Chemistry: Bulgarian Journal of Science Education, Volume 21, Number 3, 2012
Природни науки в образованието

Experiments
Учебен експеримент в природните науки

PREPARATION AND CHARACTERIZATION OF ACTIVATED CARBON DERIVED FROM RUBBER SEED COAT

[1,2]Olugbenga Solomon Bello, [2]Mohd Azmier Ahmad
[1]Ladoke Akintola University of Technology, NIGERIA
[2]Universiti Sains Malaysia, MALAYSIA

Abstract. Activated carbon was prepared from rubber seed coat (RSCAC). It was characterized using Fourier Transform Infrared (FTIR), Thermo gravimetric analysis (TGA), Braunauer Emmett Teller (BET), Scanning Electron Microscopy (SEM), Elemental Analysis (EA), pH_{pzc} and Boehmn titrations. The pore size of the adsorbent prepared lies in the mesopore region, it possess other characteristics similar to conventional commercial activated carbon (CAC). The study shows that rubber seed coat (RSC) is a good precursor that could be used in the preparation of activated carbon.

Keywords: Rubber seed coat, activated carbon, mesopore, effluents

Introduction

One of the conventional methods for removal of dyes from wastewater is adsorption. Activated carbon is a popular and an effective dye adsorbent, but it's relatively high price, high operating costs and problems associated with regeneration hampers its large-scale application. Therefore, there is a growing need in finding low cost, renewable, locally available materials as sorbent for the removal of dye colours (Walker et al., 2003; Kumar et al., 2005; Wang et al., 2005). *Hevea brasiliensis,* commonly known as rubber tree is the main source of natural rubber. The tree is cultivated in large commercial scale in several countries in the tropics amounting to 9.485 million ha worldwide.1) Apart from its latex, rubber tree has also been harnessed for its wood in making furniture and the rubber seed oil is used for manufacturing soap, paint, varnishes, fertilizer and animal feeds.2) Rubber seed coat, a waste agricultural by-product, is utilized in Malaysia to a lesser extent as fuel and manure. To produce another value added product from rubber seed coat, it is proposed to convert it to activated carbon. In this study, rubber seed coat was used as precursor in the preparation of activated carbon. The activated carbon produced was characterised and compared with the commercially available one.

Materials and methods

Preparation of adsorbent

Rubber seed coat (RSC) was washed thoroughly to remove dirt and inorganic matters from its surface. The pre-treated precursors were then dried in an oven (Model Memmert 600, Germany) at temperature of 100°C for 24 h to remove moisture. 30 g of the dried RSC was crushed using a medium size mortar and pestle. The pre-treated material was then carbonized at 700°C under nitrogen atmosphere for 1 h (first pyrolysis). A certain amount of produced char was then soaked with sodium hydroxide (NaOH) at impregnation ratio of 1:1 (NaOH pellets: char). The mixture was dehydrated in an oven overnight at 105°C; then pyrolyzed in a stainless steel vertical tubular reactor placed in a tube furnace under high purity nitrogen (99.995%) flow of 150 cm^3/min (second pyrolysis) to a final temperature of 850°C and activated for 2 h. Once the final temperature was reached, the gas flow was switched to CO_2 and activation was continued for 2 h. The activated product, referred to as RSCAC was then cooled to room temperature under nitrogen flow. Subsequently, the sample was transferred to a beaker containing a 250 ml solution of hydrochloric acid (0.1 M), stirred for 1 h. The acid was decanted off. RSCAC was then washed with hot deionized water until the pH of the washing solution reached 6.5 –7.

Characterization of adsorbent

The surface area, total pore volume and average pore diameter of the samples were determined from the adsorption isotherms of nitrogen at 77 K by using Micromeritics (Model ASAP 2020) volumetric adsorption analyzer. Mesopore volume was calculated by subtracting total volume, obtained at a relative pressure of 0.99 from the micropore volume obtained from t-plot equation. The surface morphology of the sample was examined using a scanning electron microscope (Model VPFESEM Supra 35VP). Proximate analysis was carried out using thermo gravimetric analyzer (TGA) (Model Perkin Elmer TGA7, USA). The surface chemistry characterization of RSCAC was further carried out using pH_{PZC} determination, Boehm titration and Fourier Transform Infrared Spectroscopy (FTIR) to identify its surface functional groups both qualitatively and quantitatively. The pH_{PZC}, i.e., pH of the point zero charge was measured. For this purpose, 50 mL of a 0.01M NaCl solution was placed in a 100 mL Erlenmeyer flask. Then, the pH was adjusted to successive initial values between 2 and 12, by using either NaOH or HCl, and 0.15 g of RSCAC was added to the solution. After a contact time of 48 h, the final pH was measured and plotted against the initial pH. The pH at which the curve crosses the line pH (final) = pH (initial) was taken as the pH_{PZC} of the RSCAC considered. The total surface basicity and acidity of the samples were determined by titration with NaOH and HCl using Boehm (2002) titration method. 0.15 g of RSCAC was mixed with 50 mL of 0.05N NaOH or HCl solutions for 48 h with continuous stirring. 10 mL of each filtrate were then titrated against 0.05N HCl or NaOH, using phenolphthalein as indicator. Capacities for H^+ and OH^- were then measured.

Results and discussion

Characterization of RSCAC

Proximate and elemental analysis

Table 1 presents both the proximate and elemental analyses of the adsorbent; RSCAC is suitable as precursor for preparation of activated carbon because of the high fixed carbon content. The volatile matter content decreased whereas fixed carbon increased significantly after undergoing carbonization and activation process. Similar trend was observed for the elemental analysis where the carbon content increased from 18.48 to 64.51%. This phenomenon was due to the pyrolytic effect at high temperature where most of the organic substances have been degraded and discharged both as gas and liquid tars leaving a material with high carbon content (Tan & Ani, 2003). Besides, elemental analysis showed insignificant amount of hydrogen content due to the rupture of organic molecular chains after undergoing carbonization and physiochemical activation process. Similarly, there was improvement in the carbon content after activation making the adsorbent satisfactory for dye adsorption (Mohd Din et al., 2009)

Table 1. Proximate and elemental analysis

Sample	Proximate analysis (%)				Elemental analysis (%)			
	Moisture	Volatile	Fixed Carbon	Ash	C	H	S	(N+O)[a]
Raw RSC	8.72	67.48	21.20	2.60	18.48	3.81	0.33	77.38
Char	7.15	35.05	55.39	2.41	35.15	0.43	0.06	64.36
RSCAC	4.91	18.83	73.45	2.81	64.51	0.28	0.01	35.20
CAC	-	-	-	-	94.85	0.68	0.05	4.42

[a] Estimated by difference

Surface area and pore characteristics

Table 2 shows that the BET surface area and total pore volume of RSCAC to be 782.1 m^2/g and 0.494 cm^3/g respectively. These results are comparable with the commercial activated carbon from Merck which has a BET surface area of 1000 m^2/g and a total pore volume of 0.545 cm^3/g, respectively (Tsai & Chen, 2010). RSCAC prepared in this study was of mesoporous type as its average pore diameter was 2.73nm, a value in the mesopores region according to IUPAC classification.

Table 2. Surface area and pore characteristics of RSCAC and CAC

Sample	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)
Char	208.7	0.185	2.61
RSCAC	782.1	0.494	2.73
CAC	1000	0.545	3.24

Surface acidity and basicity strengths

Table 3 lists the surface acidity and basicity strengths of RSCAC obtained via the Boehm titration method. The data in Table 3 indicated that the amounts of the acidic groups on the surface of RSCAC were more than those of basic groups. The pH$_{pzc}$ of RSAC is 4.51, meaning that the adsorbent surface is positive below this value and negative above this value. RSCAC will adsorb anionic dyes better at acidic pH and basic dyes better at high pH.

Table 3. Surface acidity and basicity strengths of RSCAC

RSCAC	Surface chemistry
Carboxylic (meq/g)	0.5421
Lactonic (meq/g)	0.3216
Phenolic (meq/g)	0.2453
Acidic (meq/g)	1.1190
Basic (meq/g)	0.1372
pH$_{pzc}$	4.51

FTIR analysis of RSCAC

An FTIR spectrum of RSCAC is shown in Fig 1. From the spectrum, the following peaks were observed. The peak at 3622 cm^{-1} was assigned to OH stretching vibration, the broad peak at 3431cm^{-1} was assigned to hydrogen bonded OH. Aromatic ring stretching or highly conjugated C=O stretching appear at 1641 cm^{-1}. Symmetric bending of C-H appears at 1435 cm^{-1}. The peak at 1035cm^{-1} was assigned to the C=O bonds of ether, ester or phenol. C-H out of plane bending in benzene derivative appears at 844 cm^{-1} while aliphatic C-H symmetric vibration appears at 796 cm^{-1} and 916 cm^{-1} respectively. RSCAC contain prominent bands which are suitable for both heavy metals and dye adsorption.

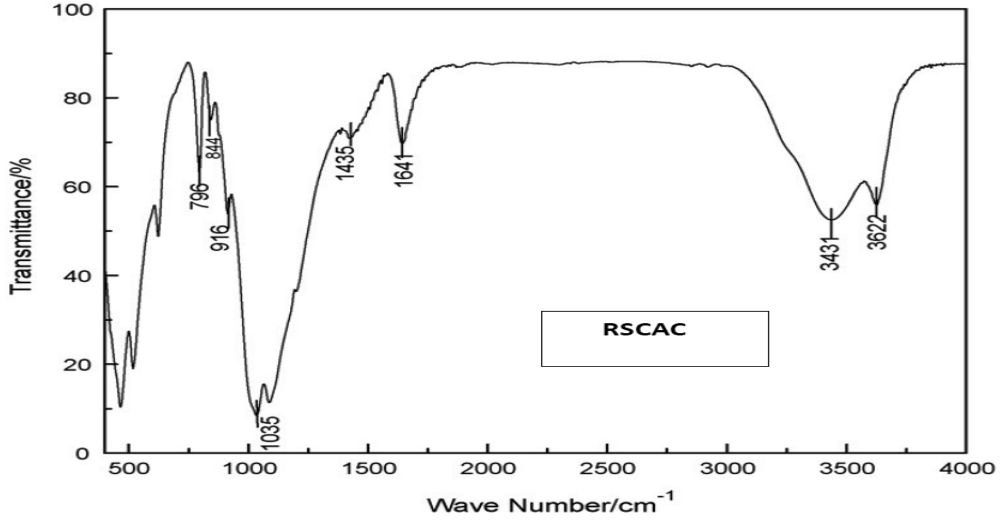

Fig. 1. FTIR spectrum of RSAC

SEM micrographs of RSCAC

From the SEM micrographs obtained (Fig. 2), raw RSC surface textures were rough, uneven, undulating and very little pores were present. After carbonization process, some irregular holes and pores were developed and found on the surfaces of the char due to the sudden burst of the thermal expansion from pyrolysis. Pore development in the char during pyrolysis was important as this would enhance the surface area and pore volume of the activated carbon after the activation process used. RSCAC contain more porous structure. This is probably due to effect of the diffusion of NaOH and CO_2 molecules into the matrix during carbonation and impregnation creating more pores in the activated carbon (Lorenc-Grabowska & Gryglewicz, 2007). Large and well-developed pores were observed on the surface of RSCAC, compared to raw RSC. SEM micrographs revealed that the combined activation process of NaOH and CO_2 were effective in creating well-developed pores on the surface of RSCAC, resulting to large surface area with good mesoporous structure.

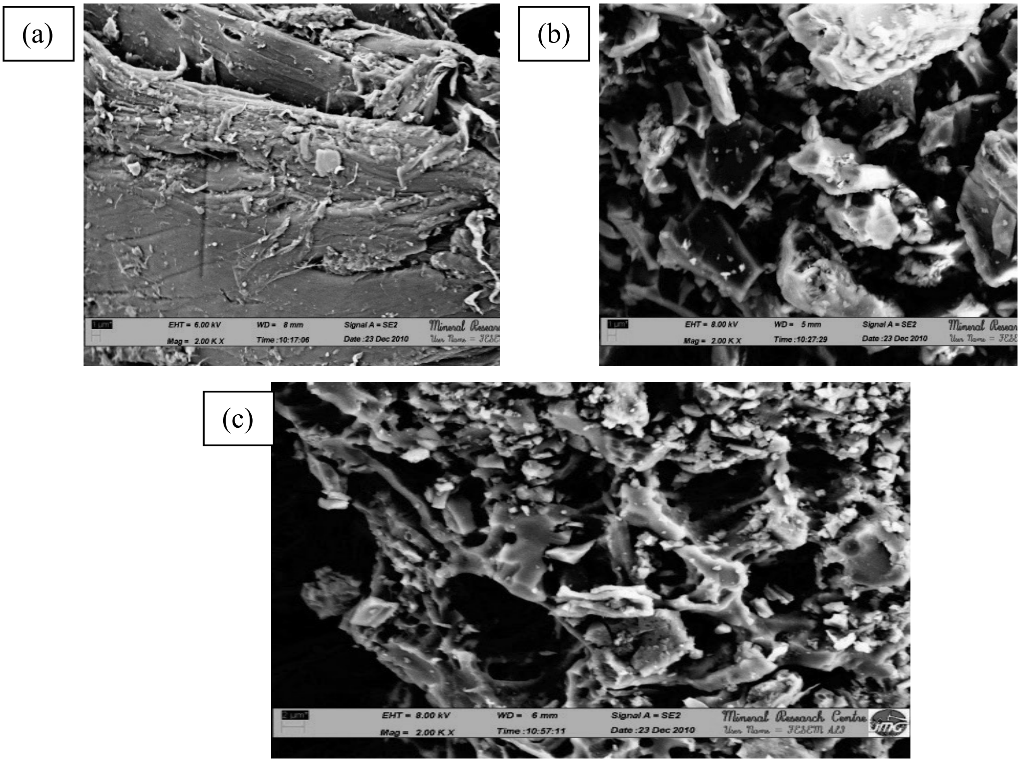

Fig. 2. Scanning electron micrographs; (a) raw RSC, (b) carbonized RSC and (c) RSCAC

Conclusion

This study revealed that RSCAC can be used as a good precursor for the preparation of activated carbon.

NOTES

1. http://www.fao.org/DOCREP/005/Y7204E/
2. Reed, C.F. (1976). *Information summaries on 1000 economic plants*. USDA.

REFERENCES

Boehm. H.P. (2002). Surface oxides on carbon and their analysis: a critical assessment. *Carbon*, *40,* 145- 149.

Kumar, K.V., Ramamurthi, V. & Sivanesan, S. (2005). Modeling the mechanism involved during the sorption of methylene blue onto fly ash. *J. Colloid Interface Sci.*, *284,* 14-21.

Lorenc-Grabowska, E. & Gryglewicz, G. (2007). Adsorption characteristics of Congo red on coal-based mesoporous activated carbon. *Dyes & Pigments, 74,* 34 - 40.

Mohd Din, A.T., Hameed, B.H. & Ahmad, A.L. (2009). Batch adsorption of phenol onto physiochemical-activated coconut shell. *J. Hazard. Mater.,161,* 1522-1529.

Tan, J.S. & Ani, F.N. (2003). Diffusional behaviour and adsorption capacity of palm shell chars for oxygen and nitrogen-effect of carbonization temperature. *Carbon*, *41,* 840- 842.

Tsai, W.T. & Chen, H.R. (2010). Removal of malachite green from aqueous solution using low cost chlorella - based biomass. *J. Hazard. Mater., 175,* 844- 849.

Walker, G.M., Hansen, L., Hanna, J.A. & Allen, S.J. (2003). Kinetics of a reactive dye adsorption onto dolomitic sorbents. *Water Res.*, *37,* 2081-2089.

Wang, S.B., Boyjoo, Y., Choueib, A. & Zhu, Z.H. (2005). Removal of dyes from aqueous solution using fly ash and red mud. *Water Res., 39,* 129 - 138.

✉ **Dr. Olugbenga Solomon Bello (corresponding author)**
Department of Pure and Applied Chemistry,
Ladoke Akintola University of Technology,
P.M.B 4000, Ogbomoso, Oyo State, Nigeria.
E-mail: osbello@yahoo.com

Mohd Azmier Ahmad
School of Chemical Engineering,
Engineering Campus,
Universiti Sains Malaysia,
14300 Nibong Tebal, Penang, Malaysia.