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PREPARATION AND CHARACTERIZATION OF PERIWINKLE SHELL ACTIVATED CARBON

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ABSTRACT

Activated carbon was prepared from periwinkle shell in this study and characterized. It was intended as alternative low-cost, environmentally friendly and readily available adsorbents for the uptake of heavy metal ions from wastewater. The periwinkle shells were collected and washed to remove inorganic impurities. It was carbonized in a horizontal tubular muffle oven for one hour 30 min at 900 ^oC. 0.1, 0.5 and 1.0 M. HNO_3 and $CaCl_2$ solutions were added into the beaker. It was allowed to stay for 48 hours and was further heated in furnace at 900 ^oC for one hour 30 min. The textural analysis, FT IR, EDX and SEM analysis of the adsorbent were carried to assess the potentials of the adsorbent in the uptake of heavy metals. The textural analysis showed specific surface area of 574.50 m^2/g. The spectra of the adsorbents were measured in the wave number range of 1000-3500cm^{-1}. The FT-IR spectrum of the activated carbon implied the presence of predominant peaks at 3388.2 cm^{-1} (–OH and –NH stretching), 2512.2 cm^{-1} (–OH stretching), 2109.7 cm^{-1} (stretching), 1796.6 cm^{-1}(–C=O Stretching). The SEM micrograph of the modified periwinkle shell (APSC) showed the rough surface texture and porosity of APSC with holes and small opening on the surface, thereby increasing the contact area, which facilitates the pore diffusion during adsorption. APSC projecting peaks in the EDX spectra indicated the presence of Ca (59.61%), O (24.34%), Al (0.20%), C (9.65%), B (3.56%), N (1.48%), Cl (0.975), and S (0.20%). APSC therefore exhibited the potential for the adsorption of heavy metals from wastewater

KEY WORDS: Activated carbon, Adsorbent, characterization, periwinkle shell

INTRODUCTION

Several treatment methods to remove heavy metal ions from wastewater have been documented in various literatures. Evaporation, filtration, rainfall, oxidation–reduction, electrochemical therapy, ion exchange, solvent extraction and activated carbon adsorption [1,2]. All of these techniques have disadvantages such as high price, low effectiveness, secondary contamination, and inapplicability to a broad spectrum of pollutants [3]. Adsorption is known to be one among the most probably appealing, effective, easy and efficient techniques [4].

Activated carbon with characteristics of high surface areas, porosity and chemical nature of their surface have made them suitable materials for heavy metals removal from industrial and domestic wastewater. Its use is not recommended because of high operational costs. The demand for a low cost and efficient adsorbent that can be applied to remove heavy metal is steadily increasing [5].

A number of separate powerful adsorbents were thought about in recent years for their potential usefulness in reducing heavy metal levels in waterways. Some of the adsorption components included bentonite, fly ash, iron oxide, red dirt and mineral carbonate [6].. Although they may have various helpful applications, their use has similar disadvantages [7-9]. So far, the development of surface modified activated carbon has generated a diversity of activated carbon with far superior adsorption capacity [10].

Due to its elevated chemical activity, efficiency, low price, no complexity of machinery and accessibility, multiple studies demonstrated that heavy metals can be removed using sorbents generated from biomass [11]. There are a lot of low-cost adsorbent materials for effluent therapy, such as fertilizer waste, biomass, tea waste, microorganisms, charcoal, ash, red mud, clay and laterite [12].

With this in mind, this study investigated the prospective use of periwinkle shell carbon as sorbents for heavy metal removal from wastewater. Periwinkles are marine mollusks (gastropods) with dense spiral shells, found mostly in the Niger Delta lagoons and mudflats between East Calabar and West Nigerian Badagry [13]. People in this region eat the edible portion as seafood and few individuals use the shell as a coarse aggregate in concrete in fields where there are no stones or granite for purposes such as paving water-logged regions [14]. A large quantity of periwinkle shell is therefore still being disposed-off as waste and has accumulated over the years in many places. The use of periwinkle shells will therefore add economic value; provide a possibly inexpensive or inexpensive material that will be used to dispose metal ions off from wastewater and assist to decrease waste disposal costs, thus creating a clean atmosphere.

MATERIALS AND METHODS

Materials

Periwinkle shells were obtained from Auchi, Edo State, Nigeria. Nitric acid (HNO_3), hydrochloric acid (HCl), calcium chloride ($CaCl_2$), and sodium hydroxide (NaOH) were products of Sigma-Aldrich, Germany.

Adsorbent Preparation

The periwinkle shells were collected, and washed to remove inorganic impurities. It was carbonized in a horizontal tubular muffle oven for one hour 30 min for 900 ^oC. Then, the materials were crushed with a mortar and ground into fine powder using a grinding machine. About 200 g of periwinkle shell carbon was separately taken into five different 500 ml beaker and 0.1, 0.5 and 1.0M. HNO_3 and calcium chloride solutions were added into the beaker until the carbons were fully submerged. It was allowed to stay for 48 h and was further heated in furnace at 900 ^oC for one hour 30 min. 0.1M sodium hydroxide and 0.1M HCl were used to stabilize the pH of carbon to neutrality.

Characterization of Adsorbent

Determination of textural characteristics

The textural characteristic of the adsorbent was determined according to modified methods of Borua et al. [15].

FT IR analysis

The infrared (IR) spectrum of activated periwinkle shell carbon and non-activated periwinkle shell carbon (NPSC) were carried out using a Perkin-Elmer model RX1 Fourier transform infrared (FT-IR) spectrometer (thane, Mumbai, India). Sample of 100-mgKBr disks containing 1% of the ground powder of each samples were prepared less than 24 hours before recording [16].

Scanning electron microscopic analysis (SEM)

The SEM was performed to examine the physical structural changes of samples using SEM (Model Phenom ProX, by phenomWorld, Einhoven, The Netherlands).

Energy dispersive X-ray (EDX) analysis)

EDX analysis was performed on APSC to access the elemental composition of the activated carbon using BRUKER EDX two-dimensionalVANTEC-500 detector [17].

RESULTS AND DISCUSSION

Selection of the Adsorbents

For all adsorbents performance studied are shown in Table 1 and in Figure 1

Table 1: Selection of the adsorbents

Adsorbents	Concentration 10mg/l		Concentration 30mg/l		Concentration 100mg/l	
	q_e(mg/g)	R_e (%)	q_e (mg/g)	R_e (%)	q_e (mg/g)	R_e (%)
10A	0.61	96.0	0.79	88.0	1.4	85.1
50A	0.60	95.5	0.84	93.0	1.55	94.0
100A	0.60	96.0	0.82	91.0	1.54	93.6
10C	0.63	100	0.90	99.9	1.64	99.9
50C	0.62	98.0	0.88	96.8	1.64	99.8
100C	0.61	96.02	0.89	87.9	1.63	99.7

The results for the capacity of adsorption and removal efficiency of the adsorbent activated with nitric acid (A), and calcium chloride (C) at the concentrations, (10A 10C, 50A 50C, 100A 100C) for the adsorption of cadmium at concentration, 10, 50 and 100mg/l were as stated in Table 1. Figure 1: shows the graphical illustration of adsorption capacity/efficiency of the adsorbents at various concentration of cadmium. However, this follows the trend, that the adsorbent 0.1C showed better adsorption capacity and performance.

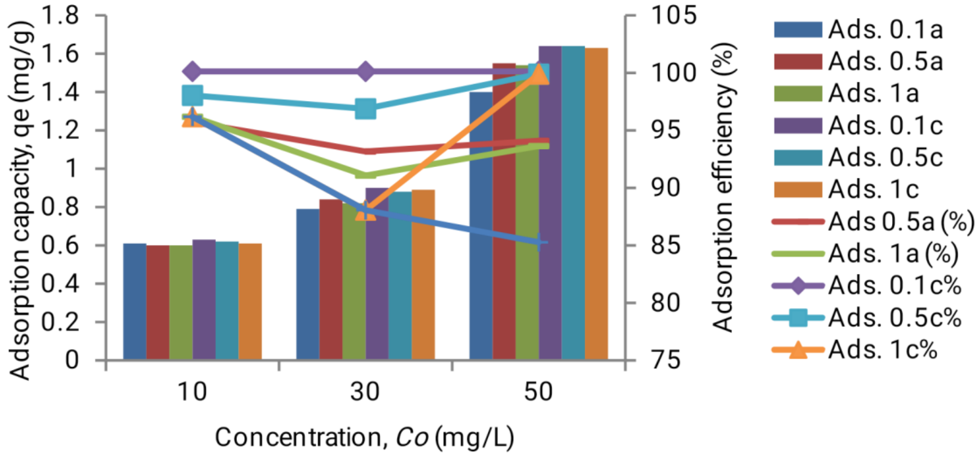

Figure 1: Selection of adsorbent

Results of the characterization of Periwinkle Shell Carbon

Surface area analysis

The textural variables of activated carbons were determined from nitrogen adsorption study. The activation of periwinkle shell by $CaCl_2$ leads to a well-developed high surface area and high mesoporosity as shown in Table 2. The activated carbon, APSC exhibits higher surface area (574.5m^{2}g^{-1}) with mesoporosity (28.58%) and average pore size (3.866nm) while non- activated, NPSC has a smaller surface area (434.9m^{2}g^{-1}) with mesoporosity (62.96%) and average pore size (5.740nm) [18]. It shows that chemical activation influences better effect in pore development in adsorbents [19]. The summaries of textural characteristics are shown on Table 2. This increase in pore distribution shows that it is a good candidate for cadmium removal.

Table 2: Textural characteristics of activated (APSC) and non-activated (NPSC)

Sample	Surface area ($S_{BET)}$,m$^{2/}$g	Average pore width(nm)	Micropore volume (cc/g)	Total pore volume (cc/g)	Mesoporosity %
APSC	574.50	3.87	0.20	0.28	28.58
NPSC	434.90	5.74	0.10	0.27	62.96

Fourier transforms infrared studies

The spectra of the adsorbents were measured in the wave number range of 1000-3500 cm^{-1}. The FTIR spectrum of APSC implies the presence of predominant peaks at 3388.2 cm^{-1} (–OH and –NH stretching), 2512.2 cm^{-1} (–OH stretching), 2109.7 cm^{-1}($-C\equiv C-$ stretching), 1796.6 cm^{-1}(–C=O Stretching) [20]. Other notable peaks are summarized in Table 3. It is visible from the Table 3 that all functional groups present are readily available for interaction with heavy metals. The observation provides that the functional groups such as NH and OH are involved in binding heavy metal ions to APSC [4, 16].

Table 3: Summary of FTIR spectra bond, frequency and functional group

Frequency, cm^{-1}	Bond	Functional group
3388.2(s,m)	O–H stretch and N–H stretch	Alcohol/phenols, amine/amides
2512.2(m)	O–H stretch	Carboxylic acids
2109.7(w)	$-C\equiv C-$ stretch	Alkynes
1796.6(s)	–C=O Stretch	Carbonyls
1636.3(w,m)	N–H bend	Amines
1394.0	C–H bend	Alkanes

m = medium, w = weak, s = strong

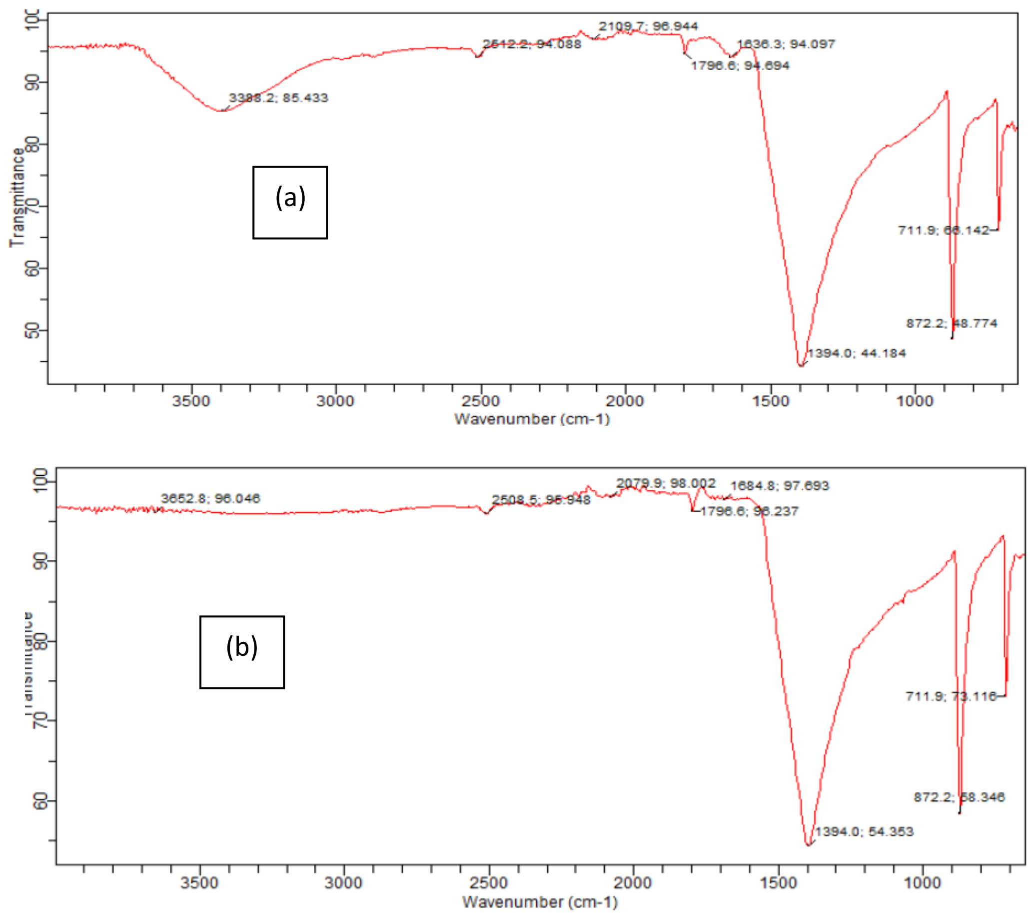

Figure 2: FITR spectrum for: (a) APSC and (b) NPSC.

Results of the scanning electron microscopic studies

The morphology of the adsorbent surface was determined using scanning electron microscopy Major changes were observed as result of modification of the adsorbent. The SEM micrograph of non-modified (NPSC) and modified periwinkle shells (APSC) are shown in Figure 3a and 3b respectively. At a magnification of 400x, the SEM micrograph of the modified periwinkle shell (APSC) shows the rough surface texture and porosity of APSC with holes and small opening on the surface, thereby increasing the contact area, which facilitates the pore diffusion during adsorption. This result agrees with the report of Olaseinde et., al. [21] and Madala et. al, [4].

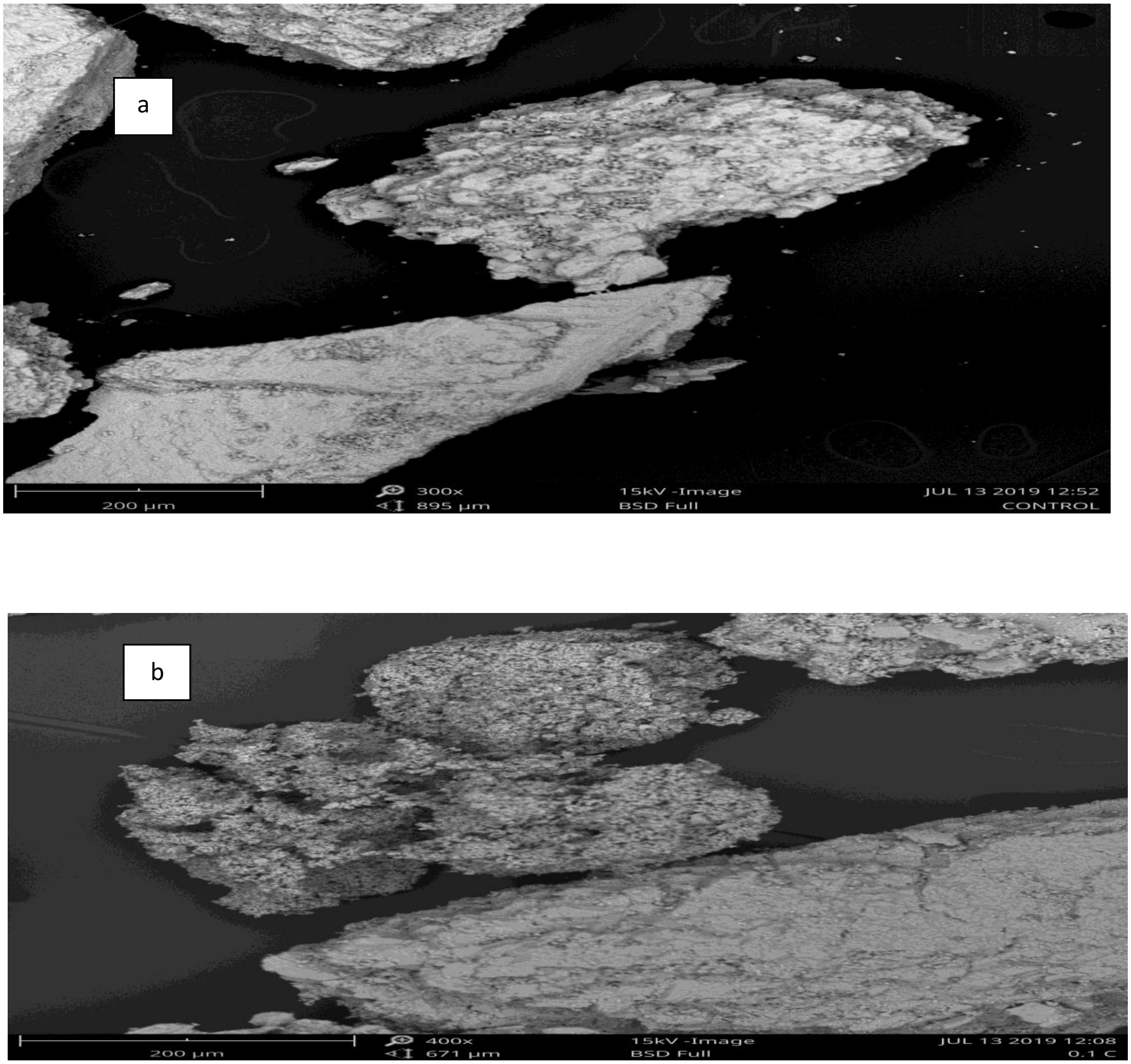

Figure 3: Scanning electron micrographs of the adsorbents (a) NPSC at 300x (b) APSC at 400x.

Results of the Energy dispersive X-ray (EDX) studies

The EDX analysis was done to obtain sample elemental composition contents of the adsorbent as shown in Figure 4. APSC projecting peaks in the EDX spectra indicates the presence of Ca(59.61%), O(24.34%), Al(0.20%), C(9.65%), B(3.56%), N(1.48%), Cl(0.975), and S(0.20%).

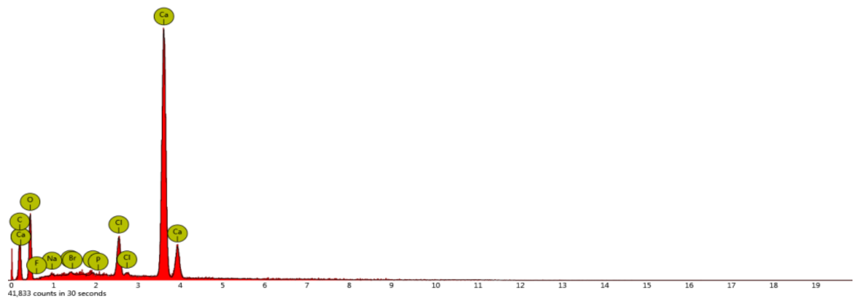

Figure 4: EDX analysis for elemental composition in the modified periwinkle shell (APSC).

CONCLUSION

The study revealed that the synthesis of activated carbon from periwinkle shell was technically feasible. The SEM showed the surface pore for heavy metals binding, FT-IR showed the functional groups present in APSC that facilitate adsorption to include: hydroxyl and amine groups. EDX spectral peak showed the elemental composition present in APSC.

Periwinkle shell could be used for industrial water treatment to eliminate low concentrations of cadmium and other heavy metal ions.

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