Rice Straw/Sewage Sludge-Based Composite Activated Carbon: Its Some Basic Properties and Adsorption Effect for Cr (VI)

Liangqian Fan 1,*, Xianda Wang 1, Wenxin Wan 2, Qin Liu 1, Jie Cai 3 and Yan Wan 1

1 College of Civil Engineering, Sichuan Agricultural University, Dujiangyan 611830, China
2 College of Environment, Sichuan Agricultural Universities, Chengdu 611130, China
3 Department of Physical and Chemical Analysis, Dujiangyan Center for Disease Control and Prevention, Dujiangyan, 611830, China
Email: flqjacky@163.com

Abstract. In this study, the rice straw/sewage sludge-based composite activated carbon (RS-SCAC) was prepared from the mixture of sewage sludge and rice straw. Some basic properties of RS-SCAC, i.e., yield, iodine number, contents of heavy metals, surface functional groups, and leaching toxicity, were characterized. Furthermore, the adsorption performance of RS-SCAC for Cr (VI) was investigated. For RS-SCAC, the yield was moderate, and the iodine number was higher than that of the sewage sludge-based activated carbon (SBAC). RS-SCAC contained a variety of heavy metals, and Zn, Fe, and Cu had the relatively high content. The surface of RS-SCAC was rich in functional groups, especially for –OH, –COOH, and –COH, which was helpful for the adsorption of polar solute. For all heavy metals except Zn in RS-SCAC, the leaching concentrations were below the limits for identifying hazardous wastes, which indicated that RS-SCAC was relatively safe. Compared with SBAC, RS-SCAC had the better adsorption effect for Cr (VI). The results indicated that RS-SCAC can be used as a safety and efficient adsorbent for Cr (VI).

1. Introduction

Sewage sludge, as a by-product of wastewater biological treatment, contains heavy metals, organic toxins, and pathogens, which has the risks of environmental pollution [1, 2]. In China, the annual sewage sludge quantity (measured by wet sludge containing 80% water) is expected to reach 50 million tons in 2020 according to the 13th Five-Year Plan. This is an urgent task for the Chinese government disposal such a huge amount of sewage sludge.

In the past decades, a large number of scholars used various methods to treat sewage sludge, such as sanitary landfill, compost, incineration, ocean dumpling, etc. [3-6]. However, these methods have some defects, such as secondary pollution and high cost. At present, the safe and low-cost treatment of sludge is attracting more and more attention. In view of this point, the preparation of activated carbon from sewage sludge has become a research hotspot. However, due to the low carbon content and high ash content of the sewage sludge [7], the performance of the sludge-based activated carbon is generally poor, not as good as commercial activated carbon, which limits its application. In recent years, sugarcane bagasse, corn straw, and coconut husk were added in sewage sludge to prepare composite activated carbons [8, 9]. These composite activated carbons displayed good performances in practical application.
In this study, rice straw was mixed in sewage sludge to prepare the rice straw/sewage sludge-based composite activated carbon (RS-SCAC). Firstly, the yield, iodine number, and contents of heavy metals in RS-SCAC were detected, and the surface functional groups of RS-SCAC were characterized by FTIR. Secondly, the heavy metal leaching toxicity of RS-SCAC was determined. At last, the difference of Cr (VI) adsorption effect between the sewage sludge-based activated carbon (SBAC) and RS-SCAC was analyzed. The objective of this study was to explore some basic properties of RS-SCAC and its adsorption effect for Cr (VI).

2. Materials and Methods

2.1. Preparation of RS-SCAC and SBAC
The sewage sludge and rice straw were grinded and sieved to 1–3 mm. Then, they were dehydrated in a drying oven (101-2AB, Zhongxinweiye Co. LTD., Beijing, China) to constant weight. After that, the sewage sludge and rice straw were mixed with a mass ratio of 8: 2 to acquire the raw material for the preparation of RS-SCAC. For the acquired raw material, 20 g sample was immersed in the 200 g/L ZnCl₂ solution for 12 h at room temperature. When the soaking time was out, the sample was filtered and dried to constant weight. And then the dried sample was poured into a steel reactor and carbonized in a muffle furnace (SX2-4-10, Shenyang Energy Saving Electric Furnace Factory, Shenyang, China) at 600 °C for 2 h. The acquired carbon material was firstly washed with 3 M HCl and then with ultrapure water for several times. The washed carbon was dried to constant weight and sieved through a 60 mesh screen. So far the preparation of RS-SCAC was finished. The prepared RS-SCAC was stored in a desiccator before use. For SBAC, the preparation method referred to that of RS-SCAC.

2.2. Yield, Iodine Number, Contents of Heavy Metals, and Surface Functional Groups
The yield was calculated with the weight of raw material and end-product. The iodine numbers was measured according to China national standards (GB/T 12496.8-2015). The contents of heavy metals (As, Cd, Cr, Cu, Mn, Ni, Pb, Fe, and Zn) were detected according to the norms of Ministry of Environmental Protection of the People’s Republic of China (HJ 781-2016) by an inductively coupled plasma spectrum analyzer (iCAP-6000, Thermo Fisher Scientific Inc., Waltham, MA, USA). The surface functional groups were characterized by a Spectrum GX spectrometer (Spectrum two, Perkin-Elmer Crop., Norwalk, Ohio, USA).

2.3. Leaching Toxicity
The leachate of RS-SCAC was prepared according to the norms of Ministry of Environmental Protection of the People’s Republic of China (HJ 557-2009). The concentrations of heavy metals (As, Cd, Cr, Cu, Mn, Ni, Pb, Fe, and Zn) in the leachate were detected by the inductively coupled plasma spectrum analyzer (iCAP-6000, Thermo Fisher Scientific Inc., Waltham, MA, USA). The detected concentrations of heavy metals were compared with the concentration limits in China national standards (GB 5085.3-2007) used for identifying hazardous wastes.

2.4. Adsorption Effect for Cr(VI)
In the experiment, 0.2829 g of K₂Cr₂O₇ was dissolved in 1 L ultrapure water to prepare the wastewater containing Cr (VI). 0.1 g of RS-SCAC and SBAC was added into 150 mL conical flask with 50 mL wastewater, respectively. The initial pH of the mixture was adjusted to 3.0. Then the mixture was reacted in a thermostatic shaker (Ts-2012c, Shanghai Baidian Instrument Equipment Co. LTD., Shanghai, China) for 24 h. In the thermostatic shaker, the temperature and shaking rate was controlled at 25 °C and 150 rpm, respectively. After that, the mixture was filtered. The residual concentration of Cr (VI) in the filtrate was detected according to China national standards (GB 7467-87) with a UV spectrophotometer (UV-1800, Mapada (Shanghai) Co. LTD., Shanghai, China) at 540 nm. The detected residual concentration was used to calculate the Cr (VI) removal percentage.
3. Results and Discussion

3.1. Yield, Iodine Number and Contents of Heavy Metals

The yield of RS-SCAC was 39.18%. The yield was roughly the same as that of other activated carbons reported in the previous studies [10, 11]. The result indicated that the preparation of RS-SCAC was feasible. The iodine numbers of RS-SCAC and SBAC are shown in figure 1. The iodine number of RS-SCAC was 438.97 mg/g, which was 1.46 times than that of SBAC (300.51 mg/g). For activated carbon, iodine number is used as a common indicator to assess its adsorption capacity [12]. The iodine number of RS-SCAC was significantly higher than that of SBAC, indicating that RS-SCAC has a better adsorption capacity than SBAC.

![Figure 1. Iodine numbers of SBAC and RS-SCAC.](image)

Sewage sludge often contains heavy metals, which has potential risks to environment. Due to sewage sludge as one main raw material for the preparation of RS-SCAC, the contents of heavy metals in RS-SCAC needed to be determined. Table 1 shows the contents of heavy metals in RS-SCAC. It can be found that there were many kinds of heavy metals in RS-SCAC. The order of the contents of heavy metals in RS-SCAC was Zn> Fe> Cu> Cr> Ni> Mn> As> Cd> Pb. The high Zn content was due to the used activator (ZnCl₂), while the high Fe content may be connected with the raw material, i.e., sewage sludge. Considering that RS-SCAC contained a certain amount of heavy metals, there was a need to assess the safety of RS-SCAC in the following section.

![Table 1. Contents of heavy metals in RS-SCAC.](table)

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| Metals (mg/g) | As  | Cd  | Cr  | Cu  | Mn  | Ni  | Pb  | Fe  | Zn  |
|---------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| RS-SCAC       | 0.0017 | 0.0002 | 0.0653 | 0.2389 | 0.0158 | 0.0313 | /  | 1.9773 | 12.5517 |
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"/" represents “not detected”

3.2. Surface Functional Groups

The surface functional groups affect the chemical properties and adsorption effect of activated carbon. The surface functional groups on RS-SCAC were characterized with FTIR. The FTIR spectra of RS-SCAC is shown in figure 2. The intense absorption bands at 3423cm⁻¹ was attributed to the stretching vibration of –OH [13]. The adsorption peak at 2925 cm⁻¹ represented the stretching vibrations of –CH and –CH₂ [14]. The peak observed at 1614 cm⁻¹ was due to the –COOH [15], and the peak observed near 1384 cm⁻¹ was connected with phenol [16]. The characteristic peak at 1089cm⁻¹ could be ascribed to the C–O bending vibration in –COH [17]. The band at around 780 cm⁻¹ was related with the out-of-plane bending mode of O–H [18]. Overall, the surface of RS-SCAC was rich in functional groups, especially for –OH, –COOH, and –COH. The main functional groups, i.e. –OH, –COOH, and –COH, were polar functional groups, which can promote the adsorption of polar solute.
3.3. Leaching Toxicity
Table 2 shows the concentrations of heavy metals (As, Cd, Cr, Cu, Mn, Ni, Pb, Fe, and Zn) in the leachate of RS-SCAC. As shown in table 2, the concentrations of As, Cd, and Ni were not detected. The concentration of Zn was much higher than that of other heavy metals. The order of the concentrations of heavy metals was Zn > Mn > Fe > Cu > Cr > Pb. Compared with the concentration limits in China national standards (GB 5085.3-2007), which were used for identifying hazardous wastes, the concentrations of all heavy metals except Zn were significantly lower than the limits. However, the concentration of Zn was only 1.46 times than its limit. The results demonstrated that RS-SCAC was relatively safe. Thus, RS-SCAC can be used as a safety adsorbent if there were no restrict limit for Zn. Moreover, the main reason for excessive Zn leaching was that ZnCl₂ was used as the activating agent. Therefore, repeated washing can be used in the process of RS-SCAC preparation to reduce Zn leaching, which is beneficial for RS-SCAC application if there were a restrict limit for Zn.

| Metal | As | Cd | Cr | Cu  | Fe  | Mn | Ni | Pb  | Zn   |
|-------|----|----|----|-----|-----|----|----|-----|------|
| Concentration (mg/L) | /  | /  | 0.039 | 0.061 | 0.077 | 1.015 | /  | 0.002 | 145.940 |
| Concentration limit (mg/L) | 5  | 1  | 15 | 100 | -   | -  | 5  | 5   | 100   |

“/” represents “not detected”
“-” represents “no limit”

3.4. Cr(VI) Adsorption Effect
The Cr (VI) removal percentages of RS-SCAC and SBAC are shown in figure 2. For RS-SCAC and SBAC, the Cr (VI) removal percentage was 41.56% and 71.66%, respectively. Overall, the Cr (VI) removal efficiency of RS-SCAC was 1.7 times than that of SBAC. For RS-SCAC, adding rice straw might lead to the increase of porosity, which further caused the rise of specific surface area. Thus the Cr (VI) removal percentage of RS-SCAC was promoted. The reason can be verified with the results of iodine number in section 3.1. Furthermore, adding rice straw might enhance the polarity of RS-SCAC, which also could improve the adsorption capacity of RS-SCAC for Cr (VI). The results in section 3.2 supported the deduction in a certain extent. Overall, RS-SCAC can be used as an efficient adsorbent for Cr (VI).
4. Conclusions
In this study, RS-SCAC was successfully prepared by adding rice straw as the carbon additive in sewage sludge. For RS-SCAC, the yield was moderate. The iodine number significantly increased compared with that of SBAC. The main functional groups on the surface of RS-SCAC were –OH, –COOH, and –COH. RS-SCAC contained a certain amount of heavy metals. Compared with the concentration limits in China national standards (GB 5085.3-2007), which were used for identifying hazardous wastes, the leaching concentrations of all heavy metals except Zn were significantly lower than the limits. The Cr (VI) removal efficiency of RS-SCAC was 1.7 times than that of SBAC. Overall, RS-SCAC can be used as a safety and efficient adsorbent for Cr (VI).

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6. References
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