



**EVALUATION OF CARBONIZED AND SURFACE-MODIFIED CARBON
PRODUCED FROM NIPA PALM (*NYPA FRUITICANS WURMB*)
LEAVES FOR THE REMOVAL OF 2-(N,N-DIMETHYL-4-
AMINOPHENYL)-AZO-BENZENE CARBOXYLIC ACID
(DMABA) IN AQUEOUS SOLUTION**

**PEREWARE ADOWEI*, AYEBBAEMI IBUTEME SPIFF and
AUGUSTUS ATAGBA ABIA**

Department of Pure & Industrial Chemistry, Faculty of Chemical Sciences, College of Natural & Applied Sciences,
University of Port Harcourt, P. M. B. 5323, PORT HARCOURT, NIGERIA

(Received : 13.05.2014; Revised : 24.05.2014; Accepted : 26.05.2014)

ABSTRACT

Batch adsorption technique was used to ascertain the most favorable conditions for the reduction of chemical oxygen demand (COD) of 2-(N,N-Dimethyl-4-aminophenyl)-azo-benzene carboxylic acid (DMABA) in aqueous solution using physically carbonized carbon (PCC) and neutral reagent surface-modified carbon (NAC) obtained from locally available and environment nuisance *Nypa fruticans* plant. The maximum adsorption capacity in terms of COD reduction of aqueous DMABA was computed by Langmuir adsorption isotherm as 62.57 and 46.11 mg/g for PCC and NAC, respectively. The most favorable agitation conditions at 30°C for the batch adsorption process were 150 rpm and 100 min. The adsorption of DMABA onto PCC and NAC was found to be physisorption, and the overall process assessed by the Gibbs free energy (ΔG°) was to some extent exergonic. The study revealed that *Nypa fruticans* plant is capable of being transformed into high-quality novel carbon for clean-up of synthetic organic chemicals (SOCs) in water and wastewater.

Key words: Nipa palm, Synthetic organic chemicals (SOCs), Activated carbon, Adsorption, Bioremediation, Wastewater.

INTRODUCTION

The biomass of Nipa palm petiole^{1,2} and shoot³ have been investigated for their prospective use as adsorbent for elimination of different metal ions in aqueous solutions. Also ethanol extract of the fruit of *Nypa fruticans* has been studied for its use as a corrosion inhibitor of Zn in acidic solution⁴. These studies indicate that the biomass of the different part of *Nypa fruticans* may possibly be employed for removal of toxic and valuable metals from aqueous systems, and could as well serve as a green corrosion inhibitor. Also the use of agro-wastes in their unprocessed form as adsorbents for metal ions elimination from aqueous solutions have been reported⁵⁻¹⁵.

However, there is very little information on their capability to remove dissolved organic compounds from aqueous solution^{16,17}. This is partly because the known sorption sites in agro-wastes are considered to be ineffective in the removal of organic compounds. In addition, due to low resistance to mechanical abrasion, agro-wastes are suitable only for a “once-and-for-all” application. In order to overcome these

problems, a great deal of attention has been drawn to the treatment of wastewaters through adsorption technology using activated carbons.

Activated carbons can be made from a variety of precursor or starting materials including coal, wood, coconut shells, water hyacinth, water spinach, sawdust, etc. by some form of activation process¹⁸⁻²³. The production of activated carbons from agro-wastes has potential economic and environmental impacts. First, it converts unwanted, low-value agro-waste to useful, high-value adsorbents. Second, activated carbons are increasingly used in water treatment to remove organic chemicals and metals of environmental and/or economic concern.

However, there are no studies at the moment using activated carbon from *Nypa fruticans* leaves as adsorbent for organic contaminant and at the same time using the chemical oxygen demand (COD) as the index of measurement. The aim of this research work is to assess the potential capability of Nipa palm leaves either surface-modified or not as adsorbent for the removal of synthetic organic chemicals (SOCs) from aqueous solutions. This paper reports the batch adsorption study of 2-(N,N-Dimethyl-4-aminophenyl)-azo-benzene carboxylic acid (DMABA) on physically carbonized carbon (PCC) and neutral reagent surface-modified carbon (NAC) of *Nypa fruticans* leaves measured as an index of chemical oxygen demand (COD) reduction.

EXPERIMENTAL

Materials and methods

Sample collection

Fresh fronds of *Nypa fruticans* were obtained during low tide at the Ogbunabali waterfront along Eastern Bypass in Port Harcourt, Nigeria. The Nipa Palm leaves were air drying and then oven dried at 70°C for several days. The stalks were carefully removed and the leaves cut into small sizes, which were further oven dried, grounded and sieved with a 2 mm mesh size sieve to obtain the biomass sample. The dried *Nypa fruticans* leaves biomass sample was carbonized in Plant Science and Biotechnology Laboratory of the University of Port Harcourt, Nigeria.

Carbonization

The dried *Nypa fruticans* leaves biomass was placed in a sealed ceramic oven and was heated gradually to 550°C and kept at this temperature for 2 hours²⁴. The sealed oven provided an oxygen-deficient condition. Under such oxygen-deficient conditions the biomass was thermally decomposed to porous carbonaceous materials and hydrocarbon compounds. This is the carbonization step of the physical activation process. The carbonized sample was sieved through a 106- μm mesh Tyler sieve and fractions < 106- μm was collected for use.

Preparation of neutral reagent surface-modified carbon

25 \pm 0.001 g carbonized material was placed in a beaker containing 50 mL of 30% H₂O₂. The content of the beaker was thoroughly mixed and heated to form a paste. The paste was transferred to a crucible and placed in a furnace and was heated at 500°C for 2 hours. After cooling to room temperature, it was washed with distilled water to neutral pH and dried on the hot plate at 100°C for up to 3hr. The final product of neutral reagent surface-modified (NAC) activated carbon were ground and sieved through a 106- μm mesh Tyler sieve. Fractions < 106- μm were collected and kept in an air-tight container for used.

Organic contaminant used in this work

The organic pollutant used in this work was 2-(N,N-Dimethyl-4-aminophenyl) azo benzene carboxylic

acid (DMABA). DMABA is a dark red crystalline powder with the following properties: Molecular formula $C_{15}H_{15}N_3O_2$, Molar mass 269.3 g mol^{-1} , Density 0.791 g/cc , Melting point $179\text{-}182^\circ\text{C}$. DMABA is a pH indicator commonly known as methyl red; it is red in pH under 4.4, yellow in pH over 6.2, and orange in between, with a pKa of 5.1.

The structure of DMABA is –

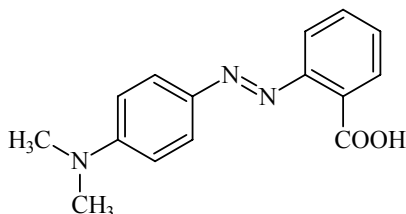


Fig. 1: Chemical structure of 2-(N,N-Dimethyl-4-aminophenyl) azo benzoic acid (DMABA)

Preparation of standard DMABA solutions

1.0 g of water soluble Na-salt of DMABA crystals were weighed on a top loading electronic balance and dissolved in 300 mL distilled water. The mixture was diluted and made up to 1000 mL giving a stock solution with concentration of 1000 mg/L. Working DMABA solutions with concentrations (mg/L) 20, 40, 60, 80, and 100 were prepared from the stock solution. The COD of the working solutions and the distilled water used were determined to give the initial COD (COD_i) and the blank COD.

Batch adsorption studies

2.0 g of each adsorbent were separately placed in a series of plastic sample containers containing 40 mL working solution of DMABA with the following concentrations (mg/L): 20, 40, 60, 80, and 100. The suspensions were shaken at room temperature ($30 \pm 2^\circ\text{C}$) using agitation speed (150 rpm) with a contact time of 100 min. After shaking the flask for 100 min, the mixtures were centrifuged for 5 min to obtain clear solutions. The clear solutions were analyzed for final COD (COD_f).

Determination of chemical oxygen demand (COD)

To determine the COD, 10 mL 0.125 M standard potassium dichromate solution was added to 20 mL of each working DMABA and the clear solutions in a 250 mL round-bottom flask. 1.0 g silver sulphate and 40 mL conc. sulphuric acid were added in small portions with careful swirling until the silver sulphate was completely dissolved. A few glass beads were added to serve as anti-bumping aid, and the flask was connected to reflux condenser. The mixture was heated gently for 10 min, after which the content of the flask was cooled. 50 mL distilled water was flushed through the condenser, and the cooling was completed under running tap water. 2 drops of indicator solution were added and the resulting mixture titrated with standardized 0.025 M ferrous ammonium sulphate (FAS) solution until there was a change in colour from yellow-green via blue-green to reddish brown. 20 mL distilled water as blank and 20 mL clear solution from batch adsorption studies were also taken through the same process and their COD values determined.

Data evaluation: The COD values of the respective solutions and blank were calculated as in Eq. (1).

$$COD \text{ as mg O}_2/\text{L} = \frac{(A - B) \times m \times 8000}{V_s} \quad \dots(1)$$

Where A = mL of ferrous ammonium sulphate (FAS) used for blank; B = mL of FAS used for sample; M = molarity of FAS; V_s = Volume of sample used (mL) and 8000 = milliequivalent weight of oxygen x 1000 mL/L.

RESULTS AND DISCUSSION

The percent reduction of chemical oxygen demand (COD) in the solutions after being contacted with PCC and NAC were estimated by Eq. (2).

$$\% \text{ COD Removed} = \frac{\text{COD}_i - \text{COD}_f}{\text{COD}_i} \times 100 \quad \dots(2)$$

Where COD_i = COD concentration of initial DMABA working solutions before interactions with the carbons (mg/L) and COD_f = COD concentration of DMABA working solutions after interactions with the carbons (mg/L)

The relationship between the initial concentration of 2-(N,N-Dimethyl-4-aminophenyl) azo benzene carboxylic acid (DMABA) and percent reduction of their respective chemical oxygen demand (COD) with physically carbonized carbon (PCC) and neutral reagent surface-modified carbon (NAC) is presented in Fig. 1. The optimal reduction in COD level for PCC and NAC were 78.86 % at an initial concentration of 80 mg/L and 83.47% at 40 mg/L, respectively. The data showed that NAC was able to reduce the COD at a lower concentration, while PCC capacity for reduction of COD was observed at higher initial concentration.

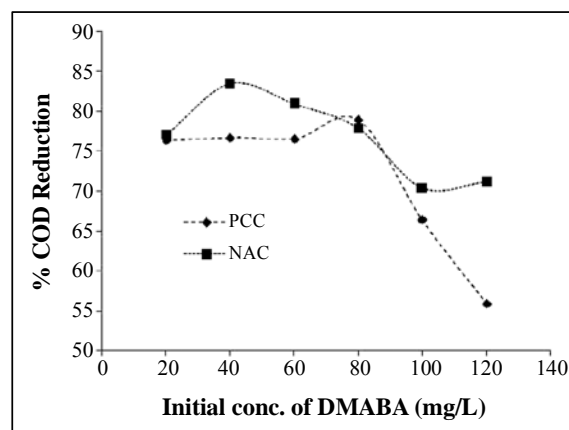


Fig. 1: COD reduction of DMABA by PCC and NAC at 30°C

The apparent capacity of PCC and NAC for COD reduction was further examined at the different concentrations. The relative amount of COD reduction the carbons during the series of batch study was calculated from a mass balance relationship as expressed in Eq. (3).

$$q_e = \frac{(\text{COD}_i - \text{COD}_f)V}{W} \quad \dots(3)$$

Where q_e = adsorption capacity or amount (mg/g) of DMABA removed at equilibrium, COD_i = COD concentration of DMABA solution before interaction with the carbons (mg O_2 /L). COD_f = COD concentration of DMABA solution after interaction with the carbons (mg O_2 /L). V = volume of the DMABA solution (L) and w = weight of the PCC or NAC carbon (g).

The behavior of the two carbons (PCC and NAC) in terms of their capacity for COD reduction was clarified by plotting initial DMABA concentrations against adsorption capacity and is presented in Fig. 2.

The data shows that, as the initial concentration of DMABA increases, the capacity for COD reduction also increases until 100 mg/L for PCC and 120 mg/L for NAC and remained nearly constant after these values. Consequently, initial DMABA concentration of 100 mg/L was used for all other batch sorption experiments. The relative amount of COD reduction with the chosen initial concentration of DMABA, gave optimum capacities of 29.83 mg/g and 20.98 mg/g for PCC and NAC, respectively. These values were taken as the optimum COD reduction capacity for the carbons prepared from *Nipa fruticans* in a batch sorption process. The data showed that PCC and NAC derived from *Nipa fruticans* had the capacity to efficiently reduce COD from aqueous solution, with no significant capacity for COD reduction with surface-modification.

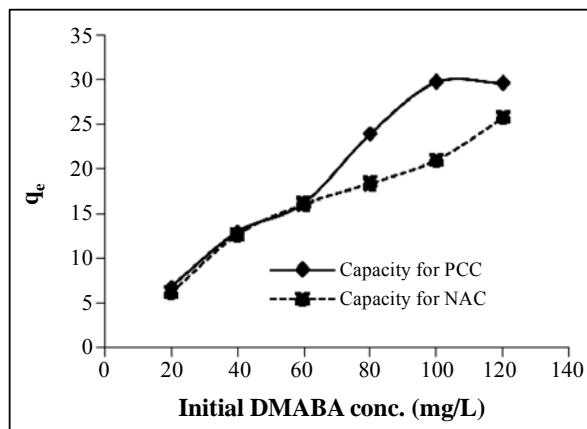


Fig. 2: Adsorption capacity of DMABA in aqueous solution by PCC and NAC at 30°C

Equilibrium sorption models

Equilibrium sorption models are fundamental criteria in the design of sorption systems and they provide in apparent formation on the sorbent-sorbate system. The batch sorption experimental data in this paper were evaluated by the Langmuir and Freundlich equilibrium sorption models.

Langmuir isotherm has a theoretical basis and assumed that a surface consists of a given number of equivalent sites where a species can physically or chemically stick. In order to facilitate the estimation of the adsorption capacity at various initial DMABA concentrations, the Langmuir adsorption isotherm, which is a typical model for monolayer adsorption was applied to the experimental data.

The Langmuir equation (Eq. 4) assumes that there is no interaction between adsorbate molecules and that once an adsorbate molecule occupies a site; no further sorption can take place at that site. Theoretically, therefore a saturation value is reached beyond which no further sorption can take place. Therefore the Langmuir equation was chosen to estimate the maximum adsorption capacity of the carbons corresponding to complete monolayer surface coverage on PCC and NAC.

$$q_e = \frac{K_L C_e q_{\max}}{1 + K_L C_e} \quad \dots(4)$$

Where K_L ($L \text{ mg}^{-1}$) is Langmuir constant representing the energy constant related to the heat of adsorption, and q_{\max} (mg/g) is the maximum COD reduction capacity upon complete saturation of the carbon surface, C_e is the equilibrium concentration representing COD_f reduction and q_e is adsorption capacity.

The linear equation of the Langmuir isotherm was employed in this study for the estimation of maximum adsorption capacity as expressed in Eq. (5).

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \quad \dots(5)$$

The Langmuir linear isotherm parameters of q_{\max} , K_L and the coefficient of determination R^2 , were evaluated from the experimental data by making a plot of specific sorption (C_e/q_e) against equilibrium COD reduction (C_e) as shown in Eq. (5).

Freundlich adsorption isotherm model is an empirical equation and can be used for non-ideal sorption that involves heterogeneous adsorption. The model is used to approximate data for physical adsorption systems especially liquids. The Freundlich isotherm has been adopted to characterize the adsorption intensity of COD reduction by fitting the experimental data. The expression for the Freundlich isotherm model is given in Eq. (6).

$$q_e = K_F (C_e)^{\frac{1}{n}} \quad \dots(6)$$

Where q_e = the adsorption capacity (mg COD removed/mg active carbon); C_e = mg COD/L removed at equilibrium; K_F and n are the Freundlich constants.

The logarithmic linear form of eqn 5 is expressed in Eq. (7).

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \dots(7)$$

The Freundlich constant K_F is the equilibrium partition coefficient related to the bonding energy. It can be defined as the adsorption or distribution coefficient and be related to the degree or extent of adsorption. The value of n indicates the affinity of the organic pollutants towards the carbon and it provides a rough estimate of the adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. In practice, large K_F values enhanced adsorption. If $n = 1$, the partition between the two phases (aqueous and solid) is independent of concentration. In this case $K_F = K$ and the isotherm is linear. A favourable adsorption corresponds to a value of $1 < n < 10$. The values of K_F and $\frac{1}{n}$ were estimated from the intercept and slope of eqn 6 after plotting $\log q_e$ against $\log C_e$.

The linear forms of the Langmuir and Freundlich adsorption isotherms at different initial concentration of 2-(N,N-Dimethyl-4-aminophenyl)-azo-benzene carboxylic acid (DMABA) on physically carbonized carbon (PCC) and neutral reagent surface-modified carbon (NAC) are presented in Figs. 3 and 4.

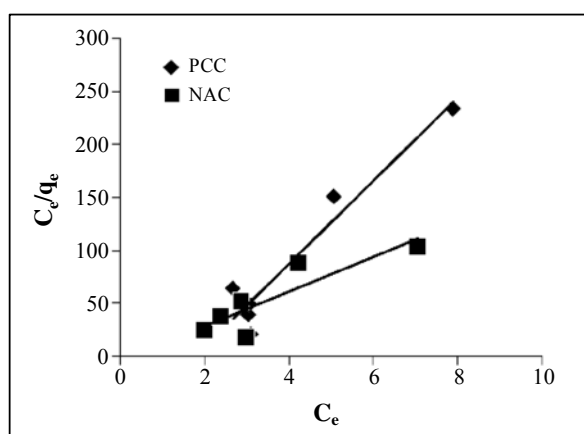


Fig. 3: Langmuir adsorption isotherm plot for COD reduction of DMABA solution by PCC and NAC produced from *Nipa fruticans*

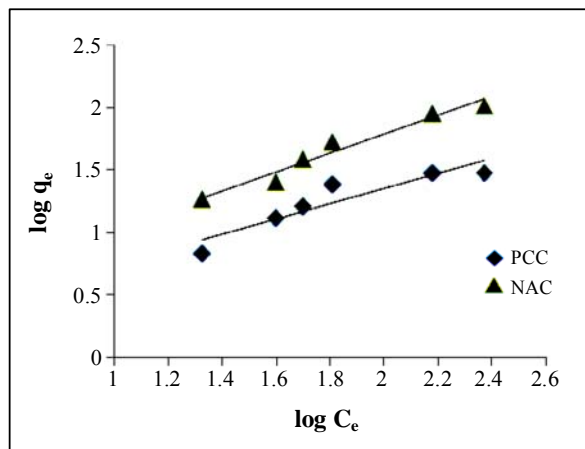


Fig. 4: Freundlich isotherm plot for COD reduction of DMABA solution by PCC and NAC produced from *Nipa fruticans*

The adsorption constants evaluated from the isotherms with correlation coefficients are shown in Table 1. The coefficient of determination (R^2) for PCC is higher than that of NAC for both Langmuir and Freundlich isotherms. The high R^2 value indicates that the equilibrium COD reduction tendency fits well for both the Langmuir and Freundlich isotherms in the concentration ranges studied, which confirms the potential ability of both carbons to significantly reduce COD of organic contaminants in aqueous solution. The Langmuir regression coefficient (R^2) values for PCC and NAC were 0.998 and 0.989, while for Freundlich model; the regression coefficient (R^2) values were 0.992 and 0.924 for PCC and NAC, respectively. Based on the regression values, the experimental data obtained from this study were more suitably described by the Langmuir isotherm model than the Freundlich isotherm.

Table 1: Langmuir adsorption isotherm parameters for PCC and NAC

Carbon s	Langmuir		R^2	Freundlich		
	q_{\max} (mg g ⁻¹)	K_L (L mg ⁻¹)		K_F	n	R^2
PCC	62.60	8.73×10^{-4}	0.998	0.207	2.917	0.992
NAC	57.83	1.996×10^{-3}	0.989	0.921	1.956	0.924

PCC = Physically carbonized carbon and
NAC = Neutral reagent surface-modified carbon

Furthermore, the maximum monolayer adsorption capacity for PCC and NAC are found in Table 1. The data indicate that PCC had higher mass capacity for DMABA (62.60 mg/g) than NAC (57.83 mg/g). The adsorption coefficient, K_L (L/g), which is related to the apparent energy of sorption was greater for NAC (1.996×10^{-3}) than PCC (8.73×10^{-4}). These adsorption coefficients values are relatively very low for both carbons, which is an indication of favourable adsorption process.

The adsorption intensities, n, for PCC (2.917) and NAC (1.956) were less than unity. This shows that the adsorption process as obtained from the Freundlich isotherm model was favourable, because favourable adsorption corresponds to a value of $1 < n < 10$. The adsorption capacity (K_F) for both samples showed that the adsorption potential of the PCC was comparable to that of the NAC in reducing COD of DMABA solutions.

Table 2: Comparison of Langmuir monolayer capacity for the removal of DMABA in aqueous solution with activated carbons from different sources

Sources of carbon	Maximum monolayer (mg/g)		Reference
	Carbonized	Chemically modified	
<i>Nipa fruticans</i>	62.60	57.58	This study
Cassava peel waste	38.60	52.90	25
<i>Cucumis sativa</i>	-	31.65	26
Annona squamosa seed	-	40.49	27
Banana Pseudostem Fibres	-	88.50	28
Sugar waste	125.00	142.85	29
Water hyacinth	23.81	-	30

The removal of DMABA from aqueous solution by a range of carbons produced from different types of precursor materials, which have been studied previously were compared with PCC and NAC (Table 2). Adsorption of methyl red from aqueous solution by activated carbon produced from cassava (*Manihot esculenta* Cranz) peel waste was investigated by Adowei and co-workers²⁵ and obtained a maximum monolayer capacity of 38.60 and 52.90 mg/g for pure and carbonized samples. Their results revealed that *Nypa fruticans* carbon has a higher sorption capacity for the same organic contaminant in aqueous solution than cassava peel waste carbon. Santhi and co-workers^{26,27} investigated the kinetic adsorption of methyl red cationic dyes from aqueous solution using activated carbon made from *Cucumis sativa* and *Annona squamosa* seed separately. They reported a maximum monolayer capacity of 31.65 mg/g for *Cucumis sativa* and 40.486 mg/g for *Annona squamosa*. Comparison of carbons produced from *Nypa fruticans* and that of *Cucumis sativa* and *Annona squamosa* seed, showed that *Nypa fruticans* is an excellent source of carbon production for removal of organic contaminants in aqueous system. The Langmuir monolayer capacity for carbon from banana pseudostem fibers was reported²⁸ as 88.50 mg/g, which is higher than PCC or NAC. In another study, Kour and co-workers²⁹ reported a maximum capacity of charred and aminated sugarcane waste as 125.0 mg/g and 142.85 mg/g, respectively, which are significantly higher than the capacity of PCC and NAC. The adsorption of methyl red by carbonized water hyacinth (*Eichornia crassipes*), which is an aquatic plant, was investigated by Tarawou and co-workers³⁰. They reported a Langmuir surface coverage of 23.81 mg/g.

Even though experimental conditions may be different for each of the comparative reports given, however, since the material being removed from aqueous solution was the same DMABA, the comparison provided an idea of the performance of carbon produced from *Nypa fruticans*. The comparative analysis with carbons produced from *Nypa fruticans* and other biomaterials indicates that the carbons obtained from *Nypa fruticans* are also capable and good adsorbents for remediation of organic contaminants in aqueous systems.

The favourability or unfavourability of the adsorption system of the DMABA onto PCC and NAC was tested using the separation index (S_i) proposed by Poots and co-workers²⁰. The dimensionless separation index, S_i , is expressed by Eq. (8).

$$S_i = \frac{1}{1 + K_L C_o} \quad \dots(8)$$

Where S_i is a dimensionless factor, C_0 is the initial adsorbate concentration and K_L is the Langmuir constant.

The dimensionless parameter, S_i , indicates that, if $S_i > 1$, there is an unfavourable interaction between adsorbate, and therefore adsorption may not be possible; if $S_i = 1$, there is a linear relationship between adsorbate and adsorbent interaction and the possible interaction is a mixture of physisorption and chemisorptions mechanism. When $0 < S_i < 1$, there is a favorable interaction between adsorbate and adsorbent, and the predominant mechanism is physisorption. If $S_i = 0$, there is an indefinite sticking between adsorbate and adsorbent, and the predominant mechanism is chemisorptions.

S_i was predicted using the Langmuir isotherm constant and the initial concentrations of DMABA (Fig. 5). The favourability of adsorption of the DMABA onto PCC and NAC showed that the sorption of DMABA on PCC and NAC increased as the initial DMABA concentration increased, indicating that adsorption is even favourable for higher initial concentrations up to a maximum of 100 mg/L.

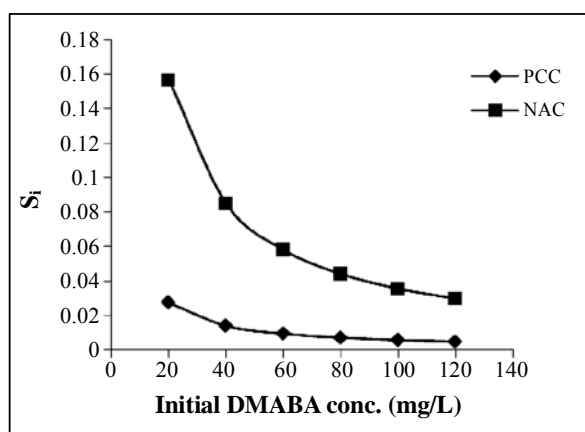


Fig. 5: Separation factor profile as a function of initial DMABA concentration

S_i values for DMABA on the PCC and NAC ranged from 0.0047-0.0288 and 0.030-0.156 respectively, indicating favourable interaction between adsorbate and adsorbent, and the predominant mechanism is physisorption.

Furthermore, the equilibrium constant, K_L , obtained from the Langmuir isotherm was used to compute the apparent Gibbs free energy ΔG° of sorption, is a fundamental criterion of spontaneity. Adsorption process is said to be spontaneously at a given temperature if ΔG° is a negative quantity. ΔG° was evaluated by using the Eq. (9).

$$\Delta G^\circ = -RT \ln K_L \quad \dots(9)$$

Where R = universal gas constant (8.314 J/mol K) and T = absolute temperature (303 K).

Values of ΔG° upto -20 KJ/mol are consistent with electrostatic interactions between sorption sites and adsorbate corresponding to physisorption, while ΔG° vales more negative than -40 KJ/mol involve charge sharing or transfer of electrons between adsorbent and adsorbate to form a coordinate bond. The negative values of ΔG° obtained for PCC (-2.52 KJ/mol) and NAC (-15.66 KJ/mol) at 30°C indicate that adsorption of DMABA by PCC and NAC is a spontaneous process with physisorption as the dominant mechanism.

CONCLUSION

The laboratory-scale batch sorption study of 2-(N,N-dimethyl-4-aminophenyl)-azo-benzene carboxylic acid (DMABA) in aqueous solution using carbonized and surface-modified carbon produced from Nipa palm (*Nypa fruticans Wurmb*) leaves indicate that *Nypa fruticans* plant has considerable potential for the treatment of organic contaminants from wastewaters. The analysis shows that the extent of COD reduction of DMABA is not greatly enhanced by surface modification of the carbon using H₂O₂.

REFERENCES

1. D Wankasi, A. I. Spiff and M. Jnr Horsfall, Adsorption of Pb²⁺ and Cu²⁺ from Aqueous Solution by Chemically Treated and Untreated Biomass of *Nypa Fruticans Wurmb*. Chem. Tech. J., **(1)**, 126-134 (2005).
2. D. Wankasi, A. I. Spiff and M. Jnr Horsfall, Desorption of Pb²⁺ and Cu²⁺ from *Nypa Fruticans Wurmb* Biomass, African J. Biotechnol., **4(9)**, 923-927 (2005).
3. D. Wankasi, A. I. Spiff and M. Jnr Horsfall, Sorption Kinetics of Pb²⁺ and Cu²⁺ from Aqueous Solution by *Nypa Palm (Nypa Fruticans Wurmb)* Shoot Biomass, Electronic J. Biotechnol., **9(5)**, 587-592 (2005).
4. K. Orubite-Okorosaye and N. C. Oforika, Corrosion Inhibition of Zinc on HCl using *Nypa Fruticans Wurmb* Extract and 1,5 Diphenyl Carbazone, J. Appl. Sci. Environ. Mgt., **8(1)**, 57-61 (2004).
5. M. Jnr Horsfall and A. A. Abia, Sorption of Cadmium (II) and Zinc (II) Ions from Aqueous Solution by Cassava Waste Biomass (*Manihot Esculenta Cranz*), Water Res., **37**, 3913-4923 (2003).
6. M. Jnr Horsfall and A. I. Siff, Adsorption of Transition Metals in Aqueous Solutions by Fluted Pumpkin (*Telfairia Occidentalis Hook f*) Waste, Electronic J. Biotechnol., **8(2)**, 163-169 (2005).
7. M. Jnr Horsfall and A. I. Spiff, Effect of Temperature on the Sorption of Pb²⁺ and Cd²⁺ from Aqueous Solutions by *Caladium Bicolor (Wild Cocoyam)* Biomass, Chemistry & Biodiversity, **2**, 1266-1276 (2005).
8. A. A. Abia, M. Jnr Horsfall and O. Didi, The use of Chemically Modified and Unmodified Cassava Waste for the Removal of Cd, Cu and Zn Ions from Aqueous Solution, Bioresource Technology, **90(3)**, 345-348 (2003).
9. J. L. Gardea-Torresdey, J. H. Gonzalez, K. J. Tiemann, O. Rodriguez and O. Gamez, Phytofiltration of Hazardous Cadmium, Chromium, Lead and Zinc Ions by Biomass of *Medicago Sativa (Alfaalfa)*, J. Hazad. Mater., **57(1-3)**, 29-39 (1998).
10. Y. S. Ho, D. A. John-Wase, C. F. Forster, Batch Nickel Removal from Aqueous Solution by Sphagnum Moss Peat, Water Research, **29(5)**, 1327-1332 (1995).
11. K. S. Low, C. K. Lee and A. C. Leo, Removal of Metals from Electroplating Waste using Banana Pith, Bioresource Technology, **51(2-3)**, 227-231 (1995).
12. G. U. Manu, C. Raji and T. S. Anirudhan, Evaluation of Coconut Husk for the Removal of Arsenic from Water, Water Research, **22(10)**, 30662-30670 (1998).
13. S. Y. Quek, D. A. J. Wase and C. F. Forster, The use of sago waste for the sorption of lead and copper. Water SA 24 (30) 251-256 (1998)
14. J. M. Randall, F. C. Reuter and A. C. Waiss, Removal of Cupric Ions from Solution by Contact with Peanut Skins, J. Appl. Poly. Sci., **19**, 156-171 (1974).

15. C. O. Okieimen and F. E. Okieimen, Enhanced Heavy Metal Sorption by Groundnut (*Arachis Hypogea*) Husks Modified with Thioglycolic Acid, *Bull. Pure Appl. Sci.*, **20C**, 13-21 (2001).
16. T. J Tarawou and M. Jnr. Horsfall, Adsorption of Methylene Blue Dye on Pure and Carbonized Waterweeds, *Bioremediation J.*, **11**, 1-8 (2007).
17. L Lei, P. A. Quinlivan and D. R. U. Knappe, Effect of Activated Carbon Surface Chemistry and Pore Structure on the Adsorption of Organic Contaminants from Aqueous Solution, Elsevier Science Ltd. *Carbon*, **40**, 2085-2100 (2002).
18. C. Namasivayam and K. Kadirvelu, Uptake of Mercury (II) from Wastewater by Activated Carbon from an Unwanted Agricultural Solid by-Product, Elsevier Science Carbon Ltd., **37**, 79-84 (1999).
19. M. M. Johns, W. E. Marshall and C. A. Toles, The Effect of Activation Method on the Properties of Pecan Shell Activated Carbon, *J. Chem. Technol. Biotechnol.*, **74**, 1037-1044 (1998).
20. V. J. P. Poots, G. McKay and J. J. Healy, Removal of Basic Dye from Effluent using Wood as an Adsorbent, *J. Water Poll. Control Fed.*, **50**, 926-/35 (1978).
21. P. K. Malik, Dye Removal from Wastewater using Activated Carbon Developed from Sawdust, Adsorption Equilibrium and Kinetics, *J. Hazard. Mater.*, B113, 81-88 (2004).
22. Y. S. Ho, W. D. A John and C. F. Forster, Batch Nickel Removal from Aqueous Solution by Sphagnum Moss Peat, *Water Research*, **29**, 1327-1332 (1995).
23. T. F. Tarawou, D. Wankasi and M. Jnr Horsfall, Column Removal of Methylene Blue using Activated Carbon Derived from Water Spinach (*Ipomoea Aquatic*), *Int. J. Biol. Chem. Sci.*, **4**, 535-545 (2010).
24. P. Marzal, A. Seco and C. Gabaldon, Cadmium and Zinc Adsorption onto Activated Carbons, Influence of Temperature, pH and Metal/Carbon Ratio, *J. Chem. Technol. Biotechnol.*, **66**, 279-285 (1996).
25. P. Adowei, M. Jnr Horsfall and A. I. Spiff, Adsorption of Methyl Red from Aqueous Solution by Activated Carbon Produced from Cassava (*Manihot Esculenta* Cranz) Peel Waste, *Innovations in Sci. Engg.*, **2(2)**, 24-33 (2012).
26. T. Santhi, S. Manonmani and T. Smitha, Removal of Methyl Red from Aqueous Solution by Activated Carbon Prepared from the *Annona Squamosa* Seed by Adsorption, *Chem. Engg. Res. Bull.*, **14**, 11-18 (2010).
27. T. Santhi, S. Manonmani, T. Smitha and K. Mahalakshmi, Adsorption Kinetics of Cationic Dyes from Aqueous Solution by Bioadsorption onto Activated Carbon Prepared from *Cucumis Sativa*, *J. Appl. Sci. Environ. Sanitation*, **4(3)**, 263-271 (2009).
28. M. H. Rosemal, M Haris and K. Sathasivam, The Removal of Methyl Red from Aqueous Solutions using Pseudostem Banana Trunk Fibers, *American J. Appl. Sci.*, **2(5)**, 209-216 (2009).
29. J. Kour, S. Pandey, P. L. Homagai, M. R. Pokhrel and K. N. Ghimire, Adsorptive Removal of Methyl Red from Aqueous Solution onto Charred and Aminated Sugarcane Waste *J. Membrane & Separation Technol.*, **2(1)**, 63-73 (2013).
30. T. F. Tarawou, M. Jr. Horsfall and José L. Vicente, The Adsorption of Methyl Red by Carbonized Water Hyacinth (*Eichornia Crassipes*), *Chemistry & Biodiversity*, **4(9)**, 2236-2245 (2007).