PREPARATION AND CHARACTERIZATION OF MODIFIED ADSORBENTS DERIVED FROM PAWPAW *(Carica papaya)* LEAF

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Abstract. The feasibility of a new and novel adsorbent was investigated by impregnation of pawpaw leaf *(Carica papaya)* in H2SO4 and NaOH respectively. The adsorbents prepared were characterized using FTIR, SEM, TGA and EDX techniques respectively. Physicochemical parameters of these adsorbents such as pH, moisture content, ash content, porosity and iodine number were also carried out; the results were then compared with the expensive commercial activated carbon (CAC) parameters. A close agreement in moisture, pH, porosity, ash content and iodine number of the acid activated pawpaw leaf (Carica papaya) shows its feasibility as a good and effective adsorbent. Conclusively, the present investigation shows that acid activated C. papaya leaf is a good and viable alternative adsorbent, which could be used in lieu of expensive CAC for adsorption processes.

Keywords: activation, adsorbent, characterization, impregnation, carica papaya, operational parameters.

1. Introduction

Recently, many synthetic processes have been tested to curtail major drawbacks of existing natural adsorbents in terms of their adsorption capacity, surface area, cation exchange capacity, stability and chemical properties than their original properties. These processes largely require intensive understanding of the adsorbent mechanisms including reactivity, affinity, stability and physico-chemical attributes [1]. Activated carbon (AC) is a solid, porous, black carbonaceous material. It is distinguished from elemental carbon by the absence of both impurities and an oxidized surface [2]. The specific properties of AC depend on both the source of the organic material (usually biomass material such as wood, peat, lignite, oil products or coal) and treatment method—typically a two-stage process: carbonization followed by activation [3]-[8]. The carbonization process enriches the carbon content and creates an initial porosity in the char while activation further develops the porosity and enhances ordering of the structure, thereby generating a highly porous solid as the final product [9].

Pawpaw *(Carica papaya)* belongs to the family of *Caricaceae,* and several species of *Caricaceae* have been used as remedy against a variety of diseases [10], [11].

Despite, the tremendous use of pawpaw fruit, little or no attention are paid to the leaves, they are left to rot thereby constituting wastes in the environment. However, to the best of our knowledge, no study has been reported on the characterization and the use of treated pawpaw leaf as adsorbent. In an attempt to place value on this waste, this paper is aimed at reporting the preparation, characterization and physico chemical properties of raw, acid and base treated pawpaw leaf and compares them with commercially available expensive activated carbon.

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2. Preparation and Activation of Activated Carbon

2.1. Modification

- Pawpaw leaves were sun dried until a constant weight is attained and pulverized.
- The dried pawpaw leaves were carbonized at 350 ^{0}C for two hours.
- Carefully weighed 25.0 ± 0.01g carbonized carbon was placed in a beaker containing 500 cm^3 of 0.3 mol/dm^3 ortho-phosphoric acid (H$_3$PO$_4$) and was thoroughly mixed and heated at 300^{0}C for thirty minutes.
- The obtained sample was washed with distilled water until constant pH of 6.7 ± 0.12 was obtained and then dried at 105 ^{0}C to constant weight.
- The carbonized sample was sieved through a 120 µm mesh Endecott sieve
- Same procedure was followed using NaOH for base activation.

2.2. Characterization

Prepared adsorbents were characterized using the following:

- Surface Morphology (SEM)
- Proximate analysis (TGA)
- Fourier transform infrared (FTIR)
- Determination of pH.
- Electron dispersive X-ray (EDX)
- Determination of the amount of iodine adsorbed

3. Results and Discussions

3.1. Characterization of PPAC Proximate Analyses of Prepared Adsorbents

Proximate content of the PPLR, PPLA and PPLB samples are shown in Table 1. PPLA was found to have the least moisture, ash content and volatile matter. However, it has the highest fixed carbon content when compared with CAC. The results showed that the moisture and volatile content decreased significantly during the activation process. During this process, organic substances in the sample become unstable and the bonding or linkage of the molecules breaks. The activation process also caused the volatile matter to be discharged as gas and liquid products leaving the material with high carbon content [12].

Table 1: Comparison of the proximate content (physicochemical) analyses of raw pawpaw (PPLR), acid activated pawpaw (PPLA), and base activated pawpaw (PPLB) with commercial activated carbon (CAC)

Properties	PPLR	PPLA	PPLB	CAC
pH	7.05 ± 0.06	6.97 ± 0.02	7.70 ± 0.16	7.0 ± 0.01
Moisture %	19.97 ± 0.09	6.76 ± 0.03	6.79 ± 0.04	6.67 ± 0.07
Ash %	17.07 ± 0.15	7.21 ± 0.07	10.78 ± 0.02	7.10 ± 0.01
Volatile %	20.2 ± 0.18	16.89 ± 0.04	29.94 ± 0.01	17.50 ± 0.03
Fixed carbon %	42.76 ± 0.03	69.14 ± 0.06	52.49 ± 0.05	68.73 ± 0.05
Iodine number	114.2 ± 0.22	197.97 ± 0.26	137.97 ± 0.21	200.36 ± 0.30

$\pm$ These values are standard errors, the experiments are carried out in triplicates.

3.2. Effect of pH

The pH of PPLR, PPLA, PPLB and CAC were found to be 7.05, 6.97, 7.70 and 7.0 respectively (Table 1). It has been reported that for most applications, carbon pH 6-8 is acceptable [13-14]. The pH values obtained are in the range of acceptable limit.

3.3. Scanning Electron Micrograph (SEM) of Prepared Adsorbents

Figure 1 shows the SEM images of raw pawpaw leaf (PPLR) base activated pawpaw leaf (PPLB) and acid activated pawpaw leaf (PPLA) samples respectively. Several large pores in a spongy shape were clearly found on the surface of the acid activated pawpaw leaves powder, PPLA, as compared with PPLB and PPL. The pores were opened on the surface of the acid activated sample, PPLA .This shows that the activation process was effective in creating well-developed pores on the surface of the acid treated sample. Similar observations were reported by Ricou-Hoeffer, *et al* 2001, Hameed, and Daud, 2008 respectively [15], [16]. These pores allowed a good surface for dyes, heavy metals and waste effluents to be trapped and adsorbed into [17].
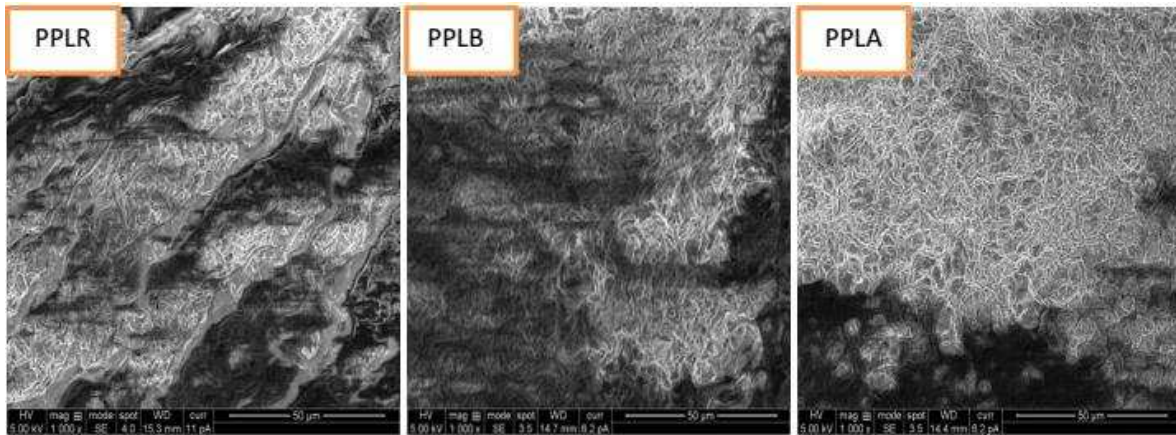

Fig. 1: The SEM micrographs of raw sample (PPLR), base activated sample (PPLB) and acid activated sample (PPLA) (Magnification x1000)
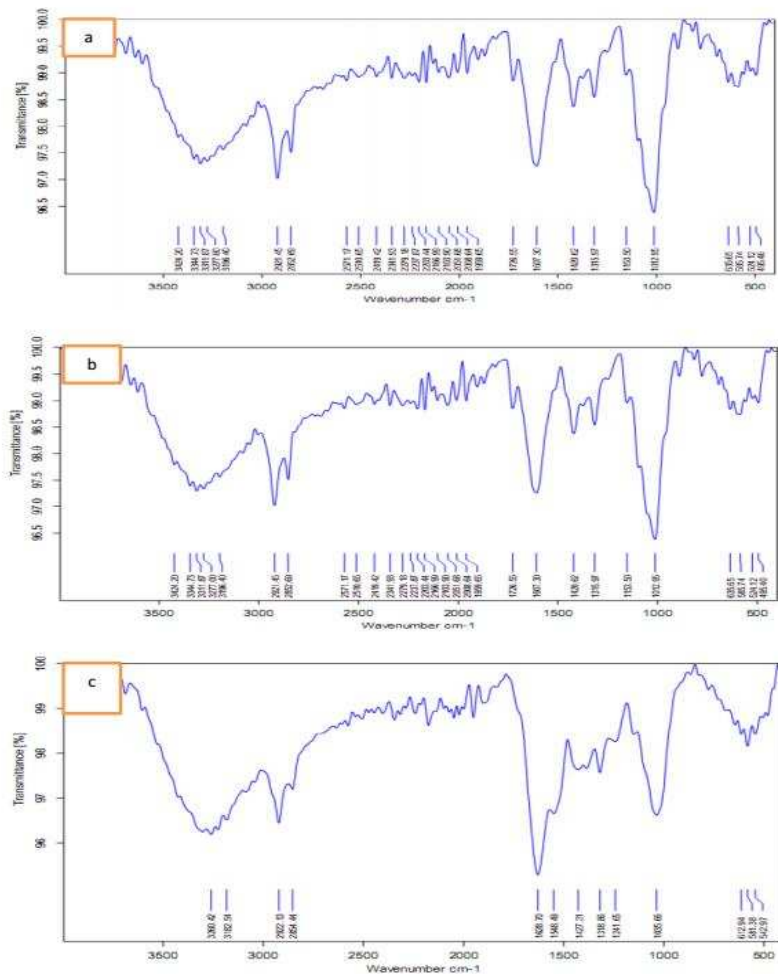

Fig. 2: Fourier Transform Infra-Red (FTIR) spectra of pawpaw leaf (a)PPLR (b)PPLB (c)PPLA

3.4. Fourier Transform Infra-Red (FTIR) Spectra of prepared adsorbents.

FTIR spectroscopic analysis indicated broad band at 3124 -3260cm^{-1}, representing bonded OH groups. The band observed at about 3344–3812 cm^{-1} was assigned to the NH stretching group. The peak observed at 2921- 2922 cm^{-1} was assigned to the aliphatic CH group. The peak observed at 2852 – 2854 cm^{-1} was assigned to the CO group. The peak around 1628 cm^{-1} corresponds to the C=O stretch. The peak observed at 1420-1318 cm^{-1} corresponds to the secondary amine group. Symmetric bending of CH$_3$ is observed to shift from 1315 to 1035 cm^{-1} and 1012 to 581 cm^{-1} respectively. The changes in FTIR spectra (Figs. 2a and 2c) confirmed the effect of activation on pawpaw leaf indicating that mostly, the bonded OH groups vibrations are due to inter- and intramolecular hydrogen bonding of polymeric compounds (macromolecular association) such as alcohols phenol and carboxylic acids as in pectin, cellulose and lignin, thus showing the presence of free hydroxyl groups on the prepared adsorbents. The same observations were reported by other researchers [18] - [20]. It was observed that there were pronounced and clear band shifts for the PPLA than PPLB when compared to PPL. The pronounced shift was due to the effect of acid activation, indicating that PPLA will be very useful in adsorption processes.
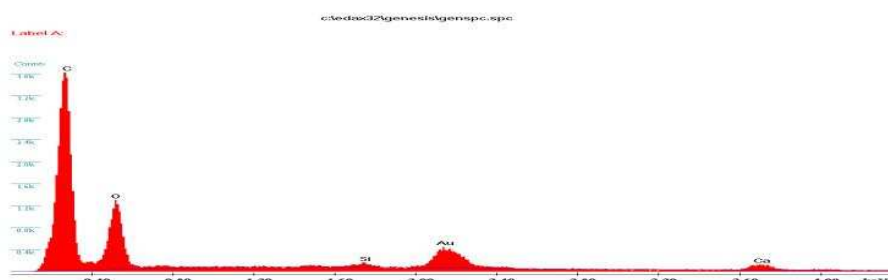
Energy Dispersive X-ray (EDX)
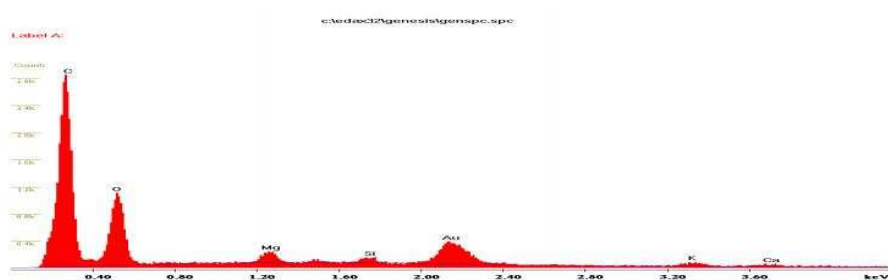
Energy dispersive X-ray (EDX) spectra of raw pawpaw leaf (PPLR)
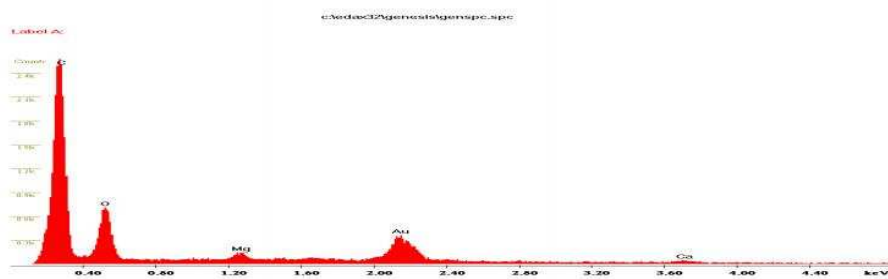
Energy dispersive X-ray (EDX) spectra of base pawpaw leaf (PPLB)

Energy dispersive X-ray (EDX) spectra of acid pawpaw leaf (PPLA)

Fig. 3: Energy dispersive X-ray (EDX) spectra of raw pawpaw leaf

Elemental analyses of prepared samples are shown in Tables 2 - 4. The result showed that the carbon content increased significantly while the other element such as oxygen (O), magnesium (Mg), silicon (Si) and calcium (Ca) decreased during the activation step. This was attributed to the decomposition of volatile compounds and degradation of organic substances during wet activation leaving behind carbon with high

purity [21]. Tables 2-4 show the variation in the amount of carbon present in different samples prepared. The sample with the highest amount of carbon present in it is said to be the most effective; that is, the higher the amount of carbon present in the sample, the more effective the sample will be as an adsorbent. It is seen from the tables below that the acid treated sample has the highest amount of carbon, so it can be concluded that it is the most viable adsorbent among the three. This is consistent with other findings reported in literature [21]-[23].

Table 2: EDX elemental analysis of raw pawpaw (PPLR)

ELEMENT	Wt%	At%	k-ratio	Z	A	F
Carbon	66.94	74.53	0.5251	1.0112	0.7800	1.0002
Oxygen	27.82	23.25	0.1061	0.9888	0.3856	1.0000
Magnesium	1.53	0.84	0.0122	0.9324	0.8550	1.0002
Silicon	0.83	0.40	0.0074	0.9290	0.9559	1.0004
Potassium	1.65	0.56	0.0146	0.8714	1.0081	1.0004
Calcium	1.22	0.41	0.0109	0.8879	1.0068	1.0000
Total	100.0	100.0				

Table 3: EDX elemental analysis of base activated pawpaw (PPLB)

ELEMENT	Wt%	At%	k-ratio	Z	A	F
Carbon	73.59	80.16	0.6231	1.0088	0.8393	1.0002
Oxygen	22.64	18.52	0.0802	0.9864	0.3590	1.0000
Silicon	0.62	0.29	0.0055	0.9267	0.9644	1.0005
Calcium	3.15	1.03	0.0282	0.8837	1.0101	1.0000
Total	100.0	100.0				

Table 4: EDX elemental analysis of acid activated pawpaw (PPLA)

ELEMENT	Wt%	At%	k-ratio	Z	A	F
Carbon	74.26	80.00	0.6363	1.0071	0.8470	1.0002
Oxygen	23.66	19.13	0.0867	0.9848	0.3720	1.0000
Magnesium	0.94	0.50	0.0075	0.9281	0.8637	1.0000
Calcium	1.14	0.37	0.0102	0.8840	1.0103	1.0000
Total	100.0	100.0				

4. Conclusion

This study shows that PPLA gave the best possible results out of the three adsorbents prepared. It also provides AC users a cost effective and environmentally friendly alternative in lieu of the expensive CAC.

5. Acknowledgements

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