

The Removal Of Some Organic Colourants In Aqueous Solutions Using Biomass And Activated Carbon Of Nipa Palm Fruit Fibre

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Abstract: The removal of Bromophenol blue (BP), Congo red (CR) and Methyl Orange (MO) by biomass and carbonized carbon of nipa palm fruit fibre was investigated in the present study. Adsorption studies were carried out by batch experiments. The effect of initial colourant concentration and adsorbent dosage was explored. The equilibrium adsorption data were analyzed using Langmuir and Freundlich isotherm. The maximum percentage of colorant reduction using nipa palm fruit fibre biomass (NFB) was obtained at an optimum dose of 4.0 g removing 83.35% of BP from aqueous solution and at 5.0 g for MO and CR removing 49.50% and 44.69% respectively whereas adsorbent dosage using nipa palm fruit carbon (NFC) was quite poor in terms of percent removal of colourants. Using the correlation coefficient values, the data for nipa fruit biomass was fitted well to Freundlich model for CR and MO while the Langmuir model was best fit for BP, the data for fruit fibre carbon fitted well for CR, BP and MO confirming the monolayer coverage of the colourant on. The capability of these adsorbents to eliminate colourants from contaminated solutions makes them acceptable for colourant treatment from industrial effluent.

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Keywords: Removal; Organic Colourant; Aqueous Solution; Biomass; Activated Carbon; Nipa Palm Fruit Fibre

Introduction

A good number of industries rely solely on the use of colourant in the manufacture of their produce, and these colourant are washed off into the waterways (Wankasi *et al.*, 2006; Kunz *et al.*, 2013). Man-made colourants are highly soluble and hence, there are frequent water pollutants and they may recurrently be found in industrial effluents (Haque *et al.*, 2011; Coruh *et al.*, 2015). Effluent containing colourants are a bit difficult to handle, as the colourants are recalcitrant organic molecules, known to be stable at elevated temperature, unchanging on exposure towards light and oxidising agents and also unresponsive towards aerobic digestion due to their molecular size and its structure (Bafuna *et al.*, 2011; Namasivayam *et al.*, 1993). The introduction of wastewaters containing organic substances into waterways depletes the dissolved oxygen (DO) present in water; the depletion in dissolved oxygen (DO) levels disrupts the well-being of aquatic microorganisms and also raises much concerns because of potential environmental problems which may lead to the reduction in population of helpful microorganisms (Umpuch *et al.*, 2013; Engwuonu, 2013). Note that this gradual depletion in dissolved oxygen (DO) rapidly increases the biological oxygen demand (BOD) and chemical oxygen demand (COD) which directly denotes the limited quantity of oxygen

needed to completely oxidise matters that are organic and present in water biologically and chemically respectively (Zulfikar *et al.*, 2013; Umpuch *et al.*, 2006). Many common and sophisticated methods for removal of colourant from wastewater have been developed but are sometimes too expensive to use, not readily available and too complex to use. Adsorption process has been proven to be the best, simple and economical choice for removal of colourant from industrial wastewaters and so researchers tends to place their focus on preparation of the cheapest, easily available adsorbent with maximum adsorption capacity (Negrulescu *et al.*, 2014; El-dars *et al.*, 2015). This paper reported the removal of organic colourants in aqueous solutions using biomass and activated carbon of Nipa Palm fruit fibre.

Experimental

Materials and methods

Sample collection

In this experiment, nipa palm fruit fibre of 10 to 15 years of age was collected from the brackish waterfronts along eastern bypass in Rivers State and transported to the laboratory.

Biomass preparation

The nipa palm fruit fibre was washed with water to remove dirt and other soluble impurities and dried under the sun for an extended period until completely

dried before separating the fibrous husk and shell, the fruit fibre was then oven dried at a temperature of 80 °C for several days to remove moisture. The nipa palm fruit fibre was further ground with a crusher and sieved with 150µm mesh size sieve to obtain biomass samples and transferred to well labelled container.

Carbonization of biomass sample

A portion of nipa palm fruit fibre biomass was placed in a well sealed ceramic oven for 2 hours at a regulated temperature to 550 °C maximum. The carbonaceous matter was allowed to cool before being sieved through 150µm mesh size and placed in a label plastic container.

Preparation of standard colourant solution

Water soluble colourant crystal (1.0 g) was 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. 20, 40, 60, 80 and 100 (mg/l) colourant solution concentrations were prepared from stock solution.

Preparation of Standard Potassium Dichromate Reagent

Standard potassium dichromate reagent was prepared by dissolving 2.4565g of $K_2Cr_2O_7$ into approximately 250 ml of distilled water in a 500 ml volumetric flask, followed by addition of concentrated sulphuric acid (83.5 ml) and mercuric sulphate (16.65 g). The mixture was allowed to dissolve completely before making up to 500 ml with distilled water.

Preparation of sulphuric acid reagent

Sulphuric acid reagent was prepared by pouring approximately 250 ml of sulphuric acid into 500 ml volumetric flask followed by addition of 2.75 g of silver sulphate (Ag_2SO_4) to dissolve in it. The mixture was stirred to dissolve completely before making up to 500 ml with sulphuric acid.

Batch experiments

Effect of concentration

Batch adsorption experiments was conducted by shaking continuously series of 100 ml Erlenmeyer flask with cork stopper containing 2 g of adsorbent (biomass and carbonized carbon of nipa palm fruit fibre) and 50 ml of stock solution with following concentrations (mg/l) 20, 40, 60, 80 and 100. The shaking proceeded for 30 minutes at agitation speed of 150 rpm at room temperature and was allow to stand for another 30 minutes after shaking to obtain a clear solution before filtering. The filtrate after adsorption was measured for final COD_f at the predetermined wavelength 420 nm using a multi parameter bench photometer.

Effect of adsorbent dose

Adsorption experiments was conducted by shaking continuously a series of 100 ml Erlenmeyer flask with cork stopper containing 1, 2, 3, 4 and 5 g of adsorbent (biomass and carbonized carbon of nipa

palm fruit fibre) and 50 ml of stock solution concentration. The shaking proceeded for 30 minutes at agitation speed of 150 rpm at room temperature and was allow to stand for another 30 minutes after shaking to obtain a clear solution before filtering. The filtrate after adsorption was measured for final COD_f at the predetermined wavelength 420 nm using a multi parameter bench photometer. (Adowei et al., 2014).

Measurement of Chemical Oxygen Demand (COD)

To measure the COD, sample (2.5 ml) was transferred to a 15 ml COD digestion tube using volumetric pipette and deionised water (25 ml) was transferred to a COD digestion tube to serve as blank. Standard dichromate reagent (2.5 ml) and Sulphuric acid reagent (2.5 ml) were slowly added to the COD digestion tubes at a tilting position, cover with its cap and shaken all together. The mixture was carefully inserted into a COD digester that has been pre-heated to a temperature of 150°C, for 2 hours.

The mixture in a COD digestion tube was allow to cool to room temperature before being placed into the cuvette holder of the multi-parameter bench photometer for COD values readings.

The quantity of colorant eliminated from aqueous solution at equilibrium by the sample (s) was calculated by the mass balance relationship.

$$q_e = \frac{(C_o - C_e)V}{w}$$

Where q_e = quantity of colorant eliminated from aqueous by sample (mg/g), C_o = initial concentration of colorant contaminated solution before contact with sample, C_e = equilibrium concentration of colorant contaminated solution after contact with sample, V = volume of colorant contaminated solution used (L), w = weight of the sample used (g). (Chu and Hashim, 2001).

The experimental data were analysed by the two commonly used adsorption isotherm models of Langmuir and Freundlich.

The Langmuir equation is expressed as;

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e}$$

Where k_L ($dm^3 g^{-1}$) is a constant that describes the energy of adsorption/desorption, q_e describes the complete adsorption on the surface of the adsorbent.

Linearization of the above equation gives

$$\frac{C_e}{q_e} = \frac{1}{q_m k_L} + \frac{C_e}{q_m}$$

The plotting of C_e/q_e against C_e gives a straight line curve with slope $\frac{1}{q_m}$ and intercept $\frac{1}{q_m k_L}$.

(Ahalya et al., 2005; Osu and Odoemelum, 2012).

The Freundlich isotherm indicates adsorption intensity of the adsorbate on the adsorbent and has purely empirical formula.

$$q_e = \frac{x}{m} = k_f C_e^{1/n}$$

Where q_e is the adsorption density (mg/g), x is the adsorbed quantity (mg), m is the mass of adsorbent (g), C_e is the concentration of the adsorbate in solution at equilibrium (mg/dm³), K_F and n are the Freundlich constants. The value of n shows the affinity of the adsorbate towards the adsorbent.

The linearised form of the Freundlich equation is:

$$\log q_e = \log K_F + 1/n \log C_e$$

Assuming the plot of $\log q_e$ against $\log C_e$ yields a straight line, then the sorption process obeys a Freundlich adsorption isotherm. The K_F value can be gotten from the intercept and $\frac{1}{n}$ value obtained from slope of the straight line (Parvathi et al., 2007; Horsfall and Abia, 2003; Osu and Odoemelam, 2012).

Results And Discussion

Effect of Biomass and Carbon Dosage on removal of colourant from aqueous solution.

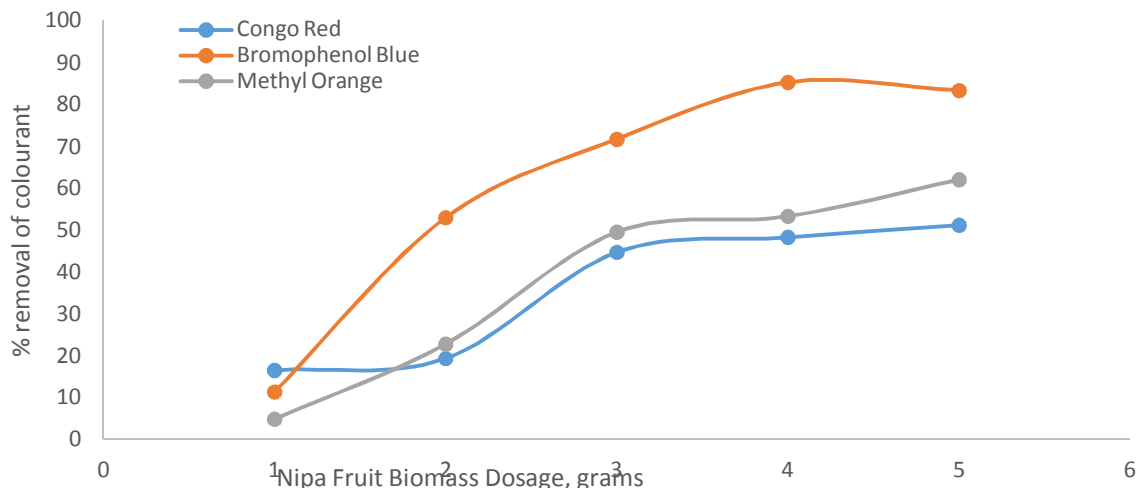


Figure 1: Effect of Nipa Fruit Biomass Dosage on the Percentage removal of colourant from Aqueous Solution at ambient temperature.

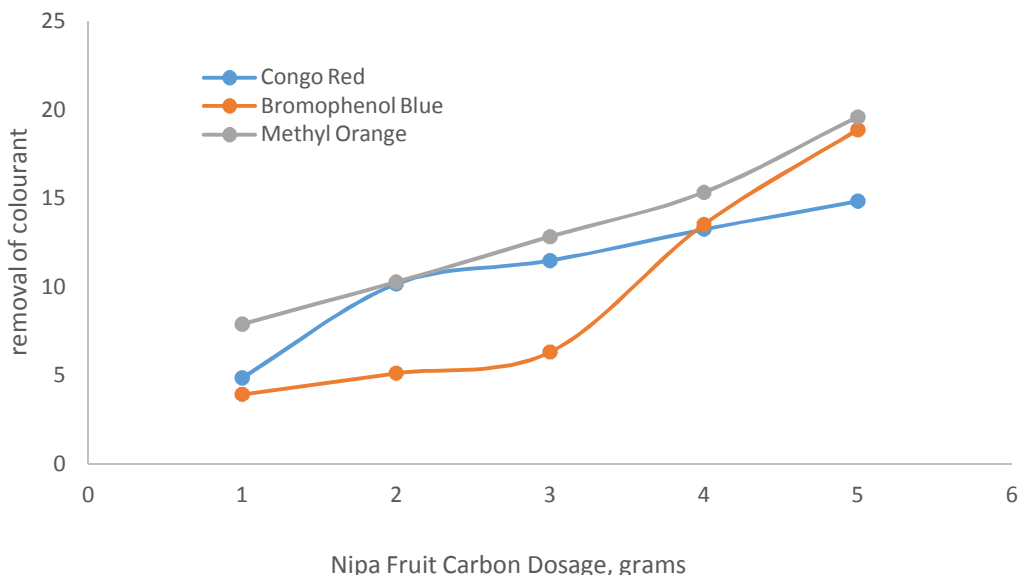


Figure 2: Effect of Nipa Fruit Carbon Dosage on the Percentage removal of colourant from Aqueous Solution at ambient temperature.

The effect of nipa fruit fibre biomass dosage on the percent removal of Methyl orange (MO), Bromophenol blue (BP) and Congo red (CR) is presented in Figure 3. The data showed that, increase

in biomass dosage from 1.0 gram to 5.0 gram resulted in a gradual increase in the amount of MO and CR being removed whereas the highest amount of BP removed was at 4.0 gram. The result from figure 3

shows that BP had the highest removal percentage of the three colourants with the highest removal of 4.0 gram of fruit fibre biomass, MO also had a higher elimination capacity at different biomass dosage than CR except with 1.0 gram of biomass where MO had the least removal percentage.

The effect of biomass dosage on the percent removal of the three colorants used in this research work is presented in Figure 4. The data showed that, increase in biomass dosage from 1.0 gram to 5.0 gram

resulted in a slight increase in the amount of colourant being removed. It is observed above that the effect of carbon dosage on the percentage removal of different colourant from aqueous solution indicated that adsorption capacity of the nipa fruit fibre carbon dosage was generally poor. MO has the highest percentage removal at 19.60%; BP was at 18.89 and CR at 14.86.

Effect of Initial Colourant Concentration on removal of Colorant from Aqueous Solution

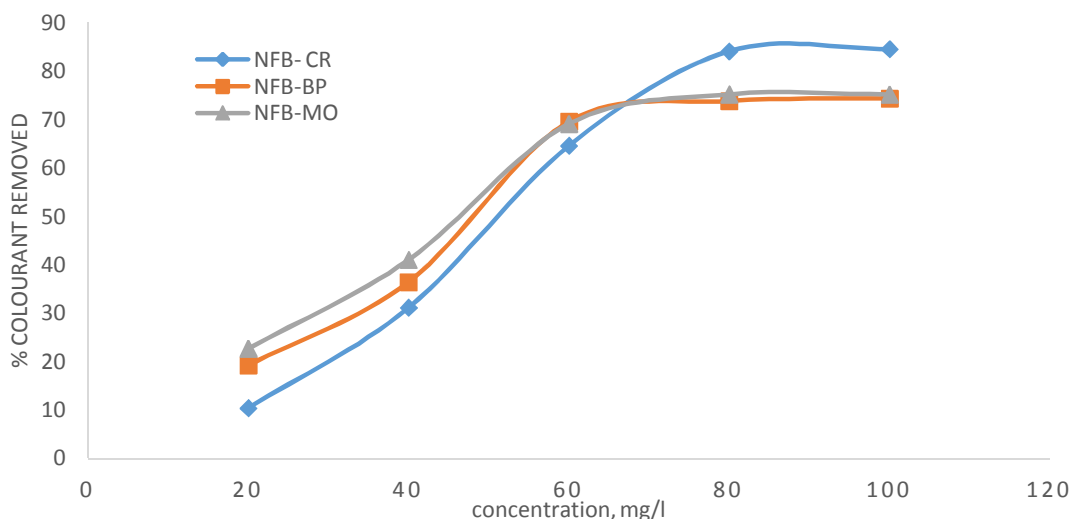


Figure 3: Effect of Concentration on Percentage Colourant removed from Aqueous Solution using Nipa Fruit Biomass at ambient temperature.

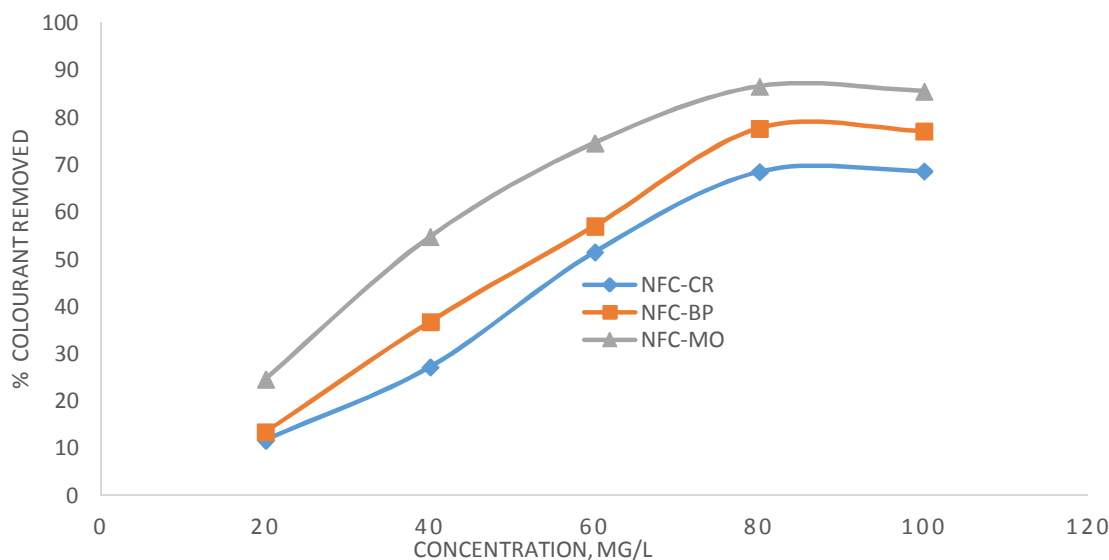


Figure 4: Effect of Concentration on Percentage Colourant removed from Aqueous Solution using Nipa Fruit Carbon at ambient temperature.

The effect of concentration on percentage colourant removed from aqueous solution using nipa fruit biomass used in this research work is presented in figure 3. The data showed that, the higher the

concentration of colourant in aqueous solution, the higher the percentage colourant removal. The adsorption capacity of nipa fruit biomass was best for CR, followed by MO and lastly, BP.

The effect of concentration on percentage colourant removal from aqueous solution using nipa fruit carbon is presented in figure 4. The optimal percentage removal of colourant from aqueous solution for MO, BP and CR were 86.55% at 80 mg/L, 77.69% at 80 mg/L and 68.65% at 100 mg/L

respectively. The data showed that nipa fruit carbon was able to eliminate colourant increasingly as we progress from initial concentration of 20 mg/l to 100 mg/L. MO was best removed at every concentration, followed BP and lastly CR.

Table 1: Computations from Langmuir and Freundlich isotherm plots for nipa fruit fibre biomass (NFB).

Colourant	Langmuir model			Freundlich model		
	q_{max}	K_L	R^2	N	K_F	R^2
CR	0.8×10^{-2}	115.3×10^{-2}	85.0×10^{-2}	10.3×10^{-2}	89.5×10^{-2}	95.1×10^{-2}
BP	0.3×10^{-2}	1057.5×10^{-2}	98.2×10^{-2}	9.5×10^{-2}	92.0×10^{-2}	31.1×10^{-2}
MO	0.3×10^{-2}	41.8×10^{-2}	49.7×10^{-2}	8.4×10^{-2}	94.4×10^{-2}	58.1×10^{-2}

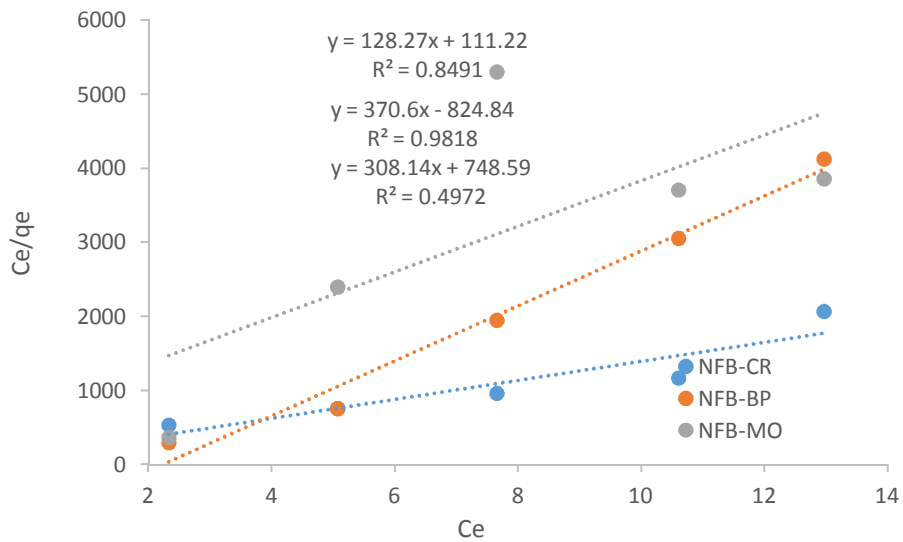


Figure 5: Langmuir Equilibrium Sorption Isotherms for removal of Colourant from Aqueous Solution using Nipa Fruit Biomass at ambient temperature.

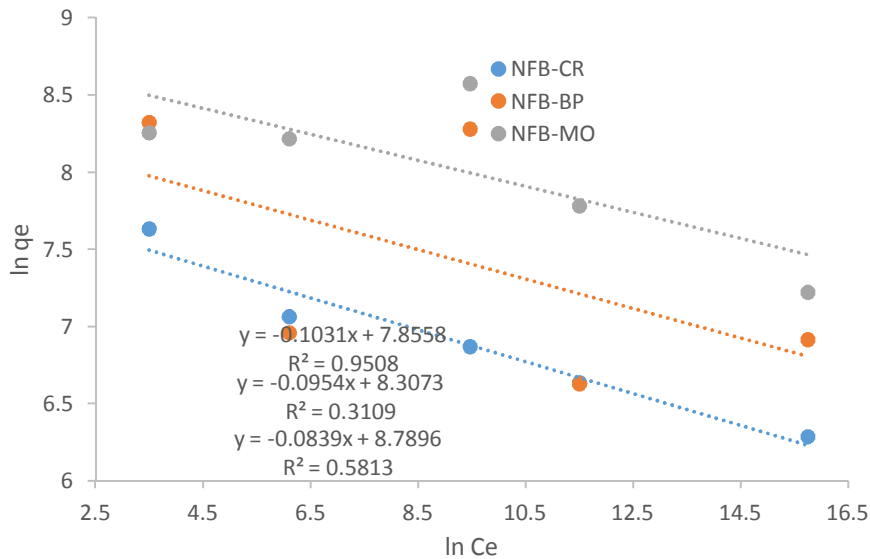


Figure 6: Freundlich Equilibrium Sorption Isotherms for removal of Colourant from Aqueous Solution using Nipa Fruit Biomass at ambient temperature.

The Langmuir and Freundlich Equilibrium Sorption Isotherms for removal of colourant from aqueous solution using nipa fruit biomass are presented in Figure 5 and 6 respectively. The adsorptions were found to be linear over the entire concentration range. The correlation coefficients for CR and MO were higher in Freundlich isotherm than Langmuir isotherm while BP is higher in Langmuir model. The r^2 indicates the ability of NFB to reduce organic contaminants in aqueous solution and shows the best fit for the models. The maximum capacity adsorption for NFB is CR (0.8×10^{-2}), BP (0.3×10^{-2}) and MO (0.3×10^{-2}).

The Langmuir constant (K_L) representing the energy constant related to the heat of adsorption was highest for BP ($1057.5 \times 10^2 \text{ Lmg}^{-1}$), compared to CR ($115.3 \times 10^2 \text{ Lmg}^{-1}$) and MO ($41.8 \times 10^2 \text{ Lmg}^{-1}$) and the Freundlich constant (K_f) expresses the extent of adsorption and was highest for MO (94.4×10^{-2}), followed by BP (92.0×10^{-2}) and CR (89.5×10^{-2}).

The Langmuir and Freundlich Equilibrium Sorption Isotherms for removal of colourant from aqueous solution using nipa fruit carbon are presented in Figure 7 and 8 respectively. The result shows that Langmuir adsorption model provides the best fit for data obtained experimentally for NFC with $r^2 > 0.8050$ for all cases than Freundlich isotherm, the Langmuir confirms the monolayer coverage of the dye on NFC and also assumes the surface to be homogeneous, with the following trend BP>CR>MO that is 0.12×10^{-2} , 0.09×10^{-2} and 0.06×10^{-2} respectively.

However, the Langmuir constant K_L representing energy constant was highest for BP (1639.9×10^2), followed by CR (1477.7×10^2) and MO (154.6×10^2). Freundlich constant K_f related to the degree or extent of adsorption was maximum for BP (103.9×10^{-2}), followed by CR (99.3×10^{-2}) and MO (99.3×10^{-2}) using NFC.

Table 2: Computations from Langmuir and Freundlich isotherm plots for nipa fruit fibre carbon (NFC).

Colourant	Langmuir model			Freundlich model		
	q_{max}	K_L	r^2	n	K_F	r^2
CR	0.09×10^{-2}	1477.7×10^2	96.2×10^{-2}	26.3×10^{-2}	99.3×10^{-2}	20.4×10^{-2}
BP	0.12×10^{-2}	1639.9×10^2	80.5×10^{-2}	42.8×10^{-2}	103.9×10^{-2}	55.1×10^{-2}
SMO	0.06×10^{-2}	154.6×10^2	93.2×10^{-2}	19.9×10^{-2}	99.3×10^{-2}	31.0×10^{-2}

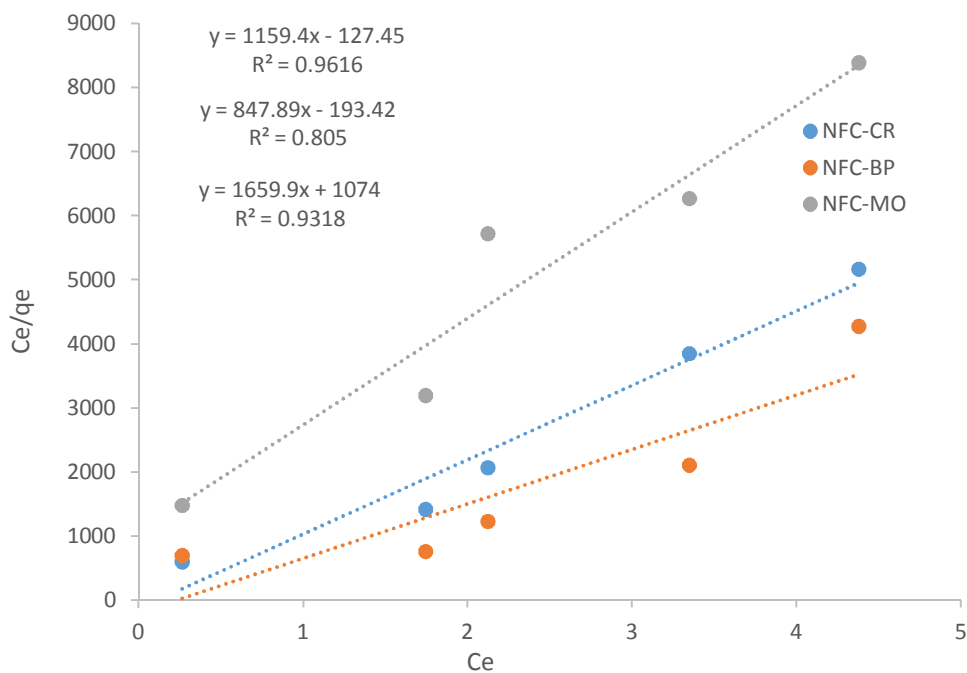


Figure 7: Langmuir Equilibrium Sorption Isotherms for removal of Colorant from Aqueous Solution using Nipa Fruit Carbon at ambient temperature.

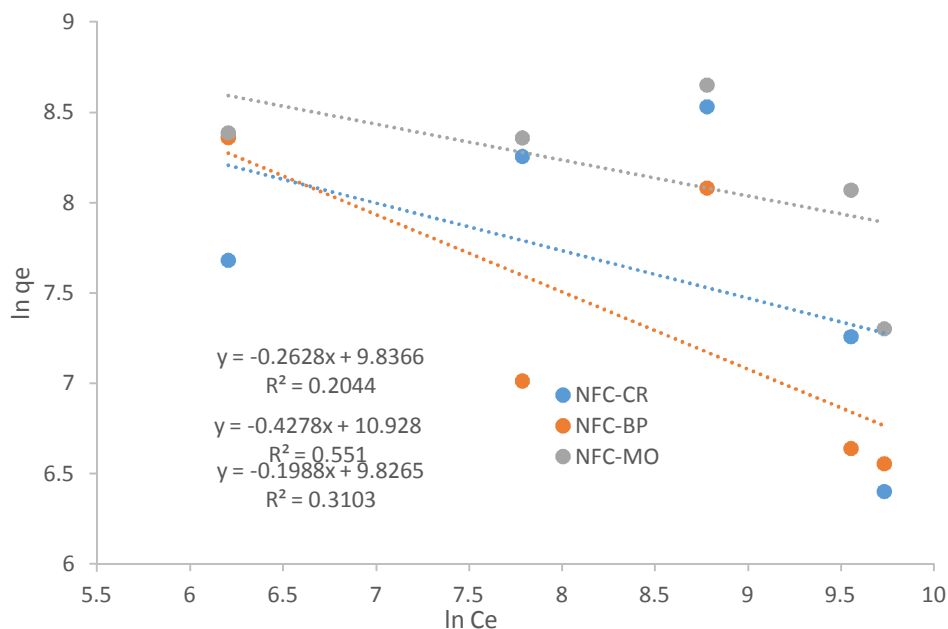


Figure 8: Freundlich Equilibrium Sorption Isotherms for Elimination of Colourant from Aqueous Solution using Nipa Fruit Carbon at ambient temperature.

Conclusion

In this work the removal of organic colourants from aqueous solution by batch adsorption experiments using nipa palm fruit fibre and carbonized carbon. This study monitored the ability of the biomaterials for removing colourants with various adsorbent dose and initial concentration. From the results obtained COD reduction of bromophenol blue, congo red and methyl red using biomass and carbonized carbon from nipa palm fruit fibre is of considerable potential for removal of colourants from waste waters.

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