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Application of Activated Carbon Prepared from Nypa Palm Seed Husk in the Adsorption of Azo Dyes from Waste Water and Evaluation of the Adsorption Isotherms

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

Nypa palm seed husk is an underutilized raw material found in Niger Delta region of Nigeria. In this research, this material was utilized as a raw material for the production of activated carbon which was used as an absorbent for the treatment of simulated wastewater containing Congo red (CR) and Methyl red (MR) (azo dyes). The effect of adsorbate concentration, absorbent dosage, adsorbent-adsorbate contact time on the adsorption of these dyes were evaluated. The results revealed that the adsorption efficiency of MR increase from 20.45 – 91.27 % and that of the CR

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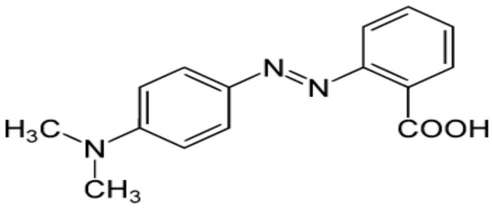
increase from 68.50 – 99.83 % when the amount of adsorbent was increased from 0.1 – 0.5 g. When adsorbent-adsorbate contact time was increased from 30 – 150 min, the adsorption efficiency increases from 20.93 – 98.94 % for MR and 58.33 – 94.83 % for CR. Also increase in the adsorbate concentration from 50 – 250 mg/L resulted in the decrease in the adsorption efficiency, from 93.16 – 76.10 % for MR and 87.68 – 73.01 mg/L for CR. Adsorption mechanism of these dyes were determined using Langmuir and Freundlich isotherms. From the values of the linear regression coefficient R^2, it was found that the adsorption of methyl red followed Freundlich isotherm while the adsorption of Congo red followed Langmuir isotherm. Hence, Nypa palm seed husk which is presently discarded as a waste material can be utilized in the preparation of activated carbon and apply in the adsorption of azo dyes from industrial effluents.

Keywords: Activated carbon; adsorption; azo dyes; adsorption isotherms; nypa palm seed husk.

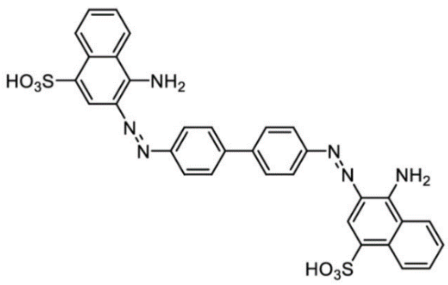
1. INTRODUCTION

"Water is essential for the very existence of life. Rapid industrialization is the major cause of wastewater generation. Untreated disposal of this wastewater into the environment has increased the pollution beyond the admissible sanitary standards. Used dyes are present in the effluents discharged from various industries like electroplating, battery, paint, plastic, paper manufacturing industries, and petrochemical process" [1]. "Dyes contamination may cause negative ecological effect since it is toxic even at very low concentrations" [1]. Dyes poisoning in human body can cause severe damage to kidney, nervous system, reproductive system, liver, and brain and may result in sickness or death. Azo dyes are widely used in the food, pharmaceutical, cosmetic, textile, and leather industries. They are synthetic dyes characterized by one (monoazo) or several intramolecular -N=N- bonds [2]. Azo dyes, if they are systemically absorbed, can be metabolized *through* azo reductases of intestinal microflora by liver cells and skin surface bacteria. This metabolism leads to aromatic amines that can be hazardous. The structure of Methyl red and Congo red dyes are given below.



Scheme 1: Methyl red

"The removal techniques of dyes from wastewater depend on the characteristic of the effluent. Different methods are used for dye removal such as solvent extraction, reverse osmosis, filtration, ion exchange etc. However, these techniques have certain disadvantages such as incomplete removal, high energy requirement and operational cost, use of toxic chemicals, and generation of toxic sludge or other waste products that again require special disposal techniques. These make most wastewater treatment processes impractical since they add to environmental damage" [3-4].



Scheme 2: Congo red

"Adsorption is a term commonly used for several different processes involving physical as well as chemical interactions between the solid surface of a material. When a solid surface is exposed to a gas or a liquid, molecules from the gas or the solution phase accumulate or concentrate on the surface of the material. The Adsorption process of wastewater treatment is a simple, cost effective and sustainable technique used for the treatment of both domestic and industrial effluents" [5-6].

Nypa palm which was introduced into the Niger Delta region of Nigeria to control erosion. Today the plant has been grown and spread over the region blocking the river estuaries and is presently a nuisance to environment and it has not been utilized for any industrial purposes [7]. Research on the pulping of this plant material have been reported [8-10]. The utilization of other parts of Nypa palm in the production of activated carbon have also been reported [11-13]. However, production of activated carbon from Nypa palm seed husk and application in the treatment of dye effluents have not reported.

Hence, this research aims at preparing the activated carbon from Nypa palm seed husk, which is presently discarded as waste material in Niger Delta region of Nigeria, and apply it in the adsorption of mono azo dye (methyl red) and diazo (Congo red) dyes and also evaluate the adsorption isotherm of the adsorption process.

2. MATERIALS AND METHODS

2.1 Sample Collection and Preparation

Nypa palm fruit bunches were harvested from a mature Nypa palm plant in Oron riverine estuary, Akwa Ibom State, Nigeria. The bunches were kept for one week for the seed to be removed. The seed husk was removed from the seed using sharp knife. It was washed with tap water and dried in the oven at 105^{o}C.

2.2 Preparation of Activated Carbon

About 100g of the sample was soaked in 1000 ml of 1 M Zinc chloride ($ZnCl_2$) at the ratio of 1:10 (w/v). The samples were heated with a heating mantle for 2 hours until it all turn to a black paste. The samples were carbonized in the muffle furnace at 500^{o}C for 2 hours. The charred products were allowed to cool to room temperature. The charred material (activated carbon) was crushed and sieved using standard sieve of 0.1mm. The activated carbon obtained was put in the air tight container pending adsorption process.

2.3 Adsorption Study

Effect of adsorbent dosage was studied by contacting 0.1 - 0.5g of the activated carbon with 50 ml of 150 mg/L of each dye solution. The mixture was agitated in a mechanical shaker for one hour. Effect of contact time was determined by contacting 0.15g of the activated carbon to 50 ml of 150 mg/L of each dye solution. It was corked and shaken for 30, 60, 90, 120 and 150 mins in a mechanical shaker. While effect of concentration was determined by contacting 0.15g of the activated carbon with 50 ml of 50, 100, 150, 200, 250 mg/L of each dye solution. The mixtures were agitating in a mechanical shaker for one hour.

After each adsorption study, each mixture was filtered and the absorbance of the resultant solutions were taken at the wavelength (λ_{max}) of 430 nm for methyl red and 495 nm for Congo red using UV/Visible spectrometer. Post adsorption concentration of each dye solution was determined from each dye using Beer Lambert Law, which is given as

$$A = \varepsilon bc$$

where A is the absorbance, ε is the molar absorptivity, b is the pathlength and c is the concentration.

The above equation was further modified to arrive at:

$$\frac{A_1}{A_2} = \frac{C_1}{C_2}$$

Where A_1 is the pre-adsorption absorbance and A_2 is the post- adsorption absorbance of dye solution, C_1 is the pre-adsorption concentration and C_2 is the post adsorption concentration of the dye solution.

Therefore, we arrived at $C_2 = \frac{C_1 X\, A_2}{A_1}$

Adsorption efficiency of the activated carbon in each adsorption process was determined using Adsorption efficiency (%) = $\frac{C_0 - C_1}{C_0}$ x 100%

Where C_o = Pre-adsorption concentration of the solution

C_1 = post-adsorption concentration of the solution.

2.3.1 Determination of absorption isotherm

Equilibrium adsorption isotherms are models used to determine the relationship between adsorbate concentration in solution and the amount of the adsorbent at equilibrium. Isotherm models provide fundamental information on the sorption mechanism and heterogeneity of the adsorbent. The isotherms model determined in this work are the Langmuir and Freundlich isotherms. This is because these two isotherm models have the ability to describe the adsorption mechanisms and experimental data with wide range of concentrations [14].

Langmuir Isotherm

This isotherm model describes monolayer adsorption of the adsorbate onto the surface of an adsorbent with the finite number of identical adsorption sites. Its assumption is that the adsorption occurs at specific homogenous sites within the adsorbent surface and the adsorbent site does not interact with Each other. The model is expressed below:

$$\frac{Ce}{qe} = \frac{1}{q_m K_L} + \frac{Ce}{q_m}$$

Where;

q_e= the quantity of adsorbate ions in (mg/g) at equilibrium.

Ce= equilibrium adsorbate concentration (mg/L),

K_L = adsorption binding energy system (L/mg),

q_m= maximum sorption capacity of the adsorbate ions from the solution (mg/g).

Freundlich Isotherm

Freundlich isotherm is an isotherm model used to describe the heterogeneity of the adsorbent surface which is an indication that the binding sites of the adsorbent are not equivalent or dependent [14].

The linear form of Freundlich isotherm below

$$\log q_e = \log K_f + 1/n \log c_e$$

Where q_e= the quantity of the adsorbate adsorbed at equilibrium (mg/g),

C_e = equilibrium concentration of the adsorbate (mg/L),
K_f = overall adsorption capacity (mg/g).

1/n = sorption intensity which is a dimensionless quantity;

3. RESULTS AND DISCUSSION

3.1 Results

The results for the adsorption of azo dyes using activated carbon prepared from Nypa Palm seed husk are presented in Table 1-3.

3.2 Adsorption Studies

The results for the comparative adsorption of two azo dyes (Methyl red and Congo red) using Nypa palm seed husk activated carbon are presented in Table 1-3. As presented in Table 1, it was observed that there is an increase in percentage adsorption with increase in the mass of the adsorbent. This is because the higher the mass of the adsorbent the greater the surface area of the adsorbent available for the adsorbate, hence the greater the adsorption efficiency. Similar results have also been reported on the adsorption of dyes using activated carbon prepared from different raw materials [15-17].

The effect of contact time on adsorption process are presented in Table 2. The results revealed that the longer the adsorbent – adsorbate contact time, the higher the adsorption efficiency. This is because at a longer adsorption time, more time has been given for the adsorbate to adsorbed onto the surface of the adsorbent. Though at a very long contact time the adsorption efficiency may decrease due the saturation of the adsorbent surface by the adsorbate and desorption may also occur especially if the adsorption mechanism is physisorption [18].

The effect of adsorbate concentration on adsorption of Methyl red and Congo red by activated carbon is presented in Table 3. The results revealed that the increase in the concentration of dyes results in the decrease in the adsorption efficiency. This is because at lower concentration lesser amount of the adsorbate molecules are present in the solution, hence greater amount of the adsorbate is being adsorbed onto the surface of the adsorbent. At higher adsorbate concentration, the adsorbent surface becomes easily saturated by the adsorbate and this results in the decrease in the adsorption efficiency [18 -19].

However, the Nypa palm seed husk activated carbon was able to adsorb methyl red and Congo red dye contaminant in the simulated industrial wastewater to various extents. At variation in adsorbent dosage, activated carbon was able to remove Congo red dye more than methyl red dye. This may be due to the availability of greater mass and surface area of the adsorbent, also Congo red with greater mass and two azo groups may easily bond to the active site of the adsorbent using the lone pair electrons on the two nitrogen atoms, hence increase in adsorbent mass greatly favours the adsorption of Congo red dye. The adsorbent was also able to remove Methyl red than Congo red dye when adsorbate-adsorbent contact time and adsorbate concentration was varied. This may be due to the lower molecular weight of methyl red compared to Congo red. As the greater amount of the dye molecules can be adsorbed onto the adsorbent surface without masking the active site of the adsorbent and without desorption.

Table 1. Effect of Adsorbent dosages on the adsorption of methyl red and Congo red

	Methyl red		Congo red	
Adsorbent Dosage (g)	Post Adsorption Concentration (mg/L)	Adsorption Efficiency (%)	Post Adsorption Concentration (mg/L)	Adsorption Efficiency (%)
0.1	119.32	20.45	47.25	68.50
0.2	51.98	65.35	12.25	91.83
0.3	19.84	86.77	9.00	94.00
0.4	15.48	89.68	6.75	95.5
0.5	13.09	91.27	0.25	99.83

Table 2. Effect of contact time on the adsorption of Methyl red and Congo red

	Methyl red		Congo red	
Time (mins)	Post Adsorption Concentration (mg/L)	Adsorption Efficiency (%)	Post Adsorption Concentration (mg/L)	Adsorption Efficiency (%)
30	118.65	20.93	62.5	58.33
60	47.22	68.52	45.0	70.00
90	21.83	85.45	29.75	80.17
120	9.92	93.38	12.75	91.50
150	1.58	98.94	7.75	94.83

Table 3. Effect of concentration on the adsorption of Methyl red and Congo red

	Methyl red		Congo red	
Pre-Adsorption Concentration (mg/L)	Post Adsorption Concentration (mg/L)	Adsorption Efficiency (%)	Post Adsorption Concentration (mg/L)	Adsorption Efficiency (%)
50	3.419	93.16	6.157	87.68
100	10.67	89.33	14.63	85.17
150	17.54	88.30	25.25	83.17
200	38.00	81.00	40.71	79.65
250	59.78	76.10	67.48	73.01

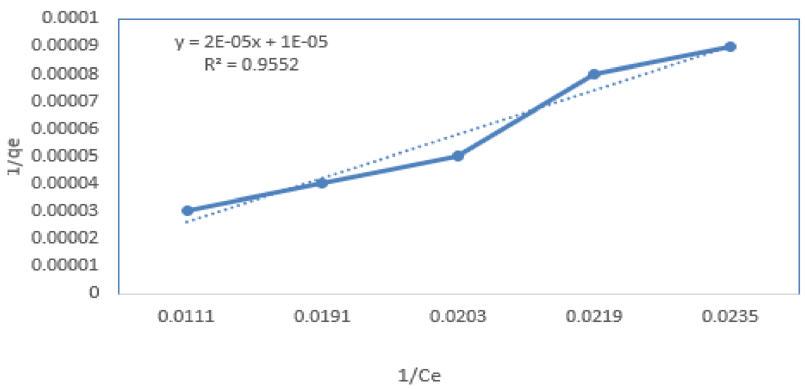


Fig. 1. Langmuir isotherm plot for the adsorption of Methyl red

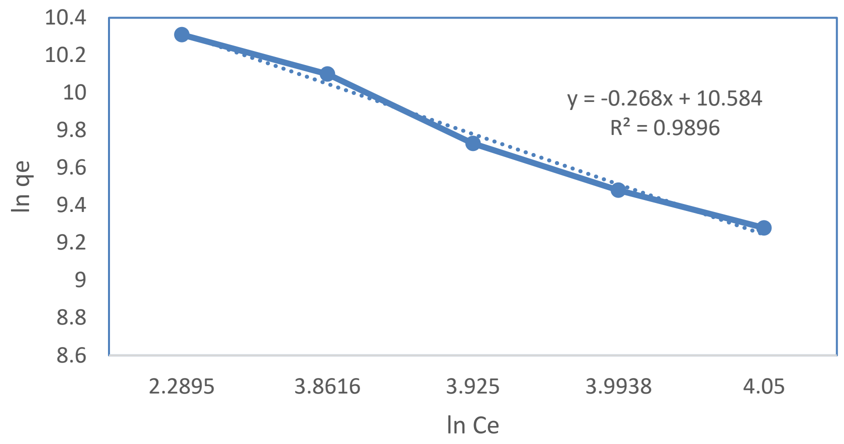


Fig. 2. Freundlich Isotherm plot for the adsorption of methyl red

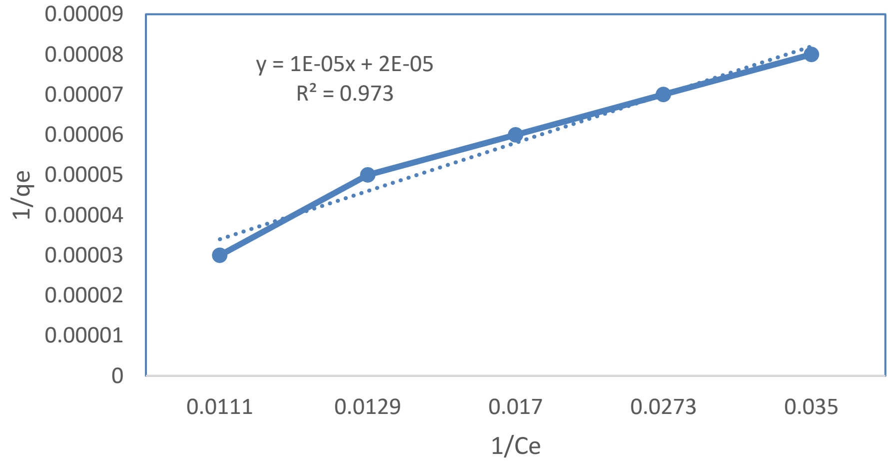


Fig. 3. Langmuir isotherm plot for the adsorption of congo red

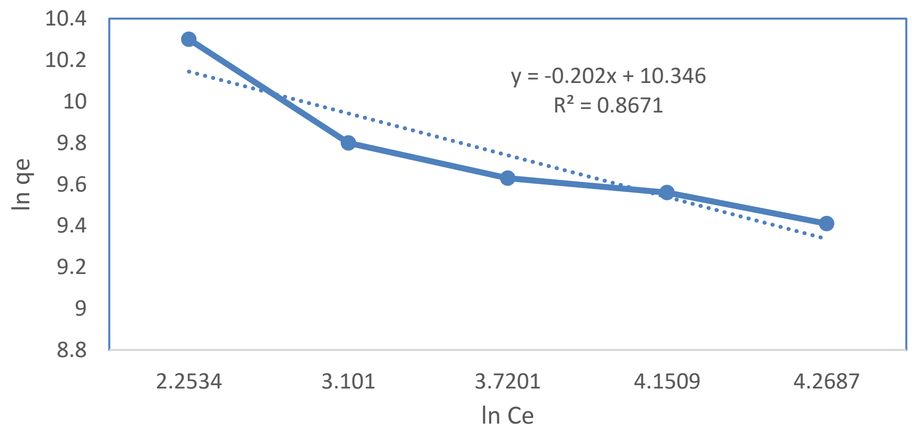


Fig. 4. Freundlich Isotherm plot for the adsorption of congo red

3.3 Isotherm Studies

Langmuir and Freundlich isotherm models were used to investigate the adsorption of Congo red and Methyl red from simulated wastewater. Figure 1 – 4, shows the plots of the Langmuir and Freundlich isotherm models for the adsorption of Congo red and Methyl red onto the adsorbent.

The linear regression R^2 values for adsorption of Congo red were 0.973 and 0.867 for Langmuir and Freundlich isotherms respectively and that of methyl red were 0.955 and 0.989 for Langmuir and Freundlich isotherm respectively. Hence, the adsorption of Congo red followed Langmuir isotherm model (R^2 = 0.973), indicating that there was a monolayer adsorption of the dye onto the surface of an adsorbent with a finite number of identical adsorption sites [15], [20]. Similar result has been reported [21-22]. Freundlich isotherms fit well for the adsorption of methyl red since its R^2 value is close to unity (0.989). This indicated that the absorbent surface was heterogeneous and the binding sites were not equivalent [15].

4. CONCLUSION

The use of Nypa palm fruit husk as a raw material for the preparation of activated carbon has been evaluated. The results revealed that the activated carbon prepared from this material can be used as an environmentally friendly, cost-effective and sustainable adsorbent for the removal of methyl red and Congo red dye contaminants from wastewater. The prepared activated carbon was used for the removal of these azo dyes at various adsorption conditions and it was found that adsorption was more effective at a lower adsorbate concentration, higher activated carbon dosage and longer contact time. Also, it was found that the activated carbon was able to remove greater percentage of methyl red than Congo red dye at variable adsorption time and dye concentration. The isotherm results revealed that the adsorption of Congo red followed Langmuir isotherm and that methyl red followed Freundlich isotherm model. Hence, the Nypa palm seed husk which is presently discarded as waste material can be converted to activated carbon and use as cost effective adsorbent for the adsorption of azo dyes from industrial effluents.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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