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Application of sonication in improving the Cu(II) adsorpptivity and recycling performance of activated carbon fibers

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Abstract
In order to enhance the adsorptivity of viscose-based activated carbon fibers (VACFs) for low-concentration Cu(II), sonication-assisted zinc chloride reactivation process and sonication-assisted-pickling regeneration process were studied in this research. This study aims to prepare a modified VACFs with high Cu(II) adsorptivity and recycling performance at the same time. As 10 wt% ZnCl2 used as activator, specific surface area, micropore volume and mesopore volume of VACFs increase by 59.33%, 37.35% and 813.87% respectively, besides, the Cu(II) adsorptivity was improved by 2.04 times through the reactivation process. Based on the sonication-assisted-pickling regeneration process, the regeneration rate was changed from 96.85% to 107.81% during 1–5 recycling times.

1. Introduction

At present, the purification of low-concentration Cu(II) is facing a series of problems such as difficult removal, high energy consumption, etc [1, 2]. Adsorption method is considered to be the most promising and practical technology in the field of low-concentration Cu(II) purification [3, 4]. As a new generation of adsorbent materials, activated carbon fibers (ACFs) have a strong adsorptivity for low concentration adsorbates due to the direct distribution of a large number of microporous structures and surface polar groups on the surface of fibers [5–9]. Howbeit, the adsorptivity of ACFs for specific adsorbate need to be enhanced by different preparation process or modification process [10–13].

In recent years, there were few studies on the modification process of activated carbon fibers for the adsorption of low-concentration Cu(II), especially the reactivation process and the regeneration process [14–17]. Chen et al [18] enhanced the Cu(II) adsorptivity of granular activated carbon by 140% through a modification methods of citric acid and there was no research on recycling performance. Mugisidi et al [19] enhanced the Cu(II) adsorptivity of activated carbon by 120% through the treatment of 15% sodium acetate. Yu et al [20] modified ACFs by nitric acid oxidation process to enhance the Cu(II) adsorptivity, which can reach 23.13 mg · g−1 and 4.55 times of pristine felts. In general, there are few studies on the preparation process and modification method to improve the Cu(II) adsorptivity and recycling performance of ACFs. The research of regeneration process of adsorbent materials for specific adsorbate is rare, especially adsorbent materials with high recyclable performance for low-concentration Cu(II) need to be exploited urgently. Advantages and defects of different regeneration technologies are shown in table 1.

Based on the traditional chemical activation technology and pickling regeneration technology, the cavitation of power ultrasound was introduced into both activation and regeneration processes to enhance the Cu(II) adsorptivity and recycling performance of ACFs simultaneously in this paper. Sonication-assisted zinc chloride reactivation process can promote the pore-forming effect of reactivation process by affecting the size and defect
of microcrystalline structure. The process parameters were optimized according to the Cu(II) adsorptivity. Micropore structure and crystal structure were studied by BET, XRD and Raman respectively. Ultimately, ACFs with high Cu(II) adsorptivity and recycling performance were synthesized under the action of cavitation, chemical activation and regeneration.

2. Experimental

2.1. Sonication-assisted zinc chloride reactivation process
Viscose-based activated carbon fibers (VACFs, specific surface area 1056 m² g⁻¹) provided by Carbon Fiber Engineering Technology Research Center of Shandong University were chosen as pristine felts. Before the process of reactivation, VACFs were pretreated at high temperature to remove the adsorbed impurities from the surface. Pretreatment of VACFs was carried out in blast oven at 403 K for 3 h.

The reactivation process is shown in figure 1. Sonication-assisted impregnation and high temperature treatment were two major steps of the novel reactivation process. Zinc chloride was used as an activator in the step of ultrasonic impregnation, and VACFs were impregnated under the aid of ultrasound field in the solution of ZnCl₂ (10 wt%) for 0, 3, 6, 9, 12 and 24 h respectively. High temperature treatment was carried out at 1023 K for 0.5 h under high purity nitrogen gas, and the heating rate was set at 3 K min⁻¹. In this study, the pristine felts and reactivated samples were recorded VACF₀ and Z-VACF-xh separately.

2.2. Sonication-assisted-pickling regeneration process
Cu(II)-absorbed VACFs under a concentration of 50 mg l⁻¹ were used as research objects for regeneration process. First of all, Cu(II)-absorbed VACFs were placed in 15 wt% nitric acid solution with a bath ratio of 1:2500. Then the nitric acid solution was placed in an ultrasonic unit at a temperature of 298 K for 3 h with a ultrasonic power of 100 W after sealing. After sonication-assisted-pickling regeneration, sufficient washing and drying for VACFs were implemented to remove the residual pickling solution on the surface sufficiently.

2.3. Evaluation of Cu(II) adsorptivity
Cu(II) concentration was proportional to the intensity of absorption wavelength, thus ultraviolet-visible spectrophotometry could determine the absorbance of Cu(II) in the wavelength range of 190–800 nm. Sodium diethyldithiocarbamate (DDTC-Na) was used as chelating agent to established a DDTC-Na-Cu(II) chelating system in an ammonia environment (pH = 9 + 1). The chelating system has the maximum absorption intensity at 452 nm. Therefore, Cu(II) standard curve (figure 2) was established by the linear variation of UV absorbance at 452 nm A (ordinate) with Cu(II) concentration (abscissa). The Cu(II) standard curve and the detailed establishment process are shown in our published articles [20].

Pretreated ACFFs pretreated samples were placed in the Cu(II) standard working fluid of 50 mg l⁻¹ (c₀) with a bath ratio of 1:1000. The samples were adsorbed in a shaking table for 2 h at 333 K with a shaking speed of 120 rpm. Upon completion of adsorption, the absorbance value at 452 nm of remaining Cu(II) solution was tested. The concentration c of remaining Cu(II) solution was calculated by equation (1) according to the Cu(II) standard curve. Cu(II) adsorption value per ACFFs unit mass Q, Cu(II) removal efficiency Ar and regeneration rate η were calculated by equations (2–4) separately. In equations (2–4), m is the dosage of ACFFs in units of g, Q₀ and Qₙ are Cu(II) adsorption values of ACFFs before and after regeneration.

\[
c(\text{Cu(II)}) = \frac{A - 0.00542}{0.1721} \times \frac{100}{N} \times 50
\]  
\[
Q = \frac{V \times (c_0 - c_f)}{m}
\]
2.4. Characterization of VACFs

Specific surface area and aperture distribution of VACFs were measured by ASAP2020 automatic surface area and mesoporous/microporous analyzer. Rigaku D/max-RC x-ray diffractometer was used to measure the crystal structure of VACFs. In this study, the scan interval was 0.02°, the scan speed was 3°/min, and the scan range was 5°–50°. Raman spectra of the samples were measured by Renishaw inVia micro-confocal Raman spectrometer. Laser excitation wavelength was 632.8 nm. Raman shift spectra were recorded in the range of 800–2000 cm⁻¹. Scan time for the sample was 20 s and exposure times was twice.

3. Results and discussion

3.1. Micropore structure and adsorption property

Micropore structure of VACFs was analyzed by N₂ adsorption test. As shown in table 2 and figure 2(c), all of specific surface area, total pore volume, ultramicropore volume, supermicropore volume and mesopore volume have a significant enhancements after the process of sonication-assisted zinc chloride reactivation, in which specific surface area and total pore volume increased by 59.33% and 41.75% respectively in table 1. The figures indicate the enlargement of total pore volume mainly focused on ultramicropores (0.1276 cm³ g⁻¹) and mesopores (0.1701 cm³ g⁻¹), which can be indicated that the reactivation process has a significant function of pore-forming and pore wall destruction in unison. Sonication-assisted propagating in liquid has the function of accelerating liquids’ mechanical motion and cavitation effect. The cavitation effect can produce local high temperature, local high pressure, strong shock wave and high speed micro-jet, which provides a high-energy reaction environment for the progress physicochemical reaction progress of graphite-like microcrystalline carbon and amorphous carbon [21, 22]. Hence, pore-forming and pore wall destruction functions exist in the reactivation process intensely and concurrently.

\[
Ar = \frac{c_0 - c_1}{c_0} \times 100\% \tag{3}
\]

\[
\eta = \frac{Q_t}{Q_0} \times 100\% \tag{4}
\]
Pore size distributions (PSDs) is shown in figure 2(a). There is no significant change in PSDs and pore volumes of micropores at different aperture are improved in the mass, in particular, pore volumes of ultramicropore at 0.51 nm became weaker after recarbonization and reactivation. The adsorption isotherms of VACFs, recarbonated VACFs and reactivated VACFs are the typical I-type isotherms (figure 2(b)). The height of equilibrium increases obviously after the reactivation process, which depends on the micropore volume and consistent with the results of figure 2(c).

As figure 2(d) shows, Cu(II) adsorption value $Q$ is greatly improved after the reactivation process and it reaches the maximum ($Q_{Z-VACF-12h} = 16.26 \text{ mg g}^{-1}$) when the time of sonication-assisted impregnation is 12 h. The diameter of free Cu(II) in aqueous phase is 0.146 nm, thus physical adsorption of VACFs for Cu(II) mainly comes from the adsorption potential of micropore structure and mesopore structure. Hence, the enhancement of Cu(II) adsorptivity is increasement of adsorption potential energy caused by the simultaneous increase of micropore volume and BET surface area. The results shows that sonication-assisted zinc chloride reactivation process is an efficient modification method to enhance the Cu(II) adsorptivity of VACFs and sonication-assisted impregnation time of 12 h has the best promotion function on the Cu(II) adsorptivity of VACFs [23–26].

Table 2. Surface structure parameters of VACFs before and after reactivation.

| Adsorbent | VACF$_0$ | Z-VACF-0h | Z-VACF-12h |
|-----------|----------|-----------|------------|
| BET surface area/m$^2$·g$^{-1}$ | 1055.65 | 1269.5 | 1681.97 |
| Total pore volume/cm$^3$·g$^{-1}$ | 0.5379 | 0.5844 | 0.7625 |
| Micropore volume/cm$^3$·g$^{-1}$ | 0.4161 | 0.5038 | 0.5715 |
| Ultramicropore volume/cm$^3$·g$^{-1}$ | 0.3401 | 0.3477 | 0.4677 |
| Supermicropore volume/cm$^3$·g$^{-1}$ | 0.0760 | 0.1561 | 0.1038 |
| Mesopore volume/cm$^3$·g$^{-1}$ | 0.0209 | 0.0605 | 0.1910 |
| Average aperture/nm | 2.8137 | 1.8412 | 1.8133 |

Figure 2. Pore structure characteristics of VACFs. (a) PSDs of micropores; (b) adsorption isotherm; (c) volumes of different pores; (d) Cu(II) adsorptivity.
3.2. Microcrystal structure

Two peaks centered at around 22° and 43° in XRD patterns of VACFs are attributed to the (002) and (101) planes of the VACFs' microcrystal structure (figure 3(a)) [7]. Microcrystal size (crystallite stack thickness $L_c$ and planar diameter $L_a$) and interlayer spacing ($d_{002}$ and $d_{101}$) were calculated by Bragg equation, Scherrer equation and Warren equation (equations 5–7) respectively.

\[
d_{002} = \frac{\lambda}{2 \sin \theta_{002}} \quad (5)
\]

\[
L_c = \frac{K\lambda}{\beta \cos \theta_{002}} \quad (6)
\]

\[
L_a = \frac{K\lambda}{\beta \cos \theta_{101}} \quad (7)
\]

As table 3 shows, both $L_c$ and $L_a$ increase during the recarbonization process, and microcrystal sizes decrease evidently with the increase of sonication-assisted impregnation time. The results shows that recarbonization process is conducive to the growth of microcrystal, on the contrary, the effects of sonication-assisted impregnation on the microcrystal size is reduced. Ultimately, the effects of two major steps are nearly cancelled out as the sonication-assisted impregnation time reaches 12 h. In addition, the interlayer spacing $d_{002}$ of the VACF$_0$ is relatively large as 0.4141 nm in comparison with 0.3354 nm graphite, and the interlayer spacing of

| Sample      | $d_{002}$/nm | $d_{101}$/nm | $L_c$/nm | $L_a$/nm |
|-------------|--------------|--------------|----------|----------|
| VACF$_0$    | 0.4141       | 0.2148       | 0.6961   | 1.3508   |
| Z-VACF-0h   | 0.4066       | 0.2104       | 0.8935   | 1.9645   |
| Z-VACF-3h   | 0.4037       | 0.2085       | 0.6699   | 1.5886   |
| Z-VACF-6h   | 0.4044       | 0.2097       | 0.6433   | 1.5192   |
| Z-VACF-9h   | 0.4066       | 0.2100       | 0.6145   | 1.4232   |
| Z-VACF-12h  | 0.4066       | 0.2112       | 0.6025   | 1.3208   |
| Z-VACF-24h  | 0.4066       | 0.2118       | 0.5773   | 1.2010   |

Figure 3. Crystal structure analysis. (a) XRD spectrums; (b) Raman spectrogram; (c) peak positions of Raman spectrogram; (d) FWHMs of Raman spectrogram.
Z-VACF-0h is decreased to 0.4066 nm by the action of recarbonization. The interlayer spacing \( d_{002} \) and \( d_{101} \) become narrow during zinc chloride reactivation process, which is cleared that the microcrystal become smaller and more disordered with sonication-assisted impregnation time increases.

In order to further analyze its crystal structure, Raman analysis is carried out in this paper. As figure 3(b) shows, there exhibit a same appearance of two obvious bands namely D-band and G-band and the intensity of the G-bands are higher than D-bands in all cases of Z-VACF-xh. Consistent with the crystal structure analysis in XRD, the disorder degree \( R \) decreases during recarbonization, increases during sonication-assisted impregnation and is positively correlated with ultrasonic immersion time. It shows that the content of amorphous carbon in Z-VACF-xh decreases. As ultrasonic impregnation time increased almost all of D-, G- and D´-band position showed a gradual downward trend (figure 3(c)), all FWHMs of first-order bands increases and the FWHMs of second-order band decreases (figure 3(d)) [27].

### 3.3. Regeneration and recycling

As figure 4 (a) shows, \( Q \) of Z-VACF-12h maintain a high Cu(II) adsorptivity on the whole with recycling times of 1–5. \( Q \) of Z-VACF-12h reaches the maximum after the twice regeneration, which is 18.57 mg g\(^{-1}\) (\( \eta = 105.93\% \)). Hence one can see that sonication-assisted-pickling regeneration process achieves efficient regenerations and enhancements of Cu(II) adsorptivity for Z-VACF-12h. Z-VACF-12h has a commendable regeneration performance and can obtain a higher Cu(II) adsorptivity by the regeneration process. Furthermore, the mass loss rate of Z-VACF-12h is small, and the average of mass loss rate is 1.64% during 1–5 recycling times (figure 4(b)). The results show that Z-VACF-12h has good regeneration performance through sonication-assisted-pickling regeneration process, and the regeneration process has a further enhance effect on the Cu(II) adsorptivity of Z-VACF-12h at the same time of achieving efficient regeneration [28].

### 4. Conclusion

The experimental results show that sonication-assisted zinc chloride reactivation process is an effective modification method to further improve the specific surface area, pore volume and Cu(II) adsorptivity of VACFs. The reactivation process can enhance specific surface area, total pore volume, ultramicropore volume, supermicropore volume and mesopore volume of VACFs at the same time. After treated by sonication-assisted zinc chloride reactivation process, the specific surface area, micropore volume and mesopore volume of VACF increase by 59.33%, 37.35% and 813.87% respectively. Based on the sonication-assisted zinc chloride reactivation process, the Cu(II) adsorptivity of VACFs after reactivation is 3.04 times as it is. In addition, Z-VACFs achieve efficient recycling performance through sonication-assisted-pickling regeneration process. During 1–5 recycling times, the regeneration rate was changed from 96.85% to 107.81%.

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