



Preparation and characterization of activated carbon from spent coffee grounds using NaOH and KCl as activating agents

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Activated carbons were prepared by double stage activation method using spent coffee grounds (SCG) as precursor. The process involved impregnation of SCG with NaOH or KCl followed by heat treatment. Proximate analysis of raw SCG was done to investigate moisture, ash, volatile matter and fixed carbon content. Characterization of the adsorbents was done through FTIR, BET and XRD analyses. Activated carbon (AC) prepared using NaOH as activating agent was used to adsorb lead (Pb(II)) from an aqueous solution. Adsorption study result showed that 98% Pb(II) could be removed with the adsorbent dose of 20 g/L and 90 min of contact time from the aqueous solution initially containing 400 mg/L of Pb(II).

Keywords: Activated carbon, double stage activation, spent coffee grounds, lead.

Introduction

Coffee is a popular beverage and almost 50% of the world's total coffee production is used for making soluble coffee. The residue left after the brewing of coffee is known as spent coffee grounds. According to the coffee market report of International Coffee Organization for December 2019 the global coffee production is estimated to be 168.71 million bags (each bag weighs 60 kg) in 2019-20. Murthy and Naidu¹ have reported that one ton of green coffee generates about 650 kg of SCG making it an abundant feed stock for AC synthesis.

Several studies have reported the use of coffee residue as a precursor for the synthesis of AC. Baquero *et al.*² chemically activated the coffee residue by H₃PO₄ to prepare AC for adsorption of phenol. Kankeu *et al.*³ produced biochar from SCG by hydrothermal method and then treating it with sodium dodecyl sulphate to remove cadmium from coal tailing leachates. The ZnCl₂ impregnated SCG was carbonized around 400 to 500°C to produce AC for heavy metal removal⁴. The ACs were obtained from SCG by impregnating it with phosphoric acid and KOH and carbonization at 600°C for the removal of lead and copper⁵; phosphoric acid for the adsorption of ethylene and n-butane⁶.

In this study, SCG was impregnated with NaOH and KCl activating agents, carbonized at 500°C to produce activated carbons referred as AC-NaOH and AC-KCl, respectively. The properties of the ACs obtained through raw SCG, AC-NaOH and AC-KCl were evaluated and compared to examine their relative characteristics. Since the BET surface area determined was higher for AC-NaOH than the other two adsorbents, it was chosen for batch removal of Pb(II) from the prepared solution.

Materials and methods

Spent coffee grounds:

Coffee beans was purchased from local market of Bilaspur, Chhattisgarh and after using them to make soluble coffee, the residue (SCG) was collected. The SCG was washed with water and sun dried for 24 h. The SCG was kept for 1 h in oven for drying at 100°C, ground and sieved to get 16 mesh size particles.

Activation process:

Activation method adopted in this study is similar to the one reported by Kalderis and coworkers⁷ for the activation of rice husk derived activated carbon. The SCG sample was impregnated with NaOH by mixing them in equal proportion

(w/w) in a glass beaker. The mixture was then added in distilled water in 10:1 (w/w) ratio of distilled water to initial SCG-NaOH mixture. The resulting solution was constantly stirred and heated at 80°C until a thick homogeneous paste was obtained. The paste was placed in a muffle furnace at 500°C for half an hour to get AC. Prepared AC termed as AC-NaOH (AC by impregnation of SCG with NaOH) was cooled at room temperature and packed in a sealed container. This process was repeated with KCl to get AC-KCl (AC by impregnation of SCG with KCl).

Characterization:

The proximate analysis of raw SCG was carried out using the standard ASTM procedures. The BET surface areas of the SCG, AC-NaOH and AC-KCl, adsorbents were determined using surface area analyzer (Model: Smart Sorb 93). Surface functional groups present on the adsorbents were determined by the FTIR spectroscopy (Bruker, Alpha Model). XRD spectra for adsorbents were obtained to understand the crystalline structure of adsorbent by using PANalytical multifunctional XRD analyzer.

Adsorption study:

In a conical flask 25 ml. of Pb(II) containing aqueous solution was mixed with fixed amount of AC-NaOH. The flask was kept in the orbital shaker for a predefined time at 30°C and constant speed of 90 rpm. After shaking and filtration of solution the concentration of Pb(II) in the filtrate was measured by using atomic absorbance spectroscopy (AAS) (Make: ECIL). Percent removal of Pb(II) and adsorbent capacity was determined by eq. (1) and eq. (2), respectively.

$$\text{Pb(II) removal (\%)} = \frac{100 (C_o - C_e)}{C_o} \quad (1)$$

$$q_e = \frac{(C_o - C_e)V}{m} \quad (2)$$

where, initial and final concentration of Pb(II) in the solution are indicated by C_o and C_e , respectively, volume of sorbate solution by V and adsorbent mass is denoted by m .

Results and discussion

Proximate analysis:

The proximate analysis showed that the raw untreated spent coffee grounds contained, moisture 10.11%, volatile matter 79.6%, ash 2.24% and the fixed carbon 8.05%. According to Indonesian National Standard, SNI 06-3730-1995 for activated carbon, the fixed carbon must be greater than 60%, whereas the moisture, ash, volatile matter content must be less than 15%, 10% and 25% respectively⁸. The moisture and volatile matter content of SCG indicated that the fixed carbon percentage could be improved to the desired standard by removing moisture and volatile matter, to make SCG a suitable precursor for AC synthesis.

BET analysis:

An insight into the active surface area is useful to analyze the mechanism of adsorption. BET surface area of SCG, AC-NaOH and AC-KCl were found to be 0.19, 2.3 and 0.41 m²/g, respectively. Although AC-NaOH has moderately higher surface area compared to the raw SCG and AC-KCl, the sur-

Table 1. FTIR peak of SCG, AC-NaOH and AC-KCl

Functional group	Peaks		
	SCG	AC-NaOH	AC-KCl
OH	3432.46	3269.19	3433.53
-CH ₂ , -CH ₃	2923.09	2977.48	2923.82
-CH	2852.82		2853.30
NH ⁺	2352.07, 2318.96	2468.30	-
C=O		1766.39, 1755.02	1697.18
C=C	1582.18, 1402.03	1455.93, 1412.21	1563.33, 1462.94
C-O	1125.18	1069.08, 1017.04	1126.11
C-O-C, C-O-H	865.87, 833.30	864.92	866.52, 757.25
N-H out-of-plane bending; NH ₂ rocking; N-H wagging	666.86	686.53, 640.73, 560.70	663.96, 619.49

face areas of the ACs prepared in this study were significantly less compared to those reported in other studies. For example, Dai *et al.*⁹ obtained 394 m²/g surface area for NaOH modified SCG (NaOH-SCG) and 422 m²/g for raw SCG. The smaller surface area of activated carbons in this study indicates that NaOH/KCl were ineffective for the activation of SCG in the process of AC synthesis⁷.

The FTIR spectra of SCG, AC-NaOH and AC-KCl for the wavelength 4000 to 400 cm⁻¹ were obtained to recognize the surface functional groups. Table 1 shows the functional groups of the three adsorbents corresponding to the peaks. Peaks at 3200 to 3500 cm⁻¹ were common in all the adsorbents that may be attributed to the stretching vibrations of O-H groups available in pectin, cellulose and lignin. Common peaks in the range of 2900–3000 cm⁻¹ reflects C-H stretching vibrations of the -CH₃ and -CH₂ groups and the peak around 2850 cm⁻¹ in SCG and AC-KCl indicated aliphatic C-H stretching from the cellulose backbone¹⁰. The peaks at 1600–1400 cm⁻¹ assert the vibration of C-C of aromatic rings and methyl⁶. The peaks from 1200 to 1000 cm⁻¹ ascribes the presence of oxygenated functional groups in open chains, for example, in hemicellulose and cellulose¹¹. The bands around 870 and 700 cm⁻¹ are due to the stretching vibration of C-O-H and C-O-C from glycosidic bonds typically available in starch¹².

XRD analysis:

XRD spectra of SCG, AC-NaOH and AC-KCl for the diffraction angle 5° to 80° are presented in Fig. 1. Difference in the diffraction pattern of the three adsorbents is clearly visible in respect of peak's intensity, shifting and disappearance. This might have resulted due to the impregnation of activating agents and the carbonization process. Increased number of peaks in AC-NaOH and AC-KCl indicated the more crystalline structure compared to SCG. Most of the peaks in AC-NaOH occurred between 28° to 50°, suggesting that structure was more amorphous as compared to SCG and AC-KCl. The peak around 30° in AC-KCl might have resulted due to impregnation of KCl.

Test for Pb(II) removal:

The highest surface area adsorbent AC-NaOH was applied in varying doses to adsorb Pb(II) from the solution having 400 mg/L of Pb(II) initially. It can be observed that with increase in dose from 12 g/L to 20 g/L, Pb(II) removal in-

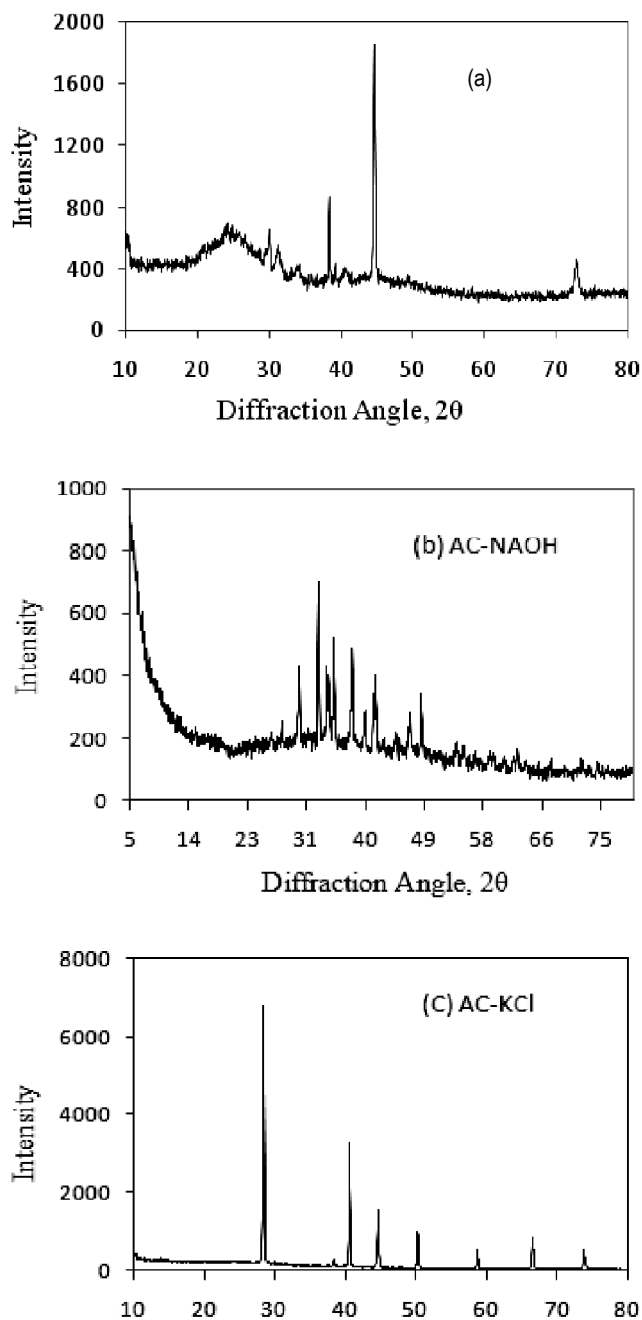


Fig. 1. XRD spectra of (a) SCG, (b) AC-NaOH and (c) AC-KCl.

creased rapidly. This could be due to the increase in number of available active and unsaturated adsorption sites with increased adsorbent amount. The results shown in Fig. 2 revealed that the 98% reduction of Pb(II) was obtained with adsorbent dose 20 g/L. Further increase in dose of adsorbent did not show any noticeable change in Pb(II) removal.

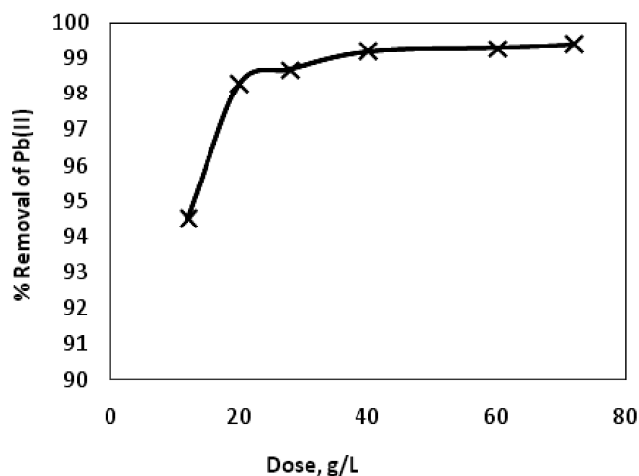


Fig. 2. Plot of effect of adsorbent dosage on Pb(II) removal (contact time 90 min, initial concentration 400 mg/L).

Optimum adsorbent capacity for adsorbent dose of 20 g/L was found 19.6 mg/g.

Conclusion

With the 16 mesh particle size of SCG, the use of NaOH or KCl as activating agent was ineffective in making of activated carbon from SCG. Among the three adsorbents, raw SCG, AC-NaOH and AC-KCl, the surface area of AC-NaOH ($2.3 \text{ m}^2/\text{g}$), was slightly higher compared to the other two adsorbents. The adsorption study revealed that 98% of Pb(II) could be removed from an initial concentration of 400 mg/L at 90 min of contact time and adsorbent dose of AC-NaOH at 20 g/L. Further studies are warranted to improve the surface

area, explore isotherm and kinetic parameters to gain further insight into the adsorption mechanism.

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