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A new preparation process of coal-based magnetically activated carbon

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Abstract Fe/C-based magnetically activated carbon (MAC) was obtained by carbonizing and activating its precursor, that was prepared by co-precipitation of anthracite coal impregnated in ferric chloride solution. The effect of the concentrations of $FeCl_3$ and pH of solution on BET surface area, pore volume and magnetic properties of the MAC was studied by BET N_2 adsorption and VSM method. The results indicated that the magnetization of MAC gradually increases with increasing concentration of $FeCl_3$ and pH value of solution, and BET surface area was inclined to fluctuation. The largest BET surface area and magnetization of MAC were 1327.5 m^2/g and 35.56 emu/g, respectively. The form of magnetic matter in the magnetically activated carbon was mainly Fe_3C by X-ray powder diffraction (XRD) and magnetic attraction test.

Key words magnetically activated carbon; coal; magnetization; specific surface area; XRD

1 Introduction

Activated carbon is an excellent adsorbent with porous structure and a great number of functional groups. It could adsorb effectively organic and inorganic pollutants and so on (Ahmad et al., 2009; Spahisa et al., 2008; Foo et al., 2010). Now, it has been widely used in water treatment areas.

The traditional filtration method of separating activated carbon has some shortages, e.g. the blockage of filters and the loss of activated carbon, which may easily result in second pollution in the water treatment process (Ai et al., 2010; Zhang et al., 2007). Rapid development of magnetic separation technology provides a new way. Activated carbon can gain magnetism through adding magnetic material (Nakayama et al., 1993). There are many studies on the preparation of magnetically activated carbon combining metal oxides (Cínthia et al., 2009; Luiz et al., 2002; Liu et al., 2010; Yang et al., 2008; Fan et al., 2007; Xing et al., 2009; Qu et al., 2002; Zhu et al., 2009; Zhang et al., 2005). The magnetic adsorbent has a better adsorption capacity, and could be recovered by magnetic separation technology (Qu et al., 2002; Zhu et al., 2009). At present, the magnetically activated carbon was chiefly prepared by the secondary disposal of activated carbon and magnetic matter. But this kind of disposal condition is relatively complex. Because of the use of adhesive and magnetic particles, some flaws appear in the magnetically activated carbon, e.g. pore plugging, smaller specific surface area and poor magnetic property (Ai et al., 2010; Xing et al., 2009; Zhang et al., 2005). In this paper, a new simple and convenient preparation method for magnetically activated carbon was studied by using coal as raw material, and $Fe(OH)_3$ as magnetism addition.

2 Experimental

2.1 Materials and instruments

High-sulfur anthracite was used as material, which was taken from the Wansheng District in Chongqing City, China. The coal was smashed, sieved (size≤120 mm), and dematerialized by HCl and HF. The demineralized coal was obtained by filtering and drying. Industrial analysis data on the dematerialized coal are presented as follows: M_{ad} 1.84%, A_d 3.21%, V_d 17.65%, F_{cd} 79.14% and S_t 4.01%.

The main instruments include a muffle furnace

(Chongqing Xinte), Micromeritics ASAP 2010, Shimadzu XRD-6000, and Lake Shore VSM 7304.

2.2 Preparation of MAC

The precursor of magnetically activated carbon [the mixture of coal and $Fe(OH)_3$] was obtained by the co-precipitation method. The detailed preparation steps are presented as follows. The demineralized coal was put into a certain concentration solution of ferric chloride before addition of sodium dodecyl sulphate. After keeping static adsorption, ammonia solution was slowly added to adjust the pH value of the solution. The magnetically activated carbon precursor was obtained by statically placing, filtrating and drying.

The magnetically activated carbon precursor was mixed with activator (KOH) and distilled water in a certain proportion, stirred into paste, and put into the muffle furnace. Under the protection of nitrogen, the mixture was carbonized for 45 minutes at 550℃, and activated for 1.5 hours at 820℃.

2.3 Characterization of MAC

Specific surface area (BET) and pore structure were measured by Micromeritics ASAP 2010 under the condition of low- temperature N_2 adsorption.

XRD analysis was conducted on Shimadzu XRD 6000 using Cu*K*α, and operated at 40 kV and 30 mA. The scanning range was from 20º to 80º with λ of 0.154 nm. Scanning mode was the continuous scan, and scanning speed was 2.0000 deg·min^{-1}.

Magnetic properties of MAC were performed on VSM-7304. And the range of adding magnetic intensities was between -12 and 12 kOe.

3 Results and discussion

3.1 Structural properties of MAC

BET surface area and pore structure of magnetically activated carbon are the main parameters for activated carbon characterization. A series of MAC prepared under various concentrations of $FeCl_3$ and pH values of solution were chosen to study its structural characteristics, and make a comparison with ordinary activated carbon. The results are listed in Table 1.

In Table 1, by a comparison with ordinary activated carbon, the total pore volume slightly increases (samples 2 and 5) or decreases within the range of 5.9%–7.8% (samples 1, 3, and 4), and the micropore volume ratios (49.3%–60.4%) are obviously lower. It can be explained as follows. The pores of MAC are mainly mesopores and micropores. And the catalysis of iron can make micropores etched into mesopores or macropores (Han et al., 2008). Altogether, $Fe(OH)_3$ breaking down and small molecules escaping in coal are beneficial to increasing or enlarging pores.

Table 1 Surface area and pore properties of MAC

Sample	Surface area ($m^2 \cdot g^{-1}$)	Total volume ($cm^3 \cdot g^{-1}$)	Micropore volume ($cm^3 \cdot g^{-1}$)	Micropore volume ratio (%)
0	1004.4	0.51	0.37	72.5
1	925.0	0.47	0.27	57.4
2	1327.5	0.67	0.33	49.3
3	909.6	0.47	0.24	51.1
4	987.4	0.48	0.29	60.4
5	1223.9	0.60	0.34	56.7

Note: 0-ordinary activated carbon;1%–3% of $FeCl_3$, 6.5 of pH; 2%–5% of $FeCl_3$, 6.5 of pH; 3%–9% of $FeCl_3$, 6.5 of pH; 4%–5% of $FeCl_3$, 3.5 of pH; 5%–5% of $FeCl_3$, 8.0 of pH.

As pH is 6.5 (samples 1, 2 and 3 in Table 1), the BET surface area inclines to fluctuate with increasing concentrations of $FeCl_3$, and becomes the highest (1327.5 m^2/g) as the concentrations reach 5%. As is seen in Table 1, BET surface areas of samples 4, 2 and 5 firstly increase and then decrease with increasing pH of the solution, and become largest as the pH value increases to 6.5. This can be attributed to two factors. Firstly, the metallic compound itself has pore structure and the catalysis of iron could make new pores emerge, and the BET of magnetically activated carbon increases. Secondly, the catalysis of iron could make micropores etched into mesopores or macropores, which will lead to the decrease of BET. When the first factor plays a major role, the BET of magnetically activated carbon will increase, but, on the contrary, the BET will decrease.

3.2 Magnetic properties of MAC

Shown in Figs. 1 and 2 are the magnetic hysteresis loops of MAC prepared under the conditions of various concentrations and pH values of $FeCl_3$ solution, respectively. The magnetic hysteresis loop is a closed curve describing magnetic hysteresis phenomenon that refers to the change of magnetization (M) lags behind the change of magnetic field strength (H) in the positive and negative demagnetization processes of magnetized magnetic material. It can reflect remanence, coercivity and magnetic characteristics. From hysteresis loops in Figs. 1 and 2, the closed curve area is very small, the hysteresis loop is long and narrow, and the hysteresis phenomenon is not obvious. After local enlarging, we can find that it has hysteresis characteristics, smaller remanence (0.02–0.54 emu/g), and coercivity (35.2–45 oe). It is proved that the MAC is a soft magnetic adsorbent. It is related to the magnetic material existence form, crystal morphology and size, and also the high dispersion of magnetic material in the carbon matrix.

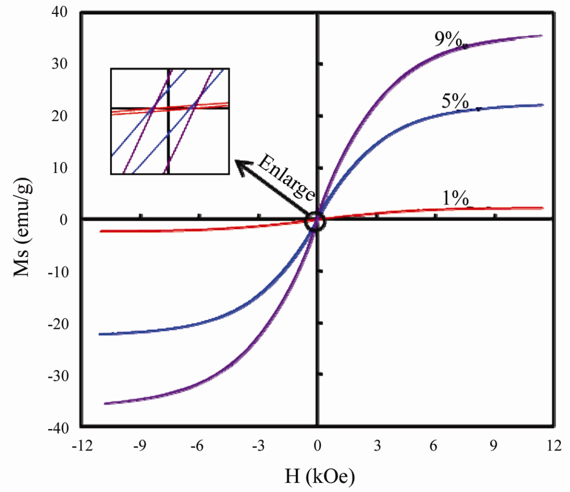

Fig. 1. Effect of the concentrations of $FeCl_3$ solution on the magnetization curve.

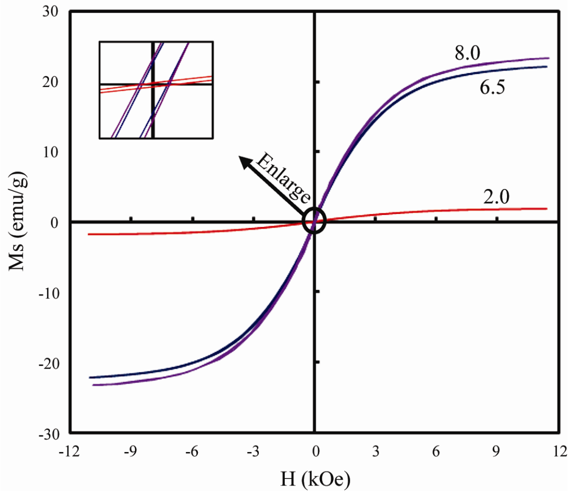

Fig. 2. Effect of pH of the solution on the magnetization curve.

From Fig. 1, the magnetization of these samples increases gradually with increasing magentic field intensity, and finally reaches the state of saturation magnetization. The saturation magnetization (Ms) increases gradually with increasing $FeCl_3$ solution concentrations, and reaches 35.56 emu/g when the concentrations of $FeCl_3$ solution are 9%. It is due to that the concentrations of $FeCl_3$ solution change will bring about the difference of $Fe(OH)_3$ content in the magnetically activated carbon precursor. And besides, this variation characteristic is similar to that of Co-based magnetically activated carbon (Fan et al., 2007) and coal-based magnetically activated carbon (Xing et al., 2009).

Fig. 2 shows that the internal magnetic domains of the prepared samples increase ceaselessly with increasing magnetic field strength. And the magnetization degree gradually increases until it reaches the state of saturation magnetization. The saturation magnetization firstly increases rapidly, then slowly, till it reaches the maximum 23.32 emu/g when the pH increases to 8. This can be explained as follows. For a certain concentration of $FeCl_3$ solution, there is initially a lot of Fe^{3+} in the solution. So abundant Fe^{3+} and OH^{1-} in the solution will quickly combine to form $Fe(OH)_3$ precipitation with increasing pH of the solution. But when pH continues to increase, Fe^{3+} will be limited in the solution combined with OH^{-}. The newly generated precipitation is gradually reduced until there is no more precipitation.

3.3 Morphological analysis of Fe in MAC

3.3.1 XRD analysis of MAC

In order to study the existing form of the magnetic material in magnetic active carbon, a kind of MAC, which was prepared under the conditions of 5% $FeCl_3$ and 6.5 of pH, was analyzed by using XRD diffraction instrument. The XRD diffraction diagram is shown in Fig. 3.

Comparing with the standard XRD card, we could find out that there are a number of diffraction peaks of Fe_3C crystal face within the range of 36° to 52° of 2θ. These peaks indicate that there are different forms of Fe_3C. In these diffraction peaks, A (103) crystal plane diffraction peak is strongest, which is located at 45° of 2θ.

In addition, it turns out that B (104) crystal face diffraction peak occurs at the diffraction angle 33° of 2θ. There may be a very little Fe_2O_3 presented in MAC. The peak intensity is relatively weak, and may be related to crystal shape and structural distribution of iron carbide crystallites in the MAC. The average grain size of microcrystalline is calculated by the Scherrer formula $D=K/FW(s)\cos\theta$ [K is a constant of 1, FW (s) is the specimen width, and θ is diffraction angle], and the results are presented as follows. The average grain size is 72 nm, and the crystal grain sizes of A (103), A (420), and A (022) crystal surfaces are respectively 64.3, 73.4, and 63.3 nm. These crystal surfaces are different in crystal grain size, which may be determined by the annealing process, temperature, time and so on.

3.3.2 Macroeconomic analysis of the existing form of iron carbide in MAC

Iron carbide is an interstitial compound formed at high temperature, with strong binding force between iron and carbon. The iron carbide is an orthorhombic

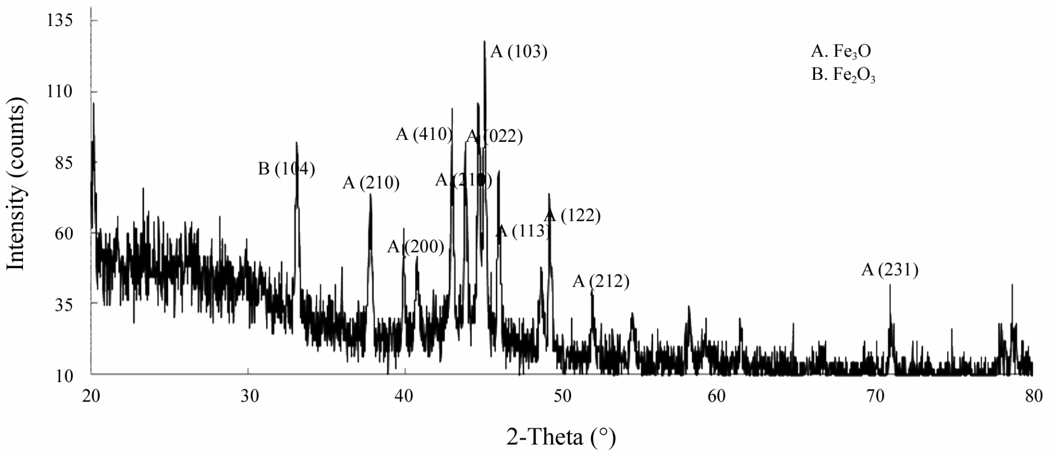

Fig. 3. XRD patters of MAC.

crystal. Each carbon atom is surrounded by 6 iron atoms located at an angle position in the crystal structure, and exhibits octahedron structure. Each iron atom is shared with two octahedrons. The related studies showed that iron carbide was formed through the carburization mechanism (Hui et al., 2003) at high temperature (t>628℃), e.g. $Fe+CO \rightarrow Fe_3C+CO_2$. So, if this was reasonable for the Fe_3C formation in the process of heat treatment, iron element was not involved in chemical bond breaking and resetting of the carbon molecular structure. Fe_3C cannot be organically united with carbon structure, and cannot be conducive to recovery.

In order to analyze the structure form and formation mechanism of magnetically activated carbon, magnet attraction idea was proposed in preliminary discussion. Specific exercises are given as follows. 2.00 g MAC, which was prepared under the conditions of 5% $FeCl_3$ and pH=6.5, attracted with a magnet wrapped with a layer of plastic film. It was observed that the MAC was attracted quickly by the magnet for a moment. The weight of the attracted magnetically activated carbon was 1.86 g, and the attraction recovery ratio was 93%. According to the attracting phenomenon and recovery ratio, it is shown that the magnetic addition of $Fe(OH)_3$ and raw coal occurred decomposition reaction, namely chemical oxidation and reduction. The iron element influenced the carbon molecular structure. Finally iron carbide was formed and connected to the carbon molecular structure during the process of carbonization and activation. These characteristics are useful for the separation and recovery of MAC during the process of water treatment. Therefore, we can find out that the best ratio of coal and iron oxide in the precursor of MAC can further improve the recovery ratio through controlling the adding amount of ferric hydroxide.

4 Conclusions

Magnetically activated carbon precursor is obtained by the co-precipitation method, and then carbonized and activated to get coal-based magnetically activated carbon. The magnetic material form in MAC is iron carbide. The average diameter of MAC is 72 nm, which is a kind of novel adsorption material connected organically with carbon structure. The specific surface area of MAC shows a fluctuation trend with increasing $FeCl_3$ concentration and the pH of the solution. When the $FeCl_3$ concentrations are 5% and pH is 6.5, the BET of MAC is the highest (1327.5 m^2/g), which increases by 32.2% as compared with the conventional activated carbon's. The saturation magnetization increases gradually with increasing $FeCl_3$ concentration and pH of the solution, and its maximum is 35.56 emu/g. The remanence and coercivity of MAC are little. From the hysteresis loop, it is shown that the magnetically activated carbon adsorbent has soft magnetic characteristics.

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