the increasing of alkaline groups would undermine the adsorption of Cr(VI). However, studies of Park et al. [28] suggested that the removal rate of AC after being treated by NaOH increased by two times, after adsorbing Cr(VI) for 170 minutes. The results showed that this may be attributed to the specific surface area and decrease of pore volume. At the same time, Chiang et al. [29] proved that under the alkaline condition, OH- will react with functional groups on the surface of the activated carbon.

3.2.3. Loaded metal modified activated carbon. The modification of loaded metal mainly takes advantage of the reducibility and adsorption characteristics of AC. During that process, the metal ions are adsorbed on the surface of AC, and then the reducing property of AC is used to reduce metal ions into ions in forms of simple substance or low valence. Due to the strong binding capacity of metal or metal ions towards absorbed substances, the adsorption capacity of AC towards absorbed substance is greatly enhanced. At present, loaded metals are commonly used, such as iron, manganese and silver [30]. Zuo et al. [31] took advantage of ferric chloride solution to modify AC, making it loaded iron oxide by the method of impregnation and roasting, and studied adsorption performance of AC towards Cr(VI) in water. The results showed that under the same conditions, virgin AC possesses a 38.6% removal rate towards Cr(VI) ion, while the removal rate of MAC was increased to 91.4%. Therefore, iron-MAC can increase the adsorption capacity towards chromium ions and improve adsorption efficiency. Leng et al. [32] studied the modification of AC through manganese ion solution with different concentrations. They thought that under the same conditions, manganese ion modified activated carbon can increase the adsorption capacity towards Cr(VI), and follow the Langmuir adsorption model. Qin et al. [33] loaded Fe\textsubscript{2}O\textsubscript{3} and MnO\textsubscript{2} onto mulberry stem to study the adsorption performance of composite adsorbent towards Cr(VI). The results showed that under the same conditions, compared with mulberry stem activated carbon, the maximum adsorption capacity of mulberry stem/iron manganese oxide composite adsorbent towards Cr(VI) was increased by 33.02%. And, after 3 times of desorption and regeneration, the regeneration and utilization efficient of composite adsorbent was 86.80%. Kakavandi et al. [34] utilized zero-valent iron and silver bimetallic nanoparticles to modify AC, and studied the Fe\textsuperscript{0}/Ag activated carbon’s performance for removing Cr(VI). The results showed that when pH value was 3, Cr(VI) adsorption effect was best, and could reach adsorption equilibrium within 60 minutes, which was in line with the Langmuir adsorption model. The maximum adsorption capacity then was 100 mg/g, and Fe\textsuperscript{0}/Ag activated carbon possesses magnetism, which helped the adsorbent regeneration. Therefore, it has great potential in application, demonstrating the trends in future.

3.2.4. Modified activated carbon by microwave treatment. Microwave modification mainly indicates that the activated carbon absorbs the energy of microwave irradiation, rises the temperature of the whole system rapidly, causes a chemical reaction between the functional groups on the surface of AC and modifier, produces chemical reaction, and further changes the structure of the functional groups on the pore surface. At the same time, the rising system temperature will promote carbonization, and lead to certain changes in the pore structure [35, 36]. Ma et al. [37] adopted nitric acid-microwave modified AC and microwave directly modified AC into their studies. The results showed that the adsorption capacity of Cr(VI) was significantly increased, with a removal rate towards Cr(VI) of 78.62%, increased by 47.49% compared with the virgin activated carbon. The adsorption capacity towards Cr(VI) of microwave directly modified AC was 22.01%, which was 2.83% less than gas-free modified carbon (removal efficiency was 24.84%). However, its removal rate towards aniline was enhanced. This showed that the microwave directly modified AC favored the adsorption of hydrophobic organic, and did not favor the adsorption and removal of metal ions in water.
4. Conclusion and prospect

Either changing the surface physical structure, or surface chemical properties of the AC, can improve the adsorption performance of AC. Activated carbons applied to remove heavy metals are mainly chemical modified ones. It is generally acknowledged that changing the surface chemical properties of AC can better the effects of removing Cr(VI) from water. Although AC enjoys extensive sources, using waste biomass to prepare AC, and improving its adsorption performance through modification, such a recycle mode of “treating wastes by wastes” is still undoubtedly one of the research trends in future.

Current methods of studying MAC to removing Cr(VI) in water are mainly oxidation modification, reduction modification, loaded metal modification, and microwave modification. Among these methods, oxidation modified activated carbon and loaded metal modified activated carbon perform better in removing Cr(VI), and thus are studied more. Through the magnetic metal nanoparticles loaded in AC, not only does it improve the adsorption performance of AC towards Cr(VI), but it is also conducive to recovery. Therefore, it has a great application value, and is one of the development trends of activated carbon.

Removal effect of MAC towards Cr(VI) is often affected by the chemical characteristics of Cr(VI), and a variety of other factors. Meanwhile, the added modified material and AC also react with each other during the process of adsorption. At present, a lot of researchers adopt artificially configured Cr(VI) solution, while the factory chromium wastewater consists of complicated composition. Hence the competition mechanism of Cr(VI), and other ions, and their effects on the adsorption performance of modified activated carbon may be an important trend in future studies.

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