Characterization of oxidized activated carbon obtained from *Astragalus* residue and its adsorption application for Cu$^{2+}$ from aqueous solution

N Feng Y Zhang and M Zhu*

School of Basic Medical Science, Ningxia Medical University, Yinchuan 750004, China

E-mail address: ncfeng@sina.com

Abstract. The activated carbon prepared by *Astragalus* residue was chemically modified with KMnO$_4$. The samples before and after modification were characterized by N$_2$ adsorption, XRD, SEM and Boehm titration. Accordingly, the original and modified-carbon materials were used for adsorption of Cu$^{2+}$ from aqueous solution. The results showed that the numbers of oxygen-containing functional groups increased and MnO$_2$ was almost uniformly deposited on the surface of activated carbon after modification by KMnO$_4$. The Langmuir isotherm provided the well description of the equilibrium adsorption giving a maximum uptake capacity for Cu$^{2+}$ as 127.71mg/g and 196.46mg/g, respectively for activated carbon before and after modification. KMnO$_4$ changed the physicochemical properties and surface texture of activated carbon significantly and enhanced adsorption capacity for Cu$^{2+}$.

1. Introduction

Heavy metal wastewater, waste residue, sludge and so on are seriously harmful to human survival and physical and mental health through soil, water, air, especially the food chain. When the copper content in the water is more than 1.5 mg/L, the white fabric can be dyed, the water has a peculiar smell and the higher concentration of copper is poisonous to the organism [1]. WHO recommends that the concentration of copper in drinking water is lower than 1.5mg/L [2]. There are different treatments for the removal of Cu$^{2+}$ from aqueous media such as ion-exchange [3], chemical precipitation [4], etc. Activated carbon adsorption is also a method for the removal of a wide variety of heavy metal ions dissolved in aqueous media. In general, activated carbon is synthesized from natural precursors, such as coal, wood or nutshells [5]. Although these materials are very successful, their widespread use is restricted due to the high cost. In addition, Carbon adsorption removes effectively organic compounds but is ineffective at removing inorganic pollutants and metals [6]. Recent years, many researchers have focused on finding economical and available materials to prepare activated carbon especially from plant biomass and biomaterial waste, such as olive stone waste residue [7], grape bagasse [8]. Activated carbon modification is gaining prominence due to the need to enable activated carbon to develop affinity for certain contaminants to cater for their removal. There are many techniques for modification, but chemical oxidation is the most common method, which presents the advantages of simple step, low cost, energy saving and introducing more oxygen-containing functional groups on the surface of activated carbon. Song *et al.* used HNO$_3$ and H$_2$O$_2$ as oxidant to modify the activated carbon, and investigated the effect of the liquid-phase oxidation on the Pb$^{2+}$ adsorption capacities of activated carbon [9]; Wang *et al.* applied activated carbon modified with KMnO$_4$ for the removal of...
Pb(II) [10]. The results showed that chemical oxidation method improved the adsorption efficiency of activated carbon for small molecules and ions.

In the present study, activated carbon was prepared from Astragalus residue, a Chinese traditional medicine-processing waste and then Astragalus residue activated carbon was modified with KMnO₄. The original and modified activated carbons were applied for the removal of Cu²⁺ in aqueous solutions.

2. Materials and methods

2.1. Fabrication of activated carbon from Astragalus residue

Astragalus residue, obtained from a local pharmaceutical company in Ningxia, China, was used as raw material for the preparation of AC by KOH activation. Astragalus residue was ground, sieved (40 mesh), washed with distilled water, and dried in the air. Then, 20 wt% KOH solution was mixed with a certain amount of astragalus residue at a ratio of 1:3 (Astragalus residue: KOH, g/mL). The KOH-impregnated sample was heated in a furnace and activated at 600°C for 80 minutes, and then the product was cooled to room temperature, soaked with 0.1mol/L HCl to remove the residual KOH and washed sequentially several times with distilled water until its filtrate reached neutral pH. The resulting activated carbon was dried at 80°C for 12h. The obtained sample is abbreviated as AC.

2.2. KMnO₄ oxidative modification of AC

AC was modified with KMnO₄ through dipping and heating methods. AC was put into 0.15 mol/L KMnO₄ solution at a ratio of 10:1 ((activated carbon: KMnO₄ solution, g/L) for 90 minutes at boiling temperature. The modification was conducted under stirring in a flask equipped with a stirrer and a reflux condenser and heated in a thermostat water bath. The modified activated carbons were washed repeatedly with distilled water until approaching neutral pH, and dried at 80°C for 12h. The sample after treatment was cooled to room temperature and stored in a desiccator for later use. This obtained sample is abbreviated as AC-Mn.

2.3. Characterization methods

The surface morphology was investigated by scanning electron microscopy (SEM, HITACHI S-3400N). The X-ray diffraction (XRD, Shimadzu XRD-6000) patterns were collected using Cu Kα radiation. The surface areas and pore characteristics of AC and AC-Mn were determined by N₂ adsorption/desorption isotherm at 77K (Micrometritics, ASAP2020). The Boehm titration method [11] was used to identify the number of oxygen-containing functional groups on the material surfaces.

2.4. Batch experiments

The adsorption capability of AC and AC-Mn toward Cu²⁺ was investigated by agitation of 0.060g of adsorbent with 30mL of Cu²⁺ solution of desired concentration in sealed conical flask using a shaking thermostat machine at a speed of 100 rpm for 1h at a pH of 5.0. Then, the mixtures were filtered using Millipore membrane, and the concentration of Cu²⁺ in the solution was measured by AAS (Persee A3 Atomic Absorption Spectrophotometer). The amount of Cu²⁺ adsorbed at equilibrium was calculated as follows:

\[
q = \frac{(c_0 - c_e)V}{m}
\]

where \(c_0\) and \(c_e\) are the initial and equilibrium Cu²⁺ ion concentrations in mg/L in the solutions respectively; \(V\) is the volume of solution in L and \(m\) is the weight of adsorbent in g.

3. Results and discussion

3.1. Characterization of adsorbents
The results of the pore structural characterization of AC and AC-Mn are listed in Table 1. AC had a large BET surface area and contains mostly micropores. The presence of micropore enhances adsorption capacity of AC, especially for small molecules or ions such as Cu$^{2+}$ [12]. KMnO$_4$ treatment led to a loss in the BET surface area, total pore volume and micropore surface area. For the initial AC, the BET surface area was 1519.53 m$^2$/g, which decreased to 774.13 m$^2$/g after modification. Total pore volume and micropore surface area also changed significantly. The results indicated that the pore structure of the AC-Mn was destroyed by KMnO$_4$ due to strong oxidation at higher temperature.

| Sample                        | AC             | AC-Mn          |
|-------------------------------|----------------|----------------|
| BET surface area(m$^2$/g)     | 1519.53        | 774.13         |
| Total pore volume(cm$^3$/g)   | 1.04           | 0.66           |
| Micropore surface area(m$^2$/g)| 1386.53        | 596.59         |
| Iodine number(mg/g)           | 1325.17        | 994.66         |
| Lactonic groups(mmol/g)       | 0.23           | 1.57           |
| Phenolic hydroxyl groups(mmol/g)| 1.07           | 0.94           |
| Carboxylic acid groups (mmol/g)| 0.42           | 2.82           |

The iodine numbers of AC and AC-Mn are summarized in Table 1. The iodine number (1325.17 mg/g) of AC was higher than the numbers of AC-Mn (994.66 mg/g). The iodine number was a measure of micropore content of the activated carbon by adsorption of iodine from solutions [13]. In the present study, the iodine numbers of AC and AC–Mn indicated that they are micropore-type activated carbon and thus suitable for the adsorption of small molecules and ions such as Cu$^{2+}$. This corresponds to the result of micropore surface area. The Boehm titration results of AC and AC-Mn are also shown in Table 1. The number of oxygen-containing functional groups, such as carboxylic, lactone groups increased after oxidation modification by KMnO$_4$. The interactions between the oxygen-containing functional groups and heavy metal ions are strong, indicating that the absorption of heavy metals by activated carbon occurs at its oxygen-containing functional groups [14]. Thus, these function groups are very useful in adsorption for heavy metal ions.

The SEM images of AC and AC-Mn are shown in Figure 1. It is apparent that the surface morphology of AC was different from that of AC-Mn. The surface of AC showed honeycomb and well-developed porous structure. After treating AC by KMnO$_4$, its surface morphology was completely changed. The grainy structure showed on AC-Mn in Figure 1b revealed that MnO$_2$ was
nearly uniformly deposited on the surface because of redox reactions through the impregnation of KMnO₄.

![Figure 2. XRD patterns of AC (a) and AC-Mn (b)](image)

The XRD spectra of AC and AC-Mn are presented in Figure 2. The diffraction spectrum of AC (Figure 2a) displayed two diffraction peaks around 26° and 43°, corresponding to the 002 and 100 diffraction of graphite [15, 16]. The 002 plane presented a narrow peak with steep rise, and the 100 plane displayed a broad small diffraction peak, these characteristics indicated that AC had the predominantly amorphous structure of carbons. The diffraction spectrum of AC-Mn is shown in Figure 2b. Compared with the AC, the 002 plane showed peaks with gradually decreased intensity, and the 100 plane had disappeared, indicating that the aligned structural domains in the carbon matrix had been destroyed in the process of oxidation–reduction; meanwhile graphitization degree was decreased [16]. However, for AC-Mn sample, the diffraction peaks at 25.91, 37.13, 42.57, 65.95 showed the presence of MnO₂ [10, 17]. These results confirmed that MnO₂ was successfully formed likely as a result of the redox reactions.

3.2. Results of adsorption experiments

The adsorption isotherms of Cu²⁺ on AC and AC-Mn with the initial concentrations of Cu²⁺ from 100 to 800 mg/L are shown in Figure 3. It shows that the adsorption capacity of Cu²⁺ on AC-Mn is higher than that of AC.

![Figure 3. Adsorption isotherms of Cu²⁺](image)

![Figure 4. Langmuir plots](image)

The experimental data of equilibrium isotherm for Cu²⁺ on AC and AC-Mn were analyzed with the most frequently used Langmuir (Eq. (2)) isotherms [18]:
\[
\frac{c_e}{q_e} = \frac{1}{q_m} + \frac{c_e}{q_m b}
\]  
(2)

where \(c_e\) (mg/L) is the equilibrium concentration of Cu\(^{2+}\) ions, \(q_e\) (mg/g) is the amount of Cu\(^{2+}\) ions adsorbed, \(q_m\) (mg/g) is the maximum adsorption capacity of Cu\(^{2+}\) ions, and \(b\) (L/mg) is the adsorption constant that relates to the affinity of the binding sites.

As shown in Table 2 and Figure 4, the adsorption patterns of Cu\(^{2+}\) on AC and AC-Mn are well fitted by Langmuir model, because the correlation coefficient (\(R^2\)) is much close to 1. According to the Langmuir isotherm, the maximum adsorption capacity of Cu\(^{2+}\) on AC-Mn was 196.46 mg/g and significantly higher than that of AC \(q_m=127.71\text{mg/g}\). A large value of \(b\) also implied strong bonding of Cu\(^{2+}\) to the AC-Mn. The oxidative modification with KMnO\(_4\) increased the number of oxygen-containing functional groups of AC-Mn, and the generation of MnO\(_2\) also improved the adsorption capacity of AC-Mn. MnO\(_2\) has a higher affinity for many heavy metals, which could be adsorbed as an inner sphere complex by surface complexation on MnO\(_2\) [19]. In last decades, there has been great interest in using MnO\(_2\) as adsorbent for the removal of various heavy metals ions [19-21].

A comparison of adsorption capacities \(q_m\) of AC-Mn and some other adsorbents reported in literatures are listed in Table 3. The adsorption capacity of AC-Mn for Cu\(^{2+}\) is higher than that of the majority of other activated carbons mentioned.

| Table 2. Langmuir parameters |
|-----------------------------|
| Adsorbent | \(q_m\) (mg/g) | \(b\) (L/mg) | \(R^2\) |
| AC-Mn     | 196.46         | 0.046         | 0.9985   |
| AC        | 127.71         | 0.024         | 0.9767   |

| Table 3. Maximum adsorption capacities for Cu\(^{2+}\) by various activated carbons |
|---------------------------------|
| Adsorbents                              | \(q\) (mg/g) | References |
|----------------------------------------|--------------|------------|
| Activated carbon from olive stone waste residue | 7.80         | [8]         |
| Activated carbon from grape bagasse     | 43.47        | [22]       |
| Activated carbon from hazelnut shell    | 39.54        | [23]       |
| Commercial activated carbon (powered)   | 5.1          | [24]       |
| Activated carbon from cassava peel      | 52.0         | [25]       |
| AC                                      | 127.71       | this study |
| AC-Mn                                   | 196.46       | this study |

4. Conclusions

*Astragalus* residue was used as a raw material for preparation of activated carbon (AC), and then AC was modified by KMnO\(_4\). AC had great BET surface area and porous honeycomb structure. KMnO\(_4\)-modified *Astragalus* residue activated carbon (AC-Mn) loaded a large amount of MnO\(_2\), produced more oxygen-containing functional groups on the basis of the AC and had lower BET surface area than AC.

AC and AC-Mn were used to adsorb Cu\(^{2+}\) in simulated wastewater. The adsorption capacity of AC–Mn for Cu\(^{2+}\) increased and became 1.56 times of that of AC because of the increase in its oxygen-containing functional groups and the emergence of MnO\(_2\) imparted onto AC by modification. Equilibrium data of Cu\(^{2+}\) on AC and AC-Mn was best fitted to the Langmuir isotherm.
Acknowledgements
This work was supported by NXYLXK2017B07 and the National Natural Science Foundation of China (No. 21667023).

References
[1] Nuhoglu Y and Oguz E 2003 Process Biochemistry 38 1627
[2] Rengaraj S, Yeon J, Kim Y, Jung Y, Ha Y and Kim W 2007 Journal of Hazardous Materials 143 469
[3] Zewail T M and Yousra N S 2015 Alexandria Engineering Journal 54 83
[4] Sis H and Uysal T 2014 Applied Clay Science 95 1
[5] Heibati B, Rodriguez-Couto S, Al-Ghouti M A, Asif M, Tyagi I, Agarwal S and Gupta V K 2015 Journal of Molecular Liquids 208 99
[6] Monsor L and Adhoum N 2002 Separation and Purification Technology 26 137
[7] Alslaibi T M, Abustan I, Ahmad M A and Foul A A 2014 Journal of Dispersion Science and Technology 35 913
[8] Demiral H and Gungor C 2016 Journal of Cleaner Production 124 103
[9] Song X, Liu H, Cheng L and Qu Y 2010 Desalination 255 78
[10] Wang Y, Wang X, Wang X, Liu M, Yang L, Wu Z, Xia S and Zhao J 2012 Colloids and Surfaces A: Physicochemical and Engineering Aspects 414 1
[11] Boehm H P 1994 Carbon 32 759
[12] An F, Cheng Y, Wu D and Wang L 2013 Adsorption 19 83
[13] Ceyhan A A, Şahin Ö, Baytar O and Saka C 2013 Journal of Analytical and Applied Pyrolysis 104 378
[14] Valle-Vigón P, Sevilla M and Fuertes A B 2013 Microporous and Mesoporous Materials 176 78
[15] Lu A and Zheng J 2001 Journal of Colloid and Interface Science 236 369
[16] Xiao Y, Long C, Zheng M, Dong H, Lei B, Zhang H and Liu Y 2014 Chinese Chemical Letters 25 865
[17] Pan N, Li L, Ding J, Li S, Wang R, Jin Y, Wang X and Xia C 2016 Journal of Hazardous Materials 309 107
[18] Allen S J and Brown P A 1995 Journal of Chemical Technology and Biotechnology 62 17
[19] Dong L, Zhu Z, Ma H, Qiu Y and Zhao J 2010 Journal of environmental sciences 22 225
[20] Gheju M, Balcu I and Mosoarch G 2016 Journal of Hazardous Materials 310 270
[21] Wang Z, Lee S W, Catalano J G, Lezama-Pacheco J S, Bargar J R, Tebo B M and Giammar D E 2013 Environmental Science & Technology 47 850
[22] Demiral H and Güngör C 2016 Journal of Cleaner Production 124 103
[23] Şayan E 2006 Chemical Engineering Journal 115 213
[24] Runtti H, Tuomikoski S, Kangas T, Lassi U, Kuokkanen Tand Rämö J 2014 Journal of Water Process Engineering 4 12
[25] Moreno-Piraján J C and Giraldo L 2010 Journal of Analytical and Applied Pyrolysis 87 188