Research Article

Surface Chemistry and Textural characterization of activated carbon prepared from animal bone chars, using potassium hydroxide (KOH) as an activating agent

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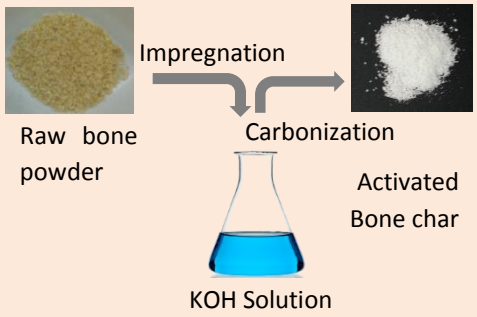
Abstract

Raw bone powder from waste cattle bones is the precursor which has been impregnated in the KOH solution. The char to KOH ratio was varied keeping the temperature constant at 600^0C with 1h residence time. The surface chemistry and the textural characterization have been studied for the activated bone chars prepared. The bone char prepared with char: KOH ratio 1:2 has a comparatively higher surface area along with the average pore volume and the micropore volume.



Keywords: Cattle bones, Chemical activation, KOH, Carbonization, Activated bone char

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Introduction

Activated carbons are considered to be versatile carbons. Since they have highly developed surface area [1, 2] they are used in numerous fields, such as separation, purification of liquids and gases, catalysts etc. The use of activated carbon is becoming restricted because of its high cost [3]. Therefore, researchers are focussing on preparing activated carbon from low cost materials such as agricultural wastes, manure, clay, fly ash and so on. They are of major importance in industrial applications because of their efficient adsorption and a well-developed porous structure [4]. Hence, their applications have been well exploited.

Activation methods are of two types; physical and chemical activation [5]. Physical activation includes carbonisation of the raw material in inert atmosphere followed by oxidation in presence of oxygen, steam or carbon dioxide [5, 6]. Chemical activation includes impregnation of the precursor in a suitable chemical agent followed by carbonisation at temperatures about 400^0- 900^0C [5].

Chemical activation is considered to be more advantageous as compared to physical activation. This includes lower activation temperature, higher yield, large surface area and short activation time [5, 7]. The chemical agents commonly used are KOH, NaOH, $ZnCl_2$, H_3PO_4 etc. Numerous studies are present in the literature where carbonaceous materials are activated using various activating agent. Among various chemical agents, KOH is readily available and has been in use since 1978 [8]. It is widely used as it can induce narrow micropores and small amount of mesopores to the precursor resulting in high surface area [7]. But the pore structure mostly depends on some of the activation parameters; such as mass ratio of KOH to carbon and activation temperature [8].

Recently, animal bone char is being considered to be a novel low cost adsorbent. This novel adsorbent has proven its efficiency in removing heavy metals [9, 10], dyes [11, 12], fluoride [13, 14] etc. from waste water. Research has been conducted to investigate the effect of activating agent on the pore volume, surface area and pore diameter. For example, Dawlet et al. prepared AC originating from sheep bones and chemically activated using $ZnCl_2$ suitable for mercury adsorption from aqueous solutions. Rezaee et al. prepared activated carbon from cattle and sheep bones activating it using acetic acid for removal of formaldehyde from air. Lurtwitayapont and Srisatit prepared activated carbon from swine bone char using NaOH as the activating agent. In their study, they focussed on the removal capacities of both bone char and activated carbon. They concluded that bone char had better adsorption efficiency.

Till this date, there are many contributions towards the activation of these carbons and they reveal few possibilities of inducing a well-developed pore network in the carbonaceous materials. Though there are a number of research contributions towards the preparation of activated carbon with various chemical agents, using KOH is limited.

In this present paper, raw cattle bone powder is utilised as the precursor for production of activated carbon and the effect of mass ratio to the texture and surface chemistry was investigated.

Experimental

Materials and Reagents

Cattle bone powder and bone char was used from our previous experiments [4]. KOH (Potassium Hydroxide- Analytical grade) was obtained from Sigma- Aldrich and deionized water (18.2 MΩ) was sourced from the laboratory MilliQ water purification system.

Precursor preparation

The raw bone powder (RBP) was used as the precursor. This was impregnated with KOH solution with a presumed carbon to KOH ratio (dry weight) (1:1, 1:2, 2:1, char/KOH) and was allowed to stand for 12 h. The resultant mass was then filtered and dried in an oven overnight. This step was then followed by carbonization in a vertical tubular furnace under limited supply of oxygen as shown in **Figure 1**. The sample with char/KOH ratio 1:1 was named as BC-1, 1:2 as BC-2, and 2:1 as BC-3 respectively. The temperature was set at 600^0C with a holding time of 1h. The samples were allowed to cool down to room temperature in a natural way and then washed thoroughly with hot distilled water so as to remove KOH from the carbon matrices. This obtained char sample was dried and stored in the desiccator for further analysis.

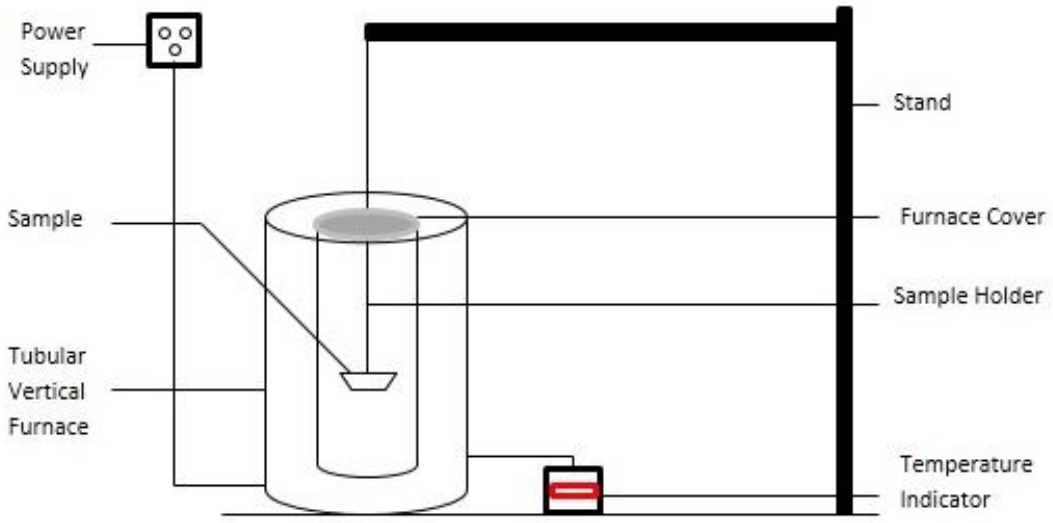

Figure 1 Vertical tubular furnace to carry out the pyrolysis process

Characterisation of Activated carbon

The textural parameters were evaluated using N_2 adsorption at 77.3 K and relative pressures (P/P0) range of 0.05-1 using Micrometrics 3Flex 3.01 instrument. All the samples, prior to analysing was outgassed under vacuum at 125^0C for 12 h. The Brunauer- Emmett- Teller (BET) surface area, average pore volume, pore diameter and t-plots were recorded from the adsorption data acquisition program.

The functional groups were determined using Furrier Transform Infrared Spectrometry (FT-IR, Spectrum 100, PerkinElmer). The Infrared spectrum was measured in the range of 380-4000 cm^{-1} with a resolution of 4 cm^{-1} and averaging over 4 scans.

Results and Discussion

Textural Characterization

The textural properties of the prepared activated bone chars were studied from N_2 adsorption isotherms using the method developed by Brunauer- Emmett Teller (BET) and *t*-plot analysis. From the adsorption data acquisition program, the surface area (S_{BET}), average pore diameter (D_p), total pore volume (V_p), micropore area ($S_{mic\text{-}area}$), exterior surface area (S_{ext}) and the micropore volume ($V_{t\text{-}plot}$) were obtained. The results have been summarised in **Table 1**. From the results obtained, the specific surface area (S_{BET}) increased with the KOH mass. The value of the total pore volume (V_p), is too low. This could be due to the penetration of metallic K into the carbon matrices, which possibly did not get removed completely. Apart from this, the reaction process majorly depends on the activation parameters such as temperature, furnace and the KOH mass [5]. These parameters can be optimised to obtain high surface area and pore volume.

In **Figure 2**, the BET plots with the linear fits are shown. For the sample having comparatively high micropore volume (BC-2), the linear region is restricted to smaller relative pressure range. To distinguish between the external surface area and the micropores, the *t*-plot method is used [15]. The micropore volume was obtained from Harkins and Jura co-relation.

Table 1 Surface Area and Pore volumes obtained from BET and t-plot method

Sample	Impregnation Ratio	BET		*t*-plot			V_p
		S_{BET} (m^2/g)	D_p (Å)	S_{ext} (m^2/g)	$S_{mic\text{-}area}$ (m^2/g)	$V_{t\text{-}plot}$ (cm^3/g)	(cm^3/g)
RBP	-	0.462	323.4	-	-	-	0.005
BC-1	1:01	10.61	112.84	7.09	3.52	0.0019	0.03
BC-2	1:02	23.96	157.69	20.13	3.83	0.002	0.09
BC-3	2:01	22.42	102.21	19.09	3.33	0.0016	0.06

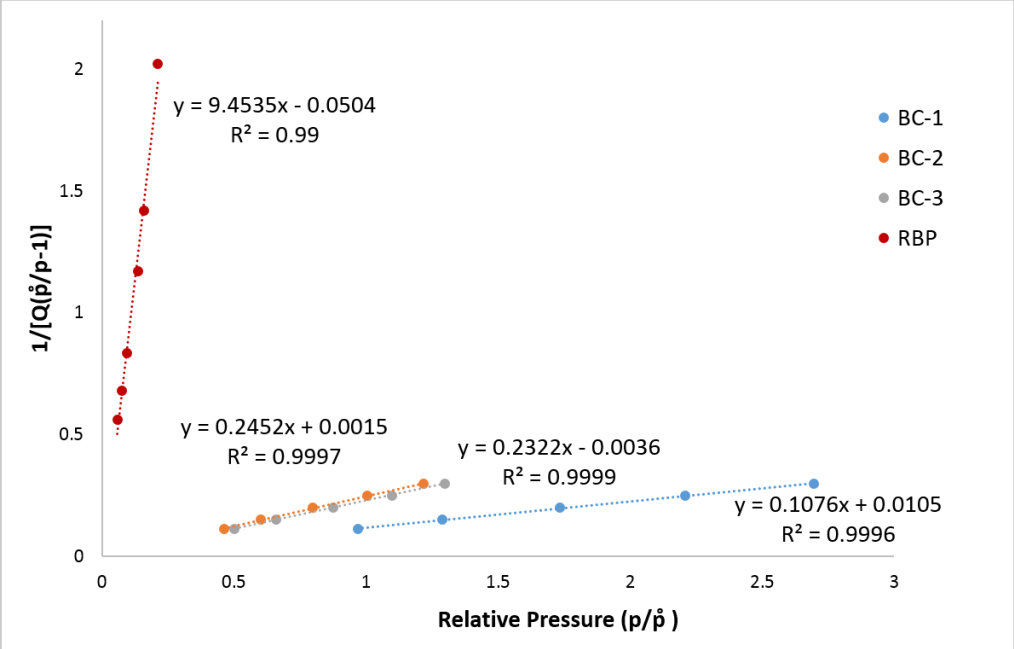

Figure 2 Linear fitted BET- Surface area plots

The *t*-plot method is usually applied to analyse hierarchical porous materials and in our case we have raw bone powder and bone char samples which after heat treatment induces meso/macropores in addition to some micropores [4]. The Multi-layer formation is modelled mathematically to calculate a layer "thickness, *t*" as a function of pressure [15]. The resulting *t*-curve is compared with the experimental isotherm in the form of a *t*-plot. That is, experimental volume adsorbed is plotted versus statistical thickness for each experimental P/P^o value. If the *t*-plot has a linear fit,

adsorption is taking place for that particular pressure range and if the sample is microporous, the linear fit does not pass through the origin and the intercept is taken as the microporous volume [15] as shown in **Figure 3**.

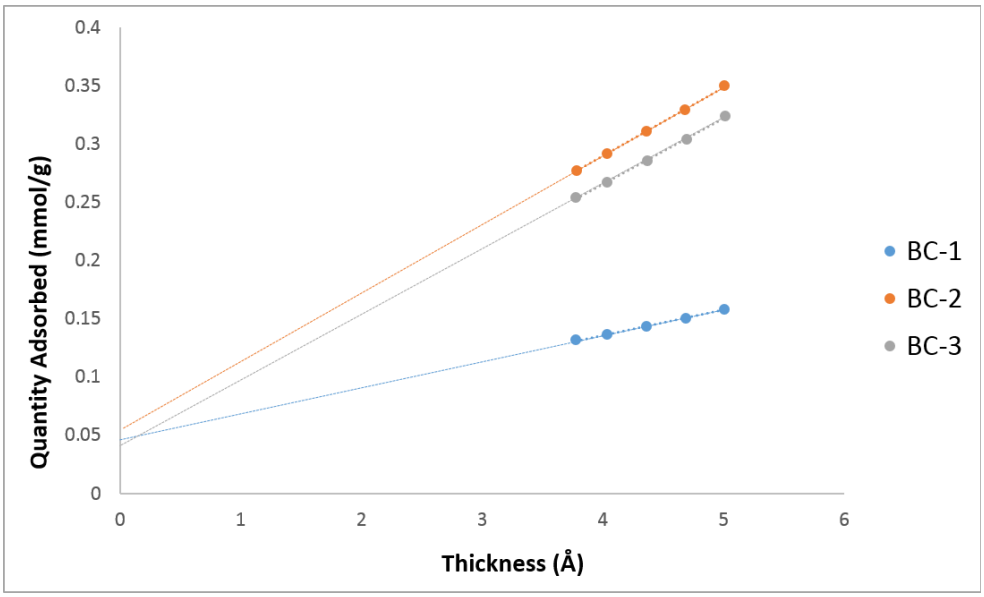

Figure 3 *t*-plot of N_2 adsorbed on BC-1, BC-2 and BC-3 using Harkins and Jura reference isotherm

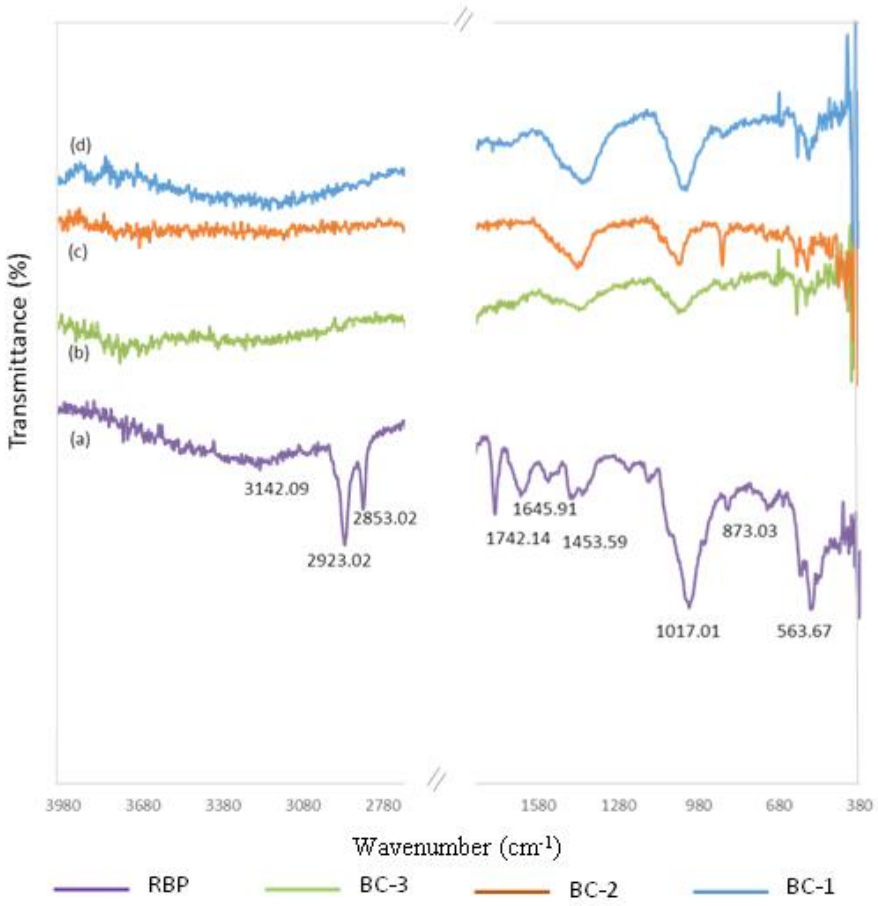

Figure 4 FT-IR of raw bone powder and activated bone chars BC-1, BC-2 and BC-3

Surface Chemistry

The FTIR spectrum of the raw bone powder and bone char samples pyrolysed with different char: KOH (dry weight) ratio was obtained. The bands were of typical hydroxyapatite as shown in **Figure 4**. This is the main component of the bone char.

The broad band observed at 3142.09 cm^{-1} is due to the presence of surface water molecules [16] whereas the wave number 1645.91cm^{-1} has been assigned to physically adsorbed water molecules [16, 17]. This peak disappears when the raw bone powder is subjected to the heat treatment at 600^0C. The C-O stretching vibrations at 1453.59 cm^{-1} has been assigned to CO_3^{2-} group, which becomes strong and intense indicating that CO_3^{2-} is present until 600^0C. This band originates due to the carbonate substitution in the crystal lattice [18]. The C=O and C=C bands corresponding to the organic matrix of the bone mineral were assigned to the wave number 1742.14 and 1645.91 cm^{-1} [14]. The peaks at 2923.02 and 2853.02 cm^{-1} has been assigned to C-H vibrations. All these peaks disappear at higher temperature, indicating its removal from the bone material. The band at 1017.01 cm^{-1} has been assigned to the P-O stretching vibration of PO_4^{3-} group. The band at 563.67 cm^{-1} corresponds to PO_4^{3-} bending vibrations. The band at 873.03 cm^{-1} has been assigned to CO_3^{2-} which is evident in all the samples prepared [18] and is more intense in BC-2. This band again originates due to the ionic substitution.

Conclusions

In conclusion, activated bone char was prepared using chemical activation method using KOH as the activating agent. Impregnation with KOH, induced the formation of micropores along with meso and macropores. The texture and the surface chemistry were analyzed with respect to the impregnation ratio of char to KOH. BC-2 which was prepared with 1:2 ratio of char: KOH had the highest BET surface area along with the micropore volume. Also the average pore volume was higher as compared to RBP, BC-1 and BC-3. Therefore, from this study it can be inferred that the chemical activation of cattle bone powder using KOH can induce the formation of micropores in the bone char increasing the surface area and pore volume.

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