PRODUCTION AND CHARACTERIZATION OF MICROWAVE ASSISTED AND CHEMICALLY IMPREGNATED BIOADSORBENT MATERIAL FROM AZADIRACHTA INDICA BARK

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A B S T R A C T

A new bioadsorbent material was developed by impregnation of carbonized Azadirachta indica bark in H2SO4 and NaOH followed by microwave treatment (MACAIB). Developed bioadsorbent was characterized using proximate and ultimate analysis. The element analysis of prepared bioadsorbent of Azadirachta indica bark shows 58.54 % carbon, 1.48 % hydrogen and 1.39 % nitrogen. The surface morphology and the chemical composition of MACAIB was analyzed by SEM and EDX, respectively. EDX results of acid-base impregnated bioadsorbent of Azadirachta indica bark have 51.10% of carbon by weight. The surface chemical nature of bioadsorbent and functional groups on the surface of the active carbon was studied by FT-IR and XRD. The Brunauer–Emmett–Teller (BET) surface area under nitrogen adsorption at -1960C of prepared adsorbent was found 65.82 m2/g. The present research work shows that acid-base impregnated bioadsorbent of Azadirachta indica bark could be employed as low cost bioadsorbent in bioengineering process in the removal of toxic pollutants from waste water.

Keywords: Bioadsorbent, Azadirachta indica, Characterization, XRD FTIR ,EDX

1Introduction

There is growing interest in using low cost, commercially available materials for the adsorption of pollutants from waste water in industrial processes. The major advantages of adsorption technologies are its effectiveness in reducing the concentration of pollutants to very low levels and the use of inexpensive adsorbent materials [1]. The use of agricultural by-products as biosorbents material to purify contaminated water has become increasingly popular through the past decade, because they are less expensive, biodegradable, abundant and efficient [2—5].

Agricultural by-products, plant and tree based materials that have been successfully used to manufacture activated carbon in the recent past years for removal of different pollutants from waste water include orange peel, Moringa oleifera tree, coffee husk, pine cone, mango peels, rice husk, periwinkle shell, coconut shell, Imperata cylindrica leaf, rubber seed coat, banana stalk, groundnut hulls, ackee apple (Blighia sapida) seeds, oil palm fruit fibre, Manilkara zapota leaf, Manilkara zapota leaf, Polyalthia Longifolia leaf, lemon leaves, Curly Kale Leaves, Eucalyptus leaves, Polyalthia longifolia leaf, Acacia arabica leaves, Aloe vera leaves, biomass of Tinospora cordifolia plant, Eichhornia crassipes Biomass, Tridax procumbens leaves, Tridax procumbens leaves, Terminalia chebula leaf, Shorearobusta leaf, Tamarindus indica fruit shell, Citrus limetta peel, Arachis hypogaea shell, Lagenaria Siceraria shell, Citrus documana fruit peel, Banana peels, Walnut Shell, Cashew nut shell, Palm kernel-shell, Betel nut coir, Lapsi (Choerospondias axillaries) seed, Phyllanthus emblica seed, Seed extracts of Moringa Oleifera, Guava seeds, Punica granatum seed, Phoenix Dactylifera (Date Plam) seeds, Cuminum cyminum seeds, Almond tree (Terminialia cattapa) bark, Vitex negundo plant bark, Drumstick (Muringa odecifera) tree bark, Acacia nilotica tree bark, Morringa Indica bark, Acacia Auriculiformis scrap wood char, stalks of Sorghum and Canola [4, 6-14].

Azadirachta indica (Neem) is a fast growing evergreen tree found commonly in Indian subcontinent. Azadirachta indica is well known in India and its neighbouring countries for more than 2000 years as one of the most versatile medicinal plants having a wide spectrum of biological activity. Every part of the tree has been used as traditional medicine for household remedy against various human ailments, from antiquity [15]. Neem has been extensively used in ayurveda, unani and homoeopathic medicine and has become a cynosure of modern medicine. More than 135 compounds have been isolated from different parts of neem with the chemical and structural diversity [15].

The objectives of this study is to contribute in the search for less expensive bioadsorbent by analyzing the bulk density, moisture content, volatile matter, ash content, pH, fixed carbon content, water and acid soluble matter by proximate analysis and elemental, BET surface, EDX, SEM, FTIR and XRD analysis.

2.Experimental

2.1. Preparation of bioadsorbent

All the chemicals used were of analytical reagent grade purchased from Merck. India Pvt. Ltd. and Sd. Fine Chemicals, and all solutions were prepared by using double distilled water throughout this study. *Azadirachta indica* bark was collected from the local area and cuts in small pieces. It was washed several times with water to remove dust and other impurities. After air drying, it was ground using domestic mixer and sieved to 300 mesh size. The sample was washed with distilled water to remove colour and dried in an oven at 80^0C for 24 hours. The dried *Azadirachta indica* bark powder was carbonized on muffle furnace for 5 Hours at 500^oC. This carbonized seed powder again activated in domestic microwave (900MW) by one minute intervals for 30 minutes. The microwave assisted carbonized *Azadirachta indica* bark then impregnated with 0.5 N sodium hydroxide and 0.5 N sulphuric acid for 24 hours respectively and washed with deionised water to remove colour and other impurities. This MACAIB was dried at 110^0C in vacuum oven for 24 hours, grind well and kept in air tight plastic bottles for further use.

2.2. Physico-chemical Characterization of bioadsorbent

2.2.1. Proximate analysis

Physico-chemical parameters such as pH, bulk density, moisture, ash, volatile matter, fixed carbon, water and acid soluble matter of MACAIB were analysed. The results of ultimate analysis obtained were presented in Table 1. The pH for the activated MACAIB bioadsorbent was determined using the Elico pH meter, model LI-120, other parameters were analyzed by using standard test methods [16-18].

2.2.2. Ultimate analysis

The Brunauer-Emmett-Teller (BET) surface area pore characteristics were determined using computer-controlled nitrogen gas adsorption analyzer at -196^0C by Quanta Chrome Nova-1000 surface analyser instrument. The elements C, H, N and S were analysed by using Elementar Vario EL III model (C-H-N Analyser). The examination and analysis of microstructure morphology of MACAIB was recorded by using Scanning Electron Microscopy (SEM), (JEOL Model JSM - 6390LV). Electron dispersive X-ray (EDX) (JEOL JSM-7600F FEG-SEM model) was used for the element and chemical characterization of the activated MACAIB. The spectral analysis was done by Fourier Transform Infrared Spectrophotometer (FTIR) (Thermo Nicolet, Avatar 370) with KBr. FTIR spectra were recorded between 4000 and 400 cm^{-1}. The FTIR spectra give information about the characteristic functional groups on the surface of activated MACAIB bio-adsorbent. The Structural integrity of the bio-adsorbent samples was checked by Powder X-ray diffraction (XRD) by Bruker AXS D8 Advance difractometer using Cu Kα radiation (λ=1.5406 A°).

3. Results & Discussion

3.1. Physico-chemical characterization

The physico-chemical characterization i.e. proximate and ultimate analysis results of chemically activated microwave assisted carbonized *Azadirachta indica* bark (MACAIB) is presented in Table 1 and 2. The moisture, ash and volatile matter contents tended to be low and the lower values of ash content, water soluble and acid soluble matter results favour the good adsorbent characteristics showing that

bioadsorbent was properly prepared. The results of proximate analysis and elemental analysis indicated that the chemical activation has successfully increased the carbon content and decreased volatile matter. The Brunauer-Emmett-Teller (BET) surface area, average pore diameter and total pore volume were found to be 65.82 (m^2/g), 99.79 (A^O) and 0.114 (cc/g) indicated that MACAIB biomaterial should be an excellent adsorbent. The pH of MACAIB bio-adsorbent has slightly alkaline nature (7.36).

Table-1 : Proximate analysis

S. N.	Parameters	Values
1	Bulk density (gm/cm^3)	0.46
2	Moisture content%	5.73
3	Ash content %	12.85
4	Volatile matter content %	16.44
5	Fixed carbon content %	64.98
6	pH	7.36
7	Water Soluble Matter (%)	0.93
8	Acid soluble matter (%)	3.87

Table -2 : Ultimate analysis

S. N.	Parameters	Values
1	Carbon %	58.54
2	Hydrogen %	1.48
3	Nitrogen %	1.39
4	Sulphur %	ND
5	Oxygen %	38.59
6	Surface Area (m^2/g)	65.82
7	Average Pore Diameter (A^O)	99.79
8	Total Pore Volume (cc/g)	0.114

3.2. Scanning Electron Microscopy (SEM) study

SEM micrographs were studied for surface and morphological characteristics of MACAIB bioadsorbent (Fig.-1 and 2). The assessment of the SEM micrographs showed that in micrographs, dark areas indicated pores and grey areas indicated the carbon matrix and showed rough surface of the adsorbent that provided large surface area. The surface structures of precursor were rough and uneven. Largely, a well-built porous surface was observed at higher magnification, and further, randomly distributed pore size was observed in the micrographs due to the modification using an activating agent and microwave treatment.

3.3. Electron Dispersive X-ray (EDX)

The EDX analysis highlighted the presence of elemental percentage compositions of carbon, oxygen and other elements in the MACAIB bioadsorbent. The EDX result of MACAIB reported in Tables 3 showing amount of different elements in the samples. The sample with the highest amount of carbon and the least amount of oxygen is said to be the most effective. It was observed that the MACAIB bioadsorbent has the highest amount of carbon by weight (51.10%) and (62.17%) by atom. Hence MACAIB can use as an efficient adsorbent for the removal of pollutants from aqueous solution.

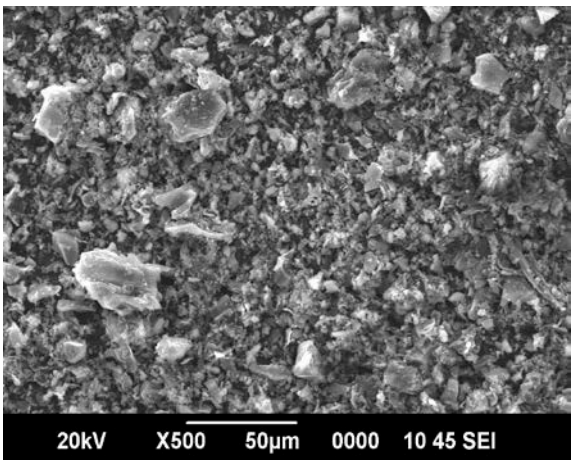

Figure 1 : SEM micrograph (50µm)

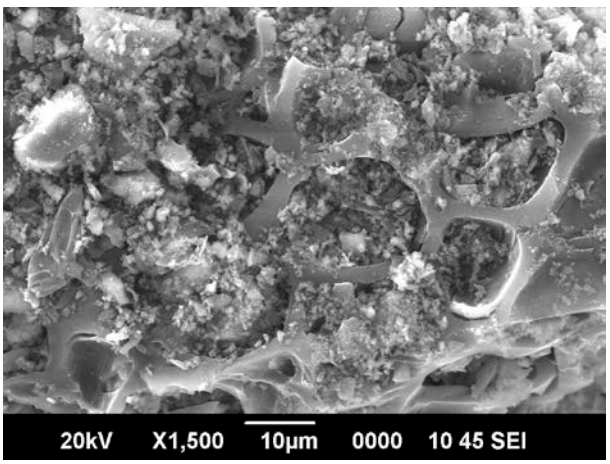

Figure 2 : SEM micrograph (10µm)

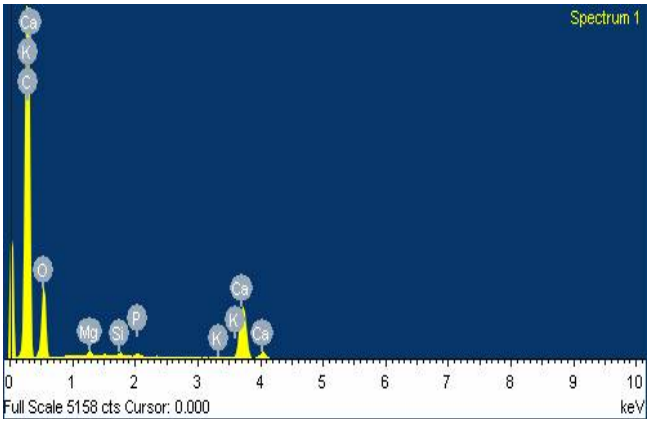

Table-3 : EDX analysis results

Element	Weight %	Atomic %
C K	51.10	62.17
O K	35.48	32.60
Mg K	0.46	0.28
Si K	0.29	0.16
P K	0.38	0.18
K K	0.31	0.12
Ca K	11.98	4.49

3.4. Fourier Transform Infrared (FTIR) spectra

The FTIR technique is an important tool to identify the characteristic functional groups present in the adsorbent. The different functional groups in MACAIB bioadsorbent were observed by FTIR spectra (Fig.-4). The number of peaks represents the adsorptive nature of MACAIB. The peaks in the region 3700 to 3400 cm^{-1} is due to the presence of –O-H and –N-H stretching vibrations. The peaks in the region 2900 to 2500 cm^{-1} represents the $–CH_2$ symmetrical and asymmetrical stretching. The peak region from 1700 to 1400 cm^{-1} indicates the presence of –C=O group of ketones, esters and –C-O-C- of ether. The peaks due to –N-H deformation and bending were observed in the region 1400 to 1500 cm^{-1}. Around 1200 to 500 cm-1 region, peaks observed due to the presence of –C=S, -C-N, -C-O, -C-C- and –C-H stretching vibrations. On the basis of the FTIR, one can confirm the potential applicability of MACAIB as a bio-adsorbent material.

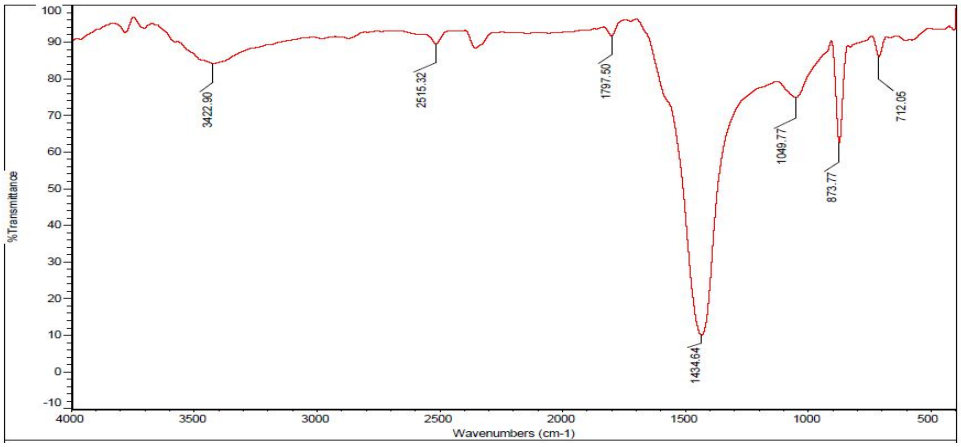

Figure 4 : Fourier Transform Infrared (FTIR) spectra of MACAIB

3.5. Powder X-ray diffraction (XRD)

Figure-5 shows the XRD pattern of the MACAIB bioadsorbent material. The powder XRD signals exhibits noise, reveals that a predominantly amorphous structure of carbon. The peaks in XRD are due to the elements like Ca, Si, K, Mg as confirmed by EDX study. In this result, it can be explained that the pyrolytic reaction of organic compounds consists of the breaking of chemical bonds with temperature and condensing further into active compounds. These compounds form typical graphitic layers and stacks of planes during carbonization [19]. Thus, the MACAIB carbon material has a completely amorphous structure, which is expected for organic materials

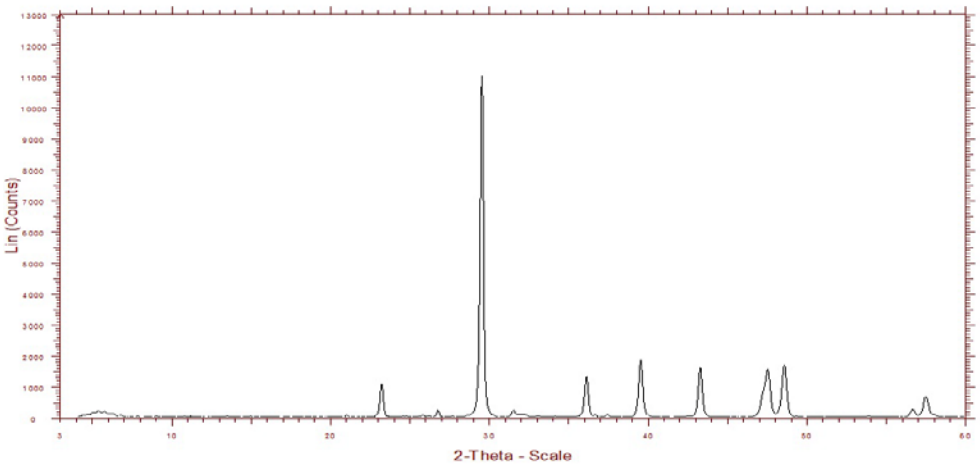

Figure 5 : Powder X-ray diffraction (XRD) of MACAIB

4. Conclusion

In this article, a new chemically impregnated and microwave assisted carbonized *Azadirachta indica* bark (MACAIB) activated carbon prepared. The developed bioadsorbent material was characterized by proximate analysis such as bulk density, moisture, ash, volatile matter, fixed carbon content, water soluble and acid soluble matter and ultimate analysis such as elemental analysis, BET surface area, average pore diameter, total pore volume, EDX, SEM, FTIR and XRD. *Azadirachta indica* bark (MACAIB) is a potential precursor adsorbent due to its high carbon content, low moisture and ash content. The irregular pores are presents on the surface of bioadsorbent indicate the feasibility of binding sites. The FTIR analysis confirmed the presence of different functional groups on the surface of adsorbent. The results of the present investigation show that MACAIB is a good precursor for preparation of potentially useful low cost adsorbent. In conclusion, *Azadirachta indica* bark can suitably considered as an alternative material for the removal of pollutants such as dyes, heavy metals, organic pollutants, biological active agents and other hazardous chemicals.

References

[1] Cafer Saka, Omer Sahin, Mehmet Masuk Kucuk, (2012), Applications on agricultural and forest waste adsorbents for the removal of lead (II) from contaminated waters, Int. J. Environ. Sci. Technol., 9, 379–394.

[2] Bailey S. E., Olin T. J., Bricka R. M., Adrian D. D., (1999), A review of potentially low-cost sorbents for heavy metals, Water. Res., 33, 2469–2479.

[3] Demirbas A., (2008), Heavy metal adsorption onto agro-based waste materials: a review, J. Hazard. Mater., 157, 220–229.

[4] Gupta V. K., Carrott P. J. M., Carrott M. M. L., Suhas R., (2009), Low-cost adsorbents: growing approach to wastewater treatment—a review, Crit. Rev. Env. Sci. Tech., 39, 783–842.

[5] Gupta S., Kumar D., Gaur J. P., (2009), Kinetic and isotherm modelling of Pb(II) sorption onto some waste plant materials, Chem. Eng. J., 148, 226–233.

[6] George Z. Kyzas, Margaritis Kostoglou, (2014), Green Adsorbents for Wastewaters: A Critical Review, Materials, 7, 333- 364.

[7] Mohapatra M., Anand S., Mishra B. K., Dion E. Giles, Singh P., (2009), Review of fluoride removal from drinking water, J. of Envir. Management, 91, 67–77.

[8] Vaishali Tomar, Surendra Prasad, Dinesh Kumar, (2013), Adsorptive removal of fluoride from water samples using Zr–Mn composite material, Microchem. J., 111, 116–124.

[9] Mirna Habuda-Stanić , Maja Ergović Ravančić, Andrew Flanagan, (2014), a review on adsorption of fluoride from aqueous solution, Materials, 7, 6317-6366.

[10] Olugbenga Solomon Bello, Kayode Adesina Adegoke, Opeyemi Omowumi Akinyunni, (2015), Preparation and characterization of a novel adsorbent from Moringa oleifera leaf, Appl. Water Sci., DOI 10.1007/s13201-015-0345-4..

[11 Telkapalliwar N. G., Shivankar V. M., (2016), Review on adsorption of

fluoride from aqueous solution by using low cost leaf based bioadsorbents, Inter. J. of Modern Trends in Eng and Res, 3(6), 40-52.

[12] Telkapalliwar N. G., Shivankar V. M., (2016), Fruit peel and shell as a low-cost bioadsorbents for fluoride removal from aqueous solution: a review, Inter. J. of Innovative Res. in Sci., Eng. and Tech., 5(6), 10248- 10257..

[13] Telkapalliwar N. G, Shivankar V. M., (2016), Growing approach in adsorption of fluoride from aqueous solution by using inexpensive seed based biomass: review, J. of Chem., Bio. and Phy. Sci., 6 (3), 946-957.

[14] Telkapalliwar N. G., Shivankar V. M., (2016), Removal of fluoride from aqueous solution by using inexpensive bark and wood based bio-adsorbent : a comprehensive review, Inter. J. of Advance Res. and Innovative Ideas in Education, 2(3), 3447- 3457.

[15] Kausik Biswas, Ishita Chattopadhyay, Ranajit K. Banerjee, Uday Bandyopadhyay, (2002), Biological activities and medicinal properties of neem (Azadirachta indica), Current Science, 82(11), 1336-1345.

[16] ISI, Activated Carbon, powdered and Granular- Methods of Sampling and Tests (Bureau of Indian Standards, New Delhi), IS877: 1989.

[17] APHA, Standard Methods for the Examination of Water and Wastewater, 17th edition (American Water Works Association, New York), 1989.

[18] Vogel A. I., A Text book of Quantitative Inorganic Analysis, 3rd edition, (ELBS, London), 1969.

[19] Ahmad M. A., Alrozi R., (2010), Optimization of preparation conditions for mangosteen peel-based activated carbons for the removal of Remazol Brilliant Blue R using response surface methodology, Chem. Eng. J., 165, 883–890.