



Adsorption of acid dyes of the monoazo and anthraquinone class from aqueous solutions using high surface area cassava peel-based activated carbon

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Received: 10th February, 2011 ; Accepted: 20th February, 2011

ABSTRACT

Cassava is one of the most important food sources in Nigeria. Cassava peel (CP) is an agricultural waste from food and starch processing industries. In this study, CP was used as a precursor for activated carbon preparation. Activated carbons were prepared from CP using both physical and chemical activation methods; they were characterized using Brunauer-Emmett Teller (BET), Fourier Transform Infrared (FTIR), Scanning Electron Microscope (SEM) and proximate analyses respectively. Their efficiencies were tested in the removal of dyes from aqueous solutions. The two activated carbons were efficient in the adsorption of eight, structurally related, acid dyes of the monoazo and anthraquinone class in aqueous solutions; the CP activated with chemical method showed higher percentage removal efficiencies (90-100%) than the physically activated one (74-89%). © 2011 Trade Science Inc. - INDIA

KEYWORDS

Cassava;
Precursor;
Activated carbon;
Dyes.

INTRODUCTION

Cassava (*Manihot esculenta* Crantz) is a storage root crop which serves as a staple foodstuff for more than 500 million people throughout tropical Africa as a result of its carbohydrate rich and low protein contents^[1]. Cassava production is high in Nigeria as it is utilized by traditional food industries, the rest are used as the raw material for cassava starch industries. Cassava starch producing operation produces large amount of cassava peels (CP) and direct discharge of these solid wastes cause environmental problems. This becomes a by-

product from cassava processing after harvest with little use, its uncontrolled spill (e.g. in rivers and streams) cause serious environmental problems.

Natural and synthetic organic dyes are extensively used in textile industries. Particularly, the acid dyes of the monoazo and anthraquinone class are used in the dyeing of wool, silk, acrylic and nylon. The discharge of colored wastewater from textile industries into rivers and lakes has caused many problems in the aquatic life because the color reduces light penetration, which has derogatory effect on the photosynthetic phenomenon^[2]. The commercial activated carbon is the most widely

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used adsorbent for the removal of such dyes, but recently some non-carbonized low cost adsorbents such as: avocado kernel^[3] banana peel^[4] coconut shell^[5] orange peel^[6] peanut hulls^[7] periwinkle shell^[8] sawdust^[9] e.t.c have been used to prepare activated carbon adsorbents. The use of waste materials from agricultural origin is an interesting alternative for the preparation of carbonaceous adsorbents.

There are two methods for preparation of activated carbon: chemical activation and physical activation. Chemical activation is known as a single step method of preparation of activated carbon in the presence of chemical agents. Physical activation involves carbonization of a carbonaceous materials followed by activation of the resulting char in the presence of activating agents such as CO₂ or steam. The chemical activation usually takes place at a temperature lower than that used in physical activation, The carbon yields of chemical activation are higher than the physical one^[10]. Chemical activation has three main advantages. Firstly, it is carried out in a single step. Secondly, carbonization and activation are united^[10]. Lastly, it is performed at relatively lower temperature when compared with physical activation; it improves pore development in the carbon structure. It involves pyrolyzing the feedstock in the presence of a chemical activating agent such as H₃PO₄, ZnCl₂, and KOH.

Although there are many studies in the literature relating to the preparation and characterization of activated carbon from agricultural wastes, to the best of my knowledge, there is no report on the preparation of the activated carbon using CP as a precursor with ZnCl₂ as chemical activating agent for the adsorption of acid dyes of the monoazo and anthraquinone class in literature. On this premise, CP obtained from cassava starch industry in Nigeria was used to prepare activated carbon using both physical and chemical activation methods. Studies were conducted on the use of activated carbons prepared from CP in the removal of eight structurally related acid dyes of the monoazo and anthraquinone class in aqueous solutions.

METHODS

Activated carbon preparation

Physical activation method

CP was first washed with water to remove dirt from

its surface and subsequently dried at 105°C for 24 h to remove the moisture content. The dried waste CP was ground into small pieces and sieved to the desired particle size of 1-2 mm and loaded in a stainless steel vertical tubular reactor placed in a tube furnace. Carbonization of the dried CP was carried out at 500°C with heating rate of 10°C min⁻¹ under purified nitrogen flow through at a flow rate of 150 cm³min⁻¹ for one hour. The resulting char was activated under the same condition, but to a final temperature of 700°C for 2 h. Once the final temperature was reached, the nitrogen gas flow was switched to CO₂ (200 cm³ min⁻¹) to complete the activation process. The activated product denoted as P-CPAC was then cooled to room temperature under nitrogen flow and then washed with hot deionized water and hydrochloric acid (0.1M) until the pH of the solution used for washing reached 6.5 - 7.0.

Chemical method

The washed and dried CP was ground and sieved to a particle size of 1-2 mm before loading it in a stainless steel vertical tubular reactor placed in a tube furnace. Carbonization step was carried out at 400°C for 30 min under nitrogen (99.99%) flow at flow rate of 150 mL min⁻¹. The char produced was impregnated with ZnCl₂ pellets (Impregnation ratio, IR= 40 (wt : %)). Deionized water was then added to dissolve all the ZnCl₂ pellets. The activation step was done using similar reactor as in carbonization step. Once the final activation temperature (700°C) was reached, the gas flow was switched from nitrogen to CO₂ at a flow rate of 150 mL min⁻¹ to complete the activation process. The activated product denoted as C-CPAC was then cooled to room temperature under nitrogen flow. Then, the sample was washed with hot deionized water and hydrochloric acid (0.1M) until the pH of the washed solution reached 6.5-7.

Reagents used

The reagents used were of analytical grade, they were supplied from BDH. The adsorbates used are Acid Blue 80, Acid Blue 32, Acid Green 25, Acid Green 27, Acid Orange 7, Acid Orange 8, Acid Orange 10 and Acid Red 1. The treatment was carried out using a batch process; 500 mg of the adsorbent was agitated at room temperature (30 ± 1°C) with 50 ml of the adsorbate for at predetermined times (30-90 mins) at 160 rpm in 250 ml conical flasks. The

supernatant was separated by centrifugation at 10,000 rpm and analyses spectrophotometrically.

ANALYSIS

The concentrations of the dyes before and after treatment were measured at their respective wavelengths spectrophotometrically. The percentage removal was calculated using the equation below

$$\% \text{ Removal} = \frac{(C_i - C_f)}{C_i} \times 100$$

where C_i and C_f (mg/L) are the concentrations of the dye before and after treatment. The experiments are conducted in triplicate and the average results are reported.

RESULTS AND DISCUSSION

Characterization of the adsorbents

The characteristics of the two adsorbents used are reported in TABLE 1. The surface area of C-CPAC was higher than P-CPAC. The high surface area of the C-CPAC was due to chemical activation using ZnCl_2 . ZnCl_2 is a dehydrating agent that penetrates deeply into the structure of the carbon causing tiny pores to develop^[11]. The addition of ZnCl_2 and the thermal treatment enhanced the attack of the chemical on the matrix of the precursor, leading to reorganization of the precursor's matrix, swelling of the particles, dehydration and gradual development of a porous structure upon activation. The volatile matter, ash and the moisture contents of C-CPAC were lower when compared to P-CPAC. The fixed carbon content of 62.52 % obtained for C-CPAC was satisfactory enough for dye adsorption. Similar result was reported in literature on the study of activated carbons by pyrolysis of cassava peel in the presence of zinc chloride^[12].

FTIR technique was used to examine the surface groups of C-CPAC adsorbent and to identify the groups responsible for dye adsorption. Infrared spectra of the adsorbent and dye-loaded adsorbent samples, before and after the adsorption process, were recorded in the range 4000–400 cm^{-1} (Figure 1). As observed for C-CPAC adsorbent after the adsorption process, the functional groups that interacted with the dye suffered a shift to lower wave numbers. Figure 1a and b shows the FTIR

TABLE 1: Characteristics of activated cassava peel carbon

Parameters	P-CPAC	C-CPAC
pH	8.38	7.14
Conductivity (ms/cm)	0.57	0.11
Moisture (%)	11.16	3.40
Volatile Matter (%)	58.30	28.20
Fixed Residue (%)	30.41	62.52
Ash Content (%)	4.56	3.20
Decolorizing power (mg/g)	6.70	44.00
Surface area (m^2/g)	250.16	834.17
Water soluble matter (%)	7.23	9.61
Acid soluble matter (%)	13.16	15.43

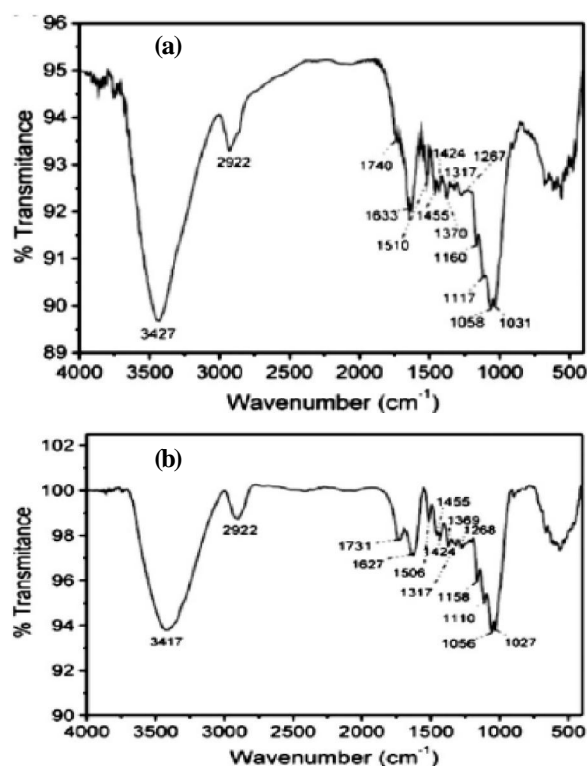


Figure 1 : FTIR spectra of C-CPAC (a) before adsorption; (b) after adsorption

vibrational spectra of the C-CPAC before the adsorption and when it was loaded with the dye after adsorption. The intense absorption bands at 3427 and 3417 cm^{-1} are assigned to O–H bond stretching, before and after adsorption, respectively. The CH_2 stretching band at 2922 cm^{-1} are assigned to asymmetric stretching of CH_2 groups which present the same wave numbers before and after the adsorption, indicating that these groups did not participate in the adsorption process. Small bands at 1740 and 1731 cm^{-1} , before and after adsorption were assigned to carbonyl groups of carboxylic acid.

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Sharp intense peaks observed at 1633 and 1627 cm^{-1} , before and after absorption, respectively, are assigned to the aromatic C=C ring stretch. In addition, there are several small bands and shoulders in the range of 1510–1424 cm^{-1} that are assigned to ring modes of the aromatic rings^[13]. The wave numbers of these bands were practically the same before and after the adsorption procedure. Small bands ranging from 1160–1031 cm^{-1} and 1158–1027 cm^{-1} before and after adsorption are assigned to C–O stretching vibrations of lignin^[13,14]. FTIR results indicate that the interaction of the dye with the C-CPAC adsorbent occur with the O–H bonds and carboxylate groups. In addition, strong bands of 1116–1061 and 1100–1026 cm^{-1} , before and after adsorption confirm the presence of C–O bond (Figure 1b)^[13] reinforcing the interaction of the dye with carboxylate groups. Scanning electron micrographs of C-CPAC (Figure 2a) and C-CPAC+Dye (Figure 2b) show drastic differences in these materials. C-CPAC is a material that has a high surface area that led to an increase in the maximum amount of dye adsorbed.

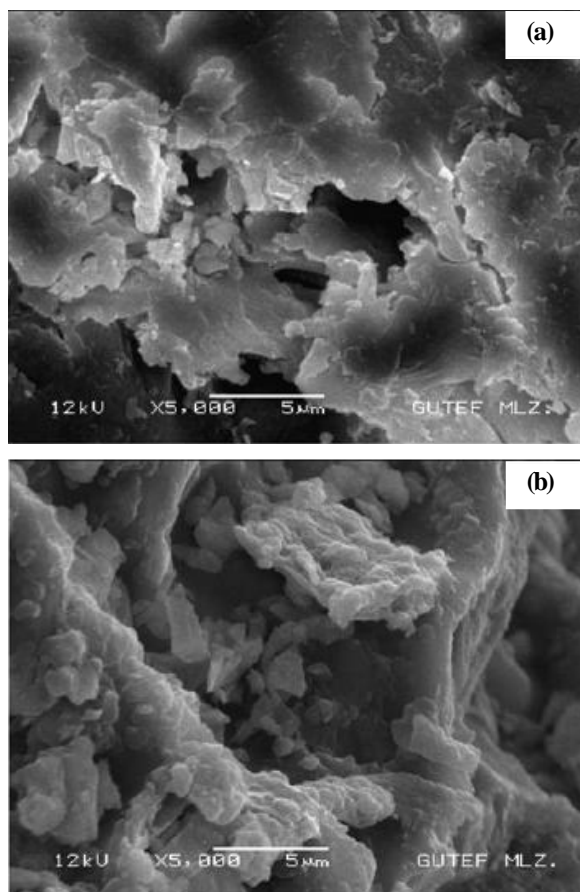


Figure 2 : SEM micrograph of (a) C-CPAC before adsorption; (b) C-CPAC after adsorption

Results presented in TABLES 2 and 3 show that the two types of activated carbon are effective in the removal of dyes from aqueous solutions. Interestingly, there was complete removal (100 %) for some of the dyes with the use of C-CPAC. Activated carbon prepared by chemical activation using ZnCl_2 was more efficient than that prepared by physical activation due to improved pore development in the carbon structure.

TABLE 2 : Removal of acid dyes from aqueous solution using P-CPAC

Dye	Initial pH	Final pH	λ_{max} (nm)	Percentage removal		
				30 mins	90 mins	120 mins
Acid Blue 80	6.4	6.8	627	65.16	84.21	85.10
Acid Blue 32	7.6	8.1	600	66.24	74.67	87.21
Acid Green 25	6.8	7.2	642	64.37	69.43	74.27
Acid Green 27	6.1	6.5	642	71.42	72.56	77.94
Acid Orange 7	6.1	6.6	490	73.17	80.21	89.43
Acid Orange 8	6.3	6.7	490	62.43	71.68	78.43
Acid Orange 10	6.1	6.5	475	58.43	68.43	74.92
Acid Red 1	6.0	6.8	506	67.32	72.16	84.76

TABLE 3 : Removal of acid dyes from aqueous solution using C-CPAC

Dye	Initial pH	Final pH	λ_{max} (nm)	Percentage removal		
				30 min	90 mins	120 mins
Acid Blue 80	6.4	8.14	627	88.21	98.24	100.00
Acid Blue 32	7.6	8.26	600	98.46	100.00	100.00
Acid Green 25	6.8	8.32	642	73.53	83.42	91.26
Acid Green 27	6.1	8.46	642	75.42	79.01	90.42
Acid Orange 7	6.1	8.52	490	82.69	100.00	100.00
Acid Orange 8	6.3	8.16	490	78.42	84.62	96.45
Acid Orange 10	6.1	8.36	475	84.21	88.63	92.18
Acid Red 1	6.0	8.21	506	91.06	98.31	100.00

CONCLUSION

In summary, pyrolysis of cassava peel impregnated with ZnCl_2 produces materials with a well-developed pore structure and high adsorption capacities, making it possible to attain surface area as high as 834.17 $\text{m}^2 \text{g}^{-1}$ (TABLE 1). The impregnation with ZnCl_2 has a strong influence on the pore structure of the activated carbon. The study showed that C-CPAC is more effective in the treatment of acid dyes of the monoazo and anthraquinone class in aqueous solutions than the P-CPAC. As a waste raw material, its application in such treat-

ment process can be commercialized.

ACKNOWLEDGEMENTS

The author gratefully acknowledge the one year Post Doctoral Fellowship jointly awarded by USM-TWAS to him (FR Number: 3240223483 in Year 2009) to complete this article. The Department of P/A Chemistry, Ladoké Akintola University of Technology, P.M.B 4000, Ogbomosho, Oyo State, Nigeria and the 12-month study leave granted him by his host institution to honor this fellowship are equally acknowledged.

REFERENCES

- [1] H.H. Yeo, T. Tetsu, O. Noboru; *Trends Anal. Chem.*, **17**, 234 (1998).
- [2] M. Arami, N. Yousefi-Limaee, N. Mohammad-Mahmoodi, N. Salman-Tabrizi; *J. Colloid Interface Sci.*, **288**, 371 (2005).
- [3] M.P. Elizalde-Gonzalez, J. Mattusch, A.A. Pelaez-Cid, R. Wennrich; *J. Anal. Appl. Pyrol.*, **78**, 185 (2007).
- [4] G. Annadurai, R.S. Juang, D.J. Lee; *J. Hazard. Mater.*, **B 92**, 263 (2002).
- [5] C. Namasivayam, M. Dinesh-Kumar, K. Selvi, R. Ashruffunissa-Begur, T. Vanathi; *Biomass Bioenergy*, **21**, 477 (2001).
- [6] R. Sivaraj, C. Namasivayam, K. Kadirvelu; *Waste Manage.*, **21**, 105 (2001).
- [7] R. Gong, Y. Ding, M. Li, C. Yang, H. Lui, Y. Sun; *Dyes Pigm.*, **64**, 187 (2005).
- [8] O.S. Bello, A.I. Adeogun, C.J. Ajaelu, E.O. Fehintola; *Chem. Ecol.*, **24**, 285 (2008).
- [9] O.S. Bello, M.A. Oladipo, M. AbdulHameed, A.O. Popoola; *Maced. J. Chem. Chem. Eng.*, **29**, 77 (2010).
- [10] A. Ahmadpour, D.D. Do; *Carbon*, **35**, 1723 (1997).
- [11] M.K.B. Gratiuto, T. Panyathanmaporn, R.A. Chinnanklang, N. Sirinuntawittaya, A. Dutta; *Bioresour. Technol.*, **99**, 4887 (2008).
- [12] J.C. Moreno-Piraján, J.L. Giraldo; *Anal. Appl. Pyrol.*, **87**, 288 (2010).
- [13] B. Smith; *Infrared Spectra Interpretation - A Systematic Approach*, CRC Press, Boca Raton, (1999).
- [14] T. Calvete, E.C. Lima, J.C.P. Cardoso, S.L.P. Vagheti, F.A. Dias, J. Pavan; *J. Environ. Manage.*, **91**, 1695 (2010).