ACTIVATED CARBON NANOFIBRES FROM GUM KONDAGOGU FOR REMEDIATION OF TOXIC METALS

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Abstract

Activated carbon (AC) from gum kondagogu (GK), a natural tree gum, was prepared by a carbonization/chemical activation process. The nanocomposite fibres contain AC, poly vinyl alcohol (PVA) and GK, which were fabricated by electrospinning. The system and the process parameters of the electrospinning were optimised to obtain smooth and uniform AC-GK/PVA composite nanofibres. The composite nanofibres with a mean diameter of 250±55 nm were obtained after cross-linking with heat treatment. Hydrophobic composite nanofibres of AC-GK/PVA were created using methane plasma treatment. Various microscopic and spectroscopic characterization techniques were used to characterize the composite nanofibres. The adsorption efficiencies of both AC-GK/PVA and GK/PVA composite nanofibres were tested on toxic metal contaminants (Pb^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, total Cr and As) in an aqueous solution and were assessed quantitatively using ICP-AES and ICP-MS. The renaissance and reusability of the composite nanofibres for consecutive operation were evaluated. The large surface area to volume ratio, extremely high stability, multi-functional groups and increased hydrophobic character of the prepared AC-GK/PVA composite nanofibres were found to be the key factors for the high adsorption/removal of toxic metals contaminant from the aqueous environment.

Keywords: Activated Carbon; Gum Kondagogu; Electrospun carbon nanofibres; Removal of toxic metals

1. INTRODUCTION

Activated carbons (ACs) are known to be the most efficient adsorbents applicable to the removal/adsorption of environmental contaminants such as toxic heavy metals, gases and organic compounds. Due to their extremely high surface area and small pore size, they express large adsorption capacities, fast adsorption kinetics and easy regeneration [1-4]. The most commonly used precursors for AC production are organic materials that are rich in carbon and low in inorganics and ash content [5]. There have been many attempts to obtain low-cost ACs from agricultural wastes such as wheat, corn straw, stones (e.g. olive, apricot, cherry, peach), sugarcane bagasse, wood (e.g. birch), husks (e.g. almond, sunflower, coconut, nuts), seeds (e.g. grape, rapeseed) or residues (e.g. cotton, olive, oat, rice) [2, 6-8]. From previous studies, the quality and characteristics of activated carbons are not only dependent on the physical and chemical properties of the starting materials but also on the preparation conditions and activation process [9, 10].

Exudate gums are hydrocolloids with complex molecular structures that are hydrophilic in nature and are extracted from trees. They have been used in food, pharmaceutical, adhesive and textile industries to stabilize emulsions and/or enhance thickening [11]. The important tree gums available in the markets are gum Arabic, gum Karaya, gum Tragacanth (GT) and gum Kondagogu (GK). Extensive research has been carried out on various aspects of these tree gums including their availability, molecular weight distribution, chemical structures and food and non-food applications [12, 13].

Heavy metals such as Pb, Cd, Cu, Ni, Zn, Cr and As pose a threat to our environmental due to inappropriate waste disposal and inadequate human usage. Adsorption and filtration are the commonly used methods for

removal of these contaminants from the aquatic system. In the present article, we report on the preparation and characterization of AC from natural tree gum (Kondagogu) using a chemical activation method. Furthermore, the AC-GK/PVA membrane was fabricated by electrospinning and was explored for the removal/adsorption of toxic metals from water.

2.   EXPERIMENTAL

2.1.   Materials and methods

GK was supplied by the DK enterprises (Hyderabad, India), poly vinyl alcohol (PVA, Mw 88,000, degree of deacetylation 88%), HCl, HNO_3, H_2SO_4, NaOH and NH_4OH were purchased from Sigma-Aldrich (USA). De-ionized water (Milli Q) was used in all of the experiments. Commercial AC was also procured from Sigma-Aldrich (USA).

The standard stock solutions of Pb, Cd, Cu, Ni, Zn, Cr and As (1.0 g L^{-1}) were prepared by dissolving the appropriate amounts of their corresponding nitrate or chloride salts in de-ionized water. The pH of the metal solution was adjusted to a preferred value with 0.1M of HCl and NaOH, respectively. The GK powder was purified by dissolution, filtration and dialysis as reported earlier [13].

2.2.   Preparation of AC from GK

The AC was prepared by carbonization and chemical activation using GK power. The dried powder (GK) was carbonized at 400 ^{0}C for 1 h in a muffle furnace (Fischer Scientific, USA) in order to produce charcoal. The charcoal was then subjected to impregnation in a NaOH solution (by a weight ratio of 4:1, NaOH to GK charcoal) at 90 ^{0}C for 24 h. In order to determine the optimum conditions for AC production, the resulting sample was activated in a muffle furnace at various activation temperatures (400 – 800 ^{0}C) and activation times (30 – 120 min.).

2.3.   Characterization of AC

The morphology of AC was analyzed by SEM (ZEISS, Ultra Plus, Germany), the functional groups by ATR-FTIR (NICOLET IZ10, USA), and surface properties by XRD (Philips PW 3020, Holland). The specific surface area using BET (Brunauer-Emmett-Teller), as well as total pore volume and average pore diameter were determined by Barrett-Joyner-Halenda (BJH) analysis using nitrogen adsorption and desorption techniques (Autosorb iQ, Quantachrome, Florida, USA). The samples were placed in an automatic surface area analyzer (Micrometrics ASAP 2000) which measures the adsorption/desorption of nitrogen gas at 77 K. The BET surface areas of the samples were calculated using N_2 adsorption data at 77 K in the relative pressure range of 0.05 to 0.25 with the help of the software. In the calculations, the cross–sectional area of the nitrogen molecule was taken to be 0.162 nm^2. The total pore volume of the adsorbed amount of N_2 was taken at a relative pressure greater than 0.98, assuming a liquid molar volume of N_2 to be 34.65 cm^3/g at 77 K.

The average pore diameter, D is calculated from the equation below

$$D = (4) \text{ X (Pore volume) / BET Area}$$

The adsorption efficiency and removal capacity of the produced AC were determined by measuring the iodine number and methylene blue number [14, 15] and these results were compared with commercially available activated carbon.

2.4.   Preparation of electrospinning mixtures of AC, GK and PVA

The GK/PVA blend solution was electrospun as reported earlier [16]. Briefly, an aqueous solution of PVA (10 wt %) was prepared by heating at 90 ^{0}C for 5 h. The PVA solution was mixed with the GK solution (1 wt %)

so that the PVA/GK weight ratio in the mixture was 80/20. Then, AC (1 wt %) was added into the mixture and the final solution was mixed thoroughly for 6 h in a magnetic stirrer for complete dissolution. The viscosity and conductivity of the mixture were determined before electrospinning.

2.5. Electrospinning

The electrospinning was carried out using a Nanospider device (Elmarco, NS IWS500U, Liberec, Czech Republic). The details of the electrospinning conditions were as follows: spinning electrode width of 500 mm, spinning distance of 130–280 mm, substrate speed of 0.015-1.95 m/min, voltage of 0-55 kV and process air flow of 20-150 m³/h. The electrospun nanofibres were cross-linked upon heat treatment at 130 °C for 1 h in an oven and were cooled to room temperature. Later, methane plasma treatment was carried out to create the hydrophobic membrane in a plasma reactor (BalTec Maschinenbau AG, Switzerland).

2.6. Adsorption study of heavy metals from an aqueous solution

Samples of the membrane (GK/PVA or AC-GK/PVA) (50 mg) were immersed into 100 mL of the metal solutions (100 mg L⁻¹) in 250 mL conical flasks. The samples were kept for 2 h at a temperature of 25±2 °C in an orbital shaker at 200 rpm (Innova-43, New Brunswick Scientific, USA). The content was then centrifuged for 5 min at 10,000×g and supernatant was collected and subsequently filtered through a 0.45 µm filter. The metal concentrations were analyzed by using ICP-MS (NexION 300 Q, PerkinElmer, USA) or ICP- AES (Optima 2100 DV, Perkin Elmer, Waltham, MA, USA).

3. RESULTS AND DISCUSSION

3.1. Proximate Analysis and Characterizations

The results of the proximate analysis of GK and AC-GK prepared from GK by the chemical activation process are given in **Table 1**. The high content of fixed carbon (20.0±0.1 wt %) and the volatile content (70.0+1.1 wt %) of GK make it a good precursor for the preparation of AC, similar to other materials used for the preparation of AC, as reported in the literature [2, 6-8].

Table 1 Proximate and ultimate analysis of GK and AC-GK)

Sample	Proximate analysis (wt %)				Ultimate analysis (wt %)			
	Moisture	Volatile	Fixed Carbon	Ash	C	H	N	O
GK	5.7±1.2	70.0±1.1	20.0±0.1	4.3±0.3	55.6±0.8	8.2±0.3	0.8±0.1	35.4±0.8
AC-GK	8.0±1.2	16.5±1.1	70±0.5	5.5±0.4	76.5±1.1	3.1±0.5	2.3±0.6	18.1±0.4

Table 2 presents the BET surface area, total pore volume and average pore diameter of purified GK and AC-GK.

Table 2 BET surface area, total pore volume and average pore diameter of GK and AC-GK

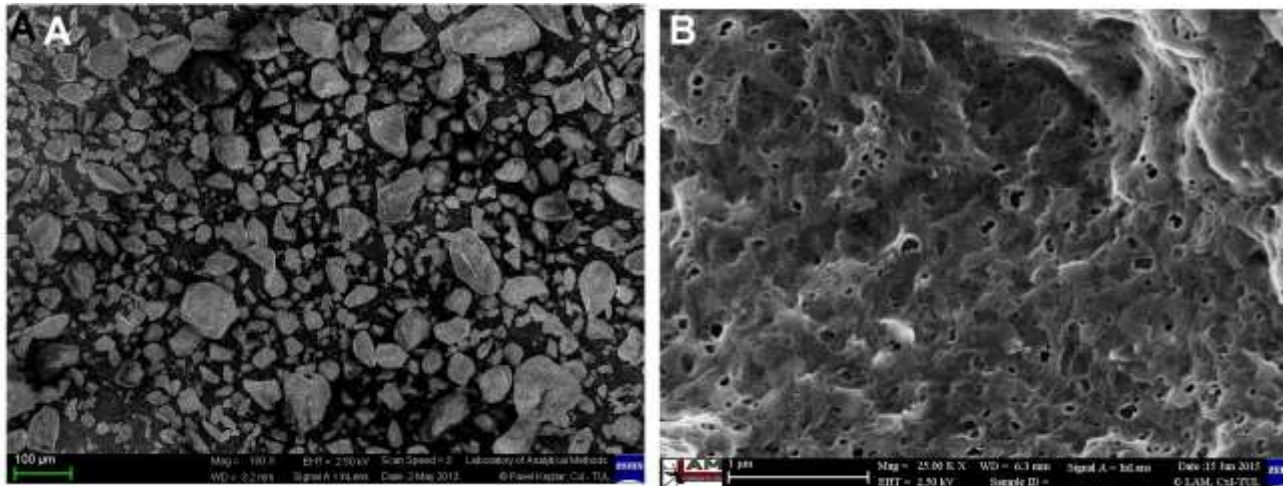| Sample	BET surface area (m²/g)	Total pore volume (cm³/g)	Average pore diameter (nm)
GK	4.05	0.025	24.6
AC-GK	750	0.358	1.9

Fig. 1 SEM pictures of (A) GK, showing irregular particle sizes and (B) AC-GK, indicating the pores on the surface

The FTIR spectra of the GK, AC-GK, commercial AC and AC-GK/PVA membranes are presented in **Fig. 2**. A broad absorption peak of GK at 3300 cm^{-1} can be observed, which is attributed to O-H stretching functional groups and the peak at 1720 cm^{-1} corresponds to C=O functional groups. The GK also shows two adsorption peaks at 1240 cm^{-1} and 1030 cm^{-1}, which represent C-O stretching functional groups. For activated carbon, most of the functional groups disappeared during the carbonization and activation process due to heating of the sample. The bands appearing at 1380 cm^{-1} and 1595 cm^{-1} are ascribed to the formation of oxygen functional groups like highly conjugated C=O stretching in carboxylic groups, and carboxylate moieties, respectively [13]. The –OH, -COO- and C=O groups presented in the AC-GK/PVA electrospun membrane can be attributed to high adsorption efficiency towards heavy metals.
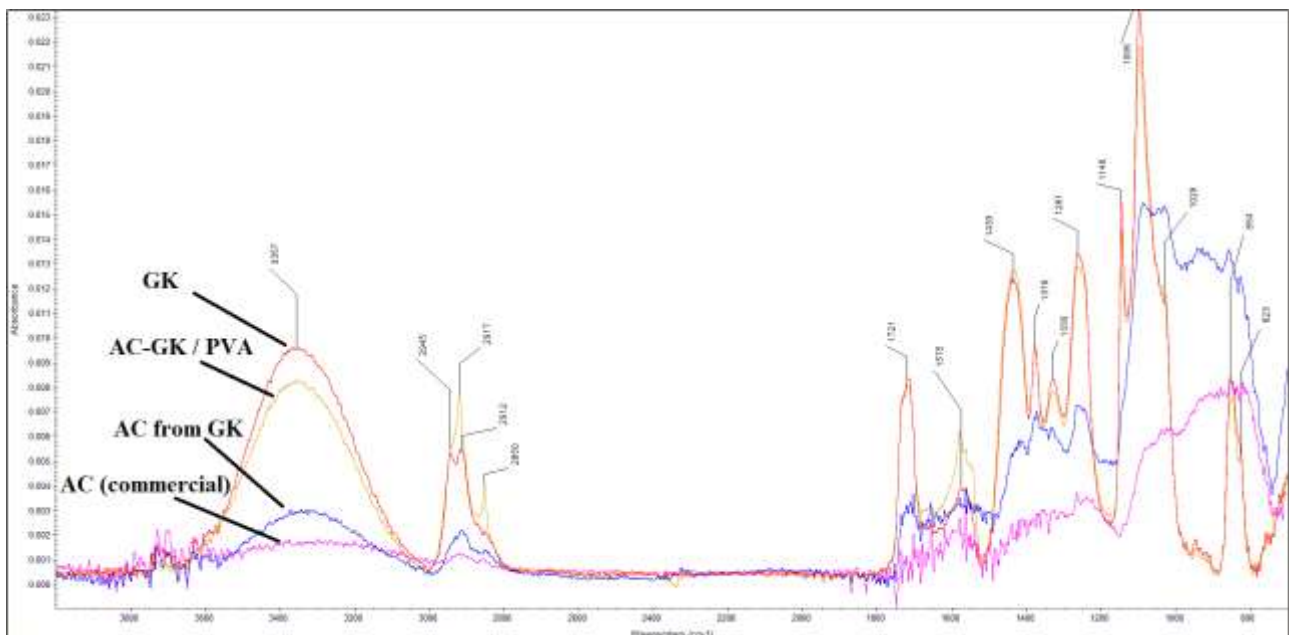

Fig. 2 ATR-FTIR spectrum indicating various functional groups present in GK, AC-GK, commercial AC and AC-GK/PVA electrospun membranes

The XRD profile of AC-GK in **Fig. 3** shows an absence of sharp peaks in the spectrum of AC, revealing the amorphous nature of the AC, which is an advantageous property of well defined adsorbents.
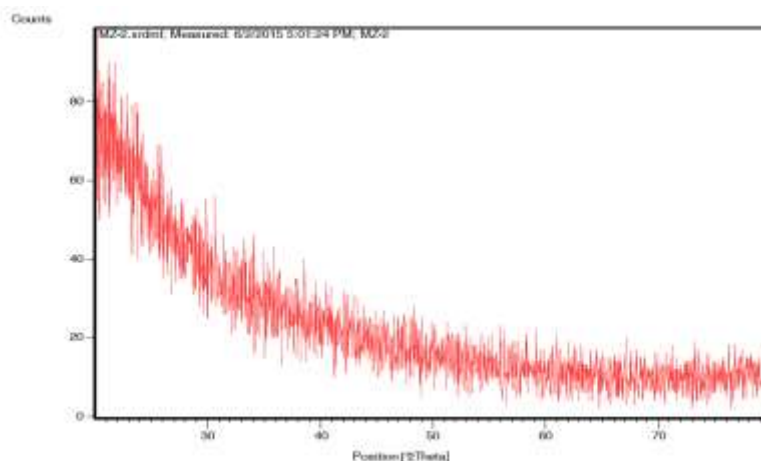
Fig. 3 XRD profile of AC-GK, indicating amorphous nature

The SEM images of electrospun PVA/GK and AC-PVA/GK nanofibres after heat and methane plasma treatment are presented in **Fig. 4** (A & B), respectively.
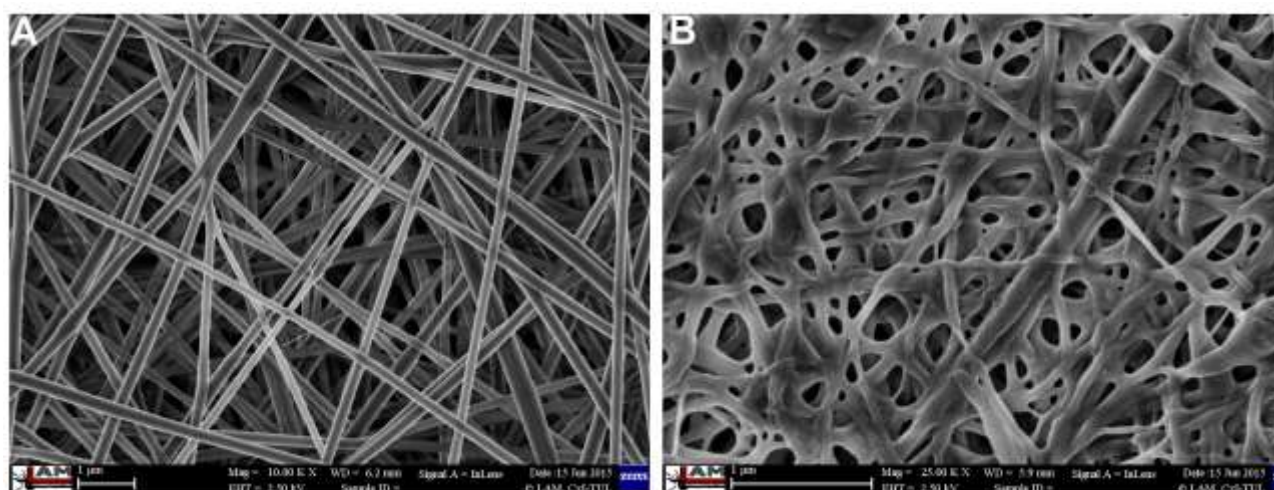

Fig. 4 SEM pictures of (A) electrospun GK/PVA fibres and (B) plasma treated AC-GK/PVA nanofibres used for metal adsorption studies

The GK/PVA blend solutions were electrospun as reported earlier [16]. In the present work, the AC particles were dispersed in a GK/PVA solution and successfully electrospun to produce nanofibres. It has been reported earlier that Gum Arabic has been the subject of interest as a dispersant for carbon nanotubes [17]. The plasma treatment modifies the surface by grafting hydroxyl (–OH), carbonyl (–C=O), and carboxylate (–COOH) groups [18].

3.2. Heavy metal adsorption onto GK/PVA and AC-GK/PVA nanofibre membranes

The aqueous mixtures of heavy metals were used to determine the competitive metal adsorption capacity of both GK/PVA and AC-GK/PVA nanofibres (**Table 3**). A pH of 5.0 was selected as the optimum pH for the adsorption of multiple metal ions onto the nanofibres. The adsorption capacity of AC-GK/PVA follows the order Pb > Cd > Ni > Cu > Zn > As > Cr at 20±2 ^{0}C and time of contact of 2 h. The adsorption capacity of AC-GK/PVA nanofibres is much higher than GK/PVA nanofibres towards the metal ions, as presented in **Table 3**.

Table 3 Heavy metal adsorption capacity (mg g^{-1}) of AC-GK/PVA and GK/PVA nanofibres as determined by ICP-MS at pH (5.0±0.1) and temperature 20±2 ^{0}C

Heavy metals	Adsorption Capacity (mg g^{-1})	
	AC-GK/PVA nanofibres	GK/PVA nanofibres
Pb	98.2±1.5	70.2±1.2
Cd	94.5±1.2	60.4±1.5
Ni	90.2±1.0	55.1±0.8
Cu	84.5±0.8	42.6±0.6
Zn	72.5±0.6	34.4±0.5
As	40.2±0.5	25.8±0.5
Cr	28.5±0.4	15.5±0.4

Previous studies on heavy metal biosorption showed that pH was an important factor affecting the adsorption process. Various nanofibre membranes based on synthetic/natural polymers such as polyacrylonitile/polypyrrole core/shell nanofibres, chitosan nanofibres, polyacroylonitile nanofibres, poly(acrylo-amidino ethylene amine) nanofibres, iron functionalized PVA nanofibres and gum karaya/PVA nanofibres were used for the removal of various different metal ions from water and it was demonstrated that the adsorption capacity depends on the functional groups present on the nanofibre membrane and the solution pH [19-23]. In the present work, acidic groups present in the GK polymer were responsible for the adsorption of heavy metals from water. In addition, multiple functional groups such as: carboxyl, hydroxyl, acetyl and cabonyl, high surface area, pore specific volume and mean pore diameter, strongly depend upon the total acidity of the surface including the functional groups. As reported in the literature, acidic functional groups such as the carboxyl group induce a negative charge on the AC surface and oxygen atoms of these functional groups donate their single pair of electrons to the metal ions, which consequently increases the cation exchange capacity of the membrane [24, 25]. Protons in the functional groups of the AC-GK/PVA membrane are exchanged with the metal ions. The chemical interaction (bond) between the metal ions and the surface acidic functional groups of the AC-GK/PVA is mainly responsible for the higher adsorption of various metal ions compared to GK/PVA nanofibres (Table 3).

4.   CONCLUSIONS

Activated carbon was successfully prepared from a natural gum kondagogu using a chemical activation process. The BET surface area, pore volume and average pore diameter of the prepared AC-GK was compared with the values of commercial activated carbon. Electrospun nanofibres of GK/PVA and AC-GK/PVA were prepared and used for the adsorptive removal of multiple toxic metals from water. GK was found to be an effective dispersion medium for AC. Ion exchange and functional group interactions and the high surface area of the AC-GK/PVA nanofibres compared to GK/PVA nanofibres were the major advantages for the multiple adsorption of heavy metals from water.

ACKNOWLEDGEMENTS

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