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Use of Activated Carbon Derived from Maize Cob and Mahogany Seed Shell for the Removal of Colour from Textile Effluent

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ABSTRACT
In the present study natural adsorbents Maize Cob (MC) and Mahogany Shells (MS) were carbonized and activated with steam/zinc chloride and sieved into 600µm particle sizes. The adsorbents were treated for the removal of colour from textile effluent at different time. These adsorbents were also evaluated at different adsorbent doses and effluent concentrations. It was found that Maize cob has the highest colour removal efficiency of 86% and also at shorter time of 25minutes compared to Mahogany shells which record 73% and at 30, respectively. Freundlich and Langmuir isotherm models were used for the mathematical description of colour adsorption equilibrium onto the adsorbents and the result obtained showed that the adsorption equilibrium data onto MC was closely fitted to the Langmuir model whereas the adsorption equilibrium data onto MS was closely fitted to the Freundlich model. Hence, adsorption of the colour onto the adsorbents is monolayer adsorption process.

Keywords: Adsorption Isotherm, Mahogany Shells, Maize Cob, % Removal, Textile Effluent

INTRODUCTION

Industrial effluents contribute enormously to water deterioration if not properly treated and discharged. Effluent is a liquid waste flowing out of a factory, farm, commercial establishment, or a household into a water body such as a river, lake, lagoon, sewer system or a reservoir (Yusuff and Sonibare, 2004). This wastewater from domestic and industrial processes increases due to the increase in population and industrial expansion.

Contaminants such as colour, heavy metals, cyanides, toxic organics, nitrogen, phosphorous, phenols and suspended solids from the industries and untreated sewage sludge from the domestic processes have become a great concern to the environment and public health. Colour is the first sign of contamination recognized in wastewater, since dye concentrations in watercourse higher than 1 mg/L caused by the direct discharges of textile effluent is highly visible and affect the aesthetic merit, water transparency and gas solubility in lakes, rivers and other water bodies (Mcurdy *et al*., 1992),

Wastewaters from textile do not only deface the look of natural waters, but are also highly toxic. Some dyes are reported to harm mammalian cells by causing kidney tumors and reproductive difficulties. These dyes are also potentially carcinogenic in many mammalian species (Yakubu *et al*., 2008). Many methods such as Physico-chemical techniques including membrane filtration, coagulation, flocculation, precipitation, adsorption, ion exchange, electrolysis, chemical reduction and Biological techniques including aerobic, anaerobic or combined aerobic/anaerobic treatment processes have been used to treat wastewaters from textile. Among these methods adsorption process is considered very effective in textile wastewater treatment. It proves superior to the other processes by being cheap, sludge free and can completely remove even minute amount of dyes in wastewaters (Yakubu *et al*., 2008).

In these regard activated carbon have long been considered the best adsorbent for the removal of organic matter in wastewater. They contain extended surface area, a lot of internal voids, high adsorption capacity and a high degree of surface activity. Agricultural by-products are renewable sources of raw materials for activated carbon production for the removal of color, dissolved metallic salts from aqueous solutions and also reduction of COD by adsorption (Ibrahim, 2014; Khan *et al*., 2004; Gregorio, 2006).

The aim of the present work is to investigate the adsorption capacity of activated carbon derived from Maize cob and Mahogany seed shells for the removal of Colour from textile effluent.

This will be achieved through the production activated carbon from Maize cob and Mahogany seed shells, determining the optimum contact time, adsorbent dose, effluent concentration and the adsorption isotherm that fit the adsorption process.

MATERIALS AND METHODS

Materials

Electric thermostatic shaker Innover 4000 from New Brunswick Scientific, UV-visible spectrophotometer Janway 6305, Muffle furnace, Portable Gallenkamp Autoclave YX 280B, Mechanical sieve, Maize cob, Mahogany shell, $ZnCl_2$ Analytical reagent from Interlabs.

Sample Collection

Textile effluent was collected from African Textile Manufacturers (ATM) Chalawa Industrial Estate Kano, from the point of discharged. Mahogany seed shells (MS) and Maize cobs (MC) were collected from B.U.K old campus and local farm in Karaye, Kano state, Nigeria, respectively. The wastewater collected was filtered using Whatman No.1 filter paper.

Carbonization and Activation of Adsorbents

Mahogany seed shells and Maize cobs were washed with distilled water to remove dirt and then air- dried. The adsorbents were carbonized in a muffle furnace at 500^0C for 1hr and 30 minutes, respectively where they completely converted to carbon and were then remove from the furnace. These adsorbents were grounded and sieved into 600µm particle sizes.

The carbonized mahogany seed shells (MS) and maize cobs (MC) were subjected to steam in an autoclave (Portable Gallenkamp Autoclave YX 280B) at 130^0C for 2hrs, the steamed treated carbons were further activated with 1M $ZnCl_2$ solution and allowed to stay overnight. The activated carbons were filtered, thoroughly washed with distilled water and dried in an oven at 100^0C for two hrs.

Colour Removal

Batch adsorption experiments were conducted to studies the influence of parameters such as; Contact Time (t), Adsorbent Dose (g) and Concentration (% Conc) on the removal of colour from textile wastewaters. 1g of the activated carbon made from MC and MS were added to polyethylene bottles with 50ml effluent at initial pH of 7.1. The bottles were kept in an Innover 4000 shaker from New Brunswick Scientific at room temperature (30 ± 2^{o}C), at a speed of 150 rpm and agitated within a specific contact time interval (5-60 mins) to study the effect of contact time and find the optimum time of the adsorption process. Other parameters such as adsorbent dose (0.5-3g) and effluents concentration (10-50%) were also studied. All the samples were filtered using whattman No.1 filter paper the filtrates were analyzed using Jenway 6305 UV-visible spectrophotometer analysis for the determination of residual colour intensities.

The percentage removals of the colour were calculated from the relation;

$$\left(\frac{C_o - C_t}{C_o} \times 100\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Where C_o and C_t are the initial and final colour concentrations of the effluent, respectively (Ibrahim and Jimoh, 2010). While the amount of colour adsorbed was calculated using the equation;

$$q_t = \frac{(C_o - C_t) \times V}{m}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Where q_e is the amount of colour adsorbed in (mg/g) of the adsorbent, C_o is the initial concentration of the colour before adsorption process, C_t is equilibrium (Residual) concentration of the colour in the filtrate after adsorption process at a given time (t), M is the mass (g) of the adsorbent, V is the volume of the solution (Opeolu *et al*., 2009).

Effect of Contact Time

A constant dose of 1g of the activated carbons (MC and MS) was transferred in to 18 polyethylene bottles containing 50ml of the effluent. The samples were shaken using an Innover 4000 electric shaker from New Brunswick Scientific at a speed of 150 rpm and different time intervals of 5, 10, 15, 20, 25, 30, 40, 50, and 60 minutes at room temperature (30 ± 2^{o}C) and $_p$H of 7.1. The samples were withdrawn from the shaker at pre-determined time interval, filtered immediately using Whatman No. 1 filter paper and the filtrates were taken for UV-visible measurements for the residual colour intensity using Janway 6305 UV-visible spectrophotometer.

Effect of Adsorbent Dose

0.5, 1, 1.5, 2, 2.5, and 3g of each of the adsorbent and 50ml of the effluent were transferred into 12 polyethylene bottles and shaken using electric shaker for 25 and 30 minutes (optimum time) for the sets of bottles containing MC and MS, respectively at room temperature and pH of 7.1. Each set was withdrawn from the shaker at its specified time and filtered using Whatman No 1 filter paper and the filtrates were analyzed for residual colour intensity by UV-visible spectrophotometer.

Effect of Concentration

The effect of concentration was studied by varying the concentration of the effluent at constant time, Adsorbent dose, pH and Temperature. 10, 20,

30, 40 and 50 percent concentrations of the effluent were prepared by putting 10, 20, 30, 40 and 50 ml of the effluent in separate bottles and making each up to 100 ml. Adsorbent dose of 2g in 50ml of the effluent were transferred into 10 polyethylene bottles and shaken using electric shaker for 25 and 30 minutes (optimum time) for the sets of bottles containing maize cob and Mahogany shells, respectively at room temperature and pH of 7.1. The samples were withdrawn from the shaker and filtered through a Whatman filter paper. The residual colour intensity was determined using UV-visible spectrophotometer.

Determination of the Adsorption Isotherm

Adsorbents weights of 2g in 50ml of the effluent were used for adsorption isotherms studies with a contact time of 25 minutes. Each set was withdrawn from the shaker after its specified time and filtered through a Whatman filter paper. The residual colour concentration of the effluent was determined using UV-Visible spectrophotometer.

RESULTS AND DISCUSSION

Effect of Contact Time

The contact time was evaluated as one of the important parameters affecting the adsorption efficiency (Mane and Bhusari, 2012). Fig. 1 is a graphical representation of effect of contact time on the uptake of colour from textile effluent by the activated carbon made from (MC) and (MS).

It was observed from Fig. 1 that the process of adsorption was high at initial stage which then gradually became steady after sometime, the rapid uptake at the initial stage may be due to the presence of plenty of readily accessible sites suggesting possible adsorptive forces (Van der Waals) between dyes and adsorbent molecules, leading to saturation, which resulted in the steady uptake as process proceeds and after equilibrium was attained, the uptake rate gradually decreased with time indicating desorption of the dye molecule with time as the adsorption force (Van der Waals) existing between adsorbent and adsorbate became weak (Weba, 1972). Similar phenomenon was observed by Sharma and Kaur (2011) where sugarcane bagasse was found to be effective in removal of Erythrosine B. and Methylen Blue from aqueous waste and the data reveals rate of adsorption increased initially as the contact time increased which then became almost constant. This is due to aggregation of dye molecules with the increase in contact time. This aggregation negates the influence of contact time as the pores get filled up and start offering resistance to diffusion of aggregated dye molecules in the adsorbent.

It was found that in figure 1 the optimum time duration required for colour removal in textile effluent were 25 and 30 minutes for maize cob and mahogany shell, respectively.

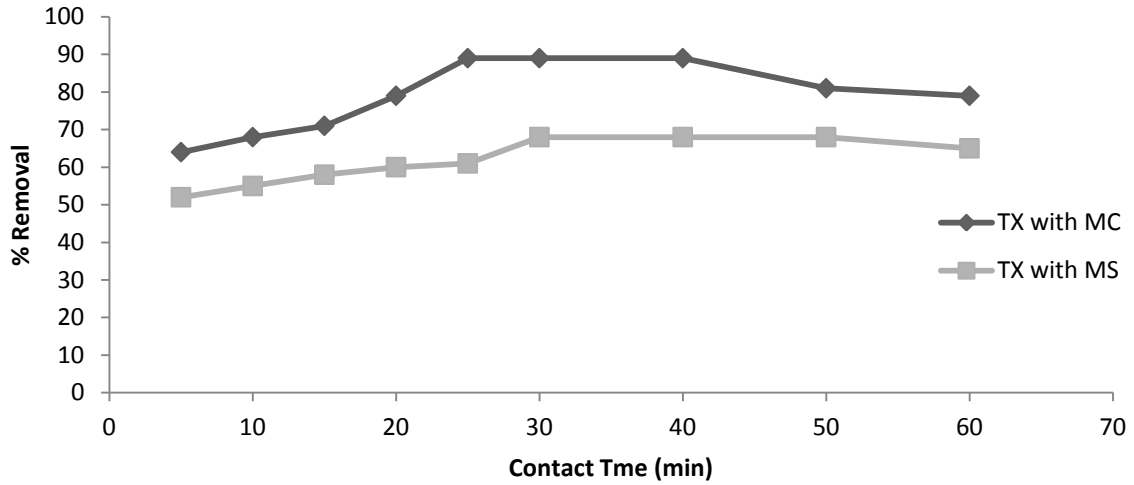

Fig. 1: Effect of Contact Time for the Removal of Colour from Textile Effluent with Maize Cob and Mahogany Shell

Effect of Adsorbent Dose

Fig. 2 shows the increase in colour removal with increase in adsorbent dosage, similar result was also reported by Mane and Bhusari (2012). It can be seen that, the uptake of the colour by both adsorbents increased as the adsorbent dosage increased from 0.5g to 2g, which can be attributed to the increase in active surface sites (Ibrahim, 2014). Similarly, from Fig. 2 the maximum colour removal from textile effluent with maize cob was 86% at 2g for 25minutes, whereas with mahogany shell was 73% at 2g for 30minutes.

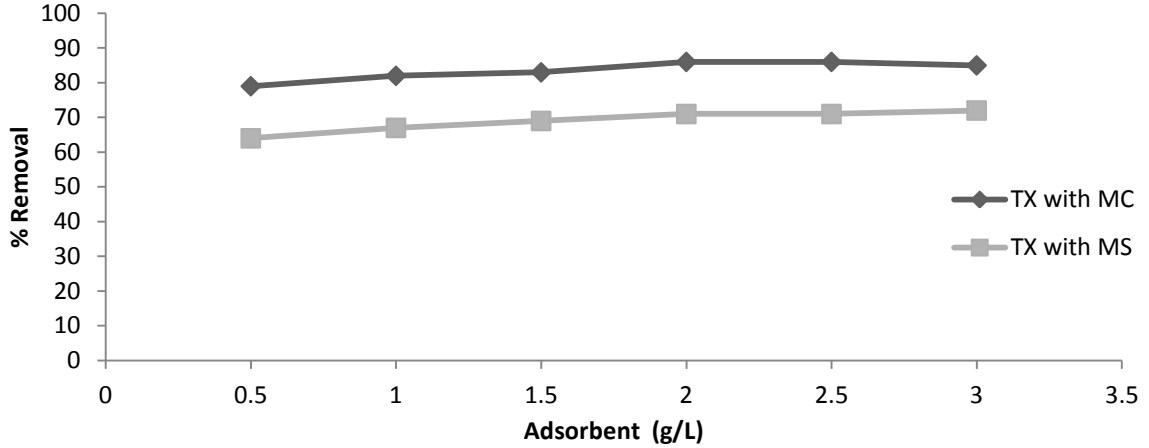

Fig. 2: Effect of Adsorbent Dose for the Removal of Colour from Textile Effluent with Maize Cob and Mahogany Shell

Effect of Concentration

Fig. 3 shows an increase in the colour uptake as the initial dye concentration in percentage of effluent increased. This could be due to the increase in the driving forces of the concentration gradient as an increased the dye initial concentration. This result is similar to what was reported by Mathivanan and Saranathan (2015). The colour uptake increased gradually from 83% to 89% for maize cob and 65% to 72% for mahogany shell.

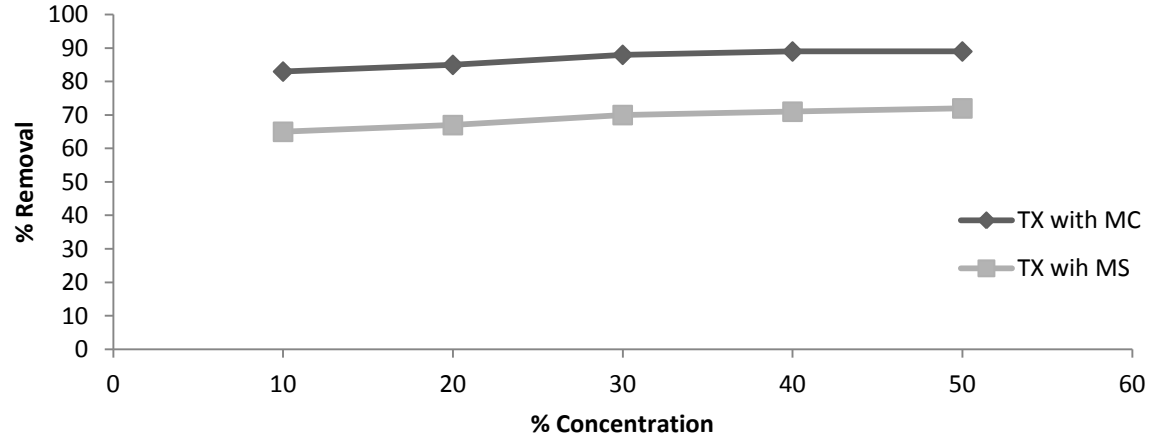

Fig. 3: Effect of Initial Concentration on the Removal of Colour from Textile Effluent Using Activated Carbon Obtained from MC and MS

Adsorption Isotherms

Adsorption isotherms are important to predict how adsorbates will interact with adsorbents. The equilibrium data obtained on effect of percentage concentration were applied on linearized Freundlich and Langmuir isotherm equations.

The Langmuir and Freundlich isotherms are the most commonly used for solid-liquid phase isotherms. These isotherms relate the amount of colour adsorbed per unit weight of the adsorbent, (mg/g) to the colour concentration at equilibrium, C_e (mg/l).

Freundlich isotherm model describes non-ideal sorption onto heterogeneous surfaces involving multilayer sorption.

The isotherm model is defined as;

$$q_e = K_F C_e^{1/n} \quad \ldots\ldots (3)$$

Its linearized form is given as

$$\ln q_e = K_F + 1/n \ln C_e \quad \ldots\ldots (4)$$

Where q_e is the amount of dye adsorbed per unit weight of the adsorbent (mg/g), C_e is dye concentration at equilibrium (mg/l), n is constant related to adsorption efficiency and energy of adsorption or adsorption capacity of the adsorbent and may determine linear (n = 1), chemosorption (n < 1) or physisoption (n > 1) process.

According to the Langmuir model, adsorption occurs uniformly on the active sites of the adsorbent, and once the adsorbate occupies a site, no further sorption can take place at that site (Weber 1972).

The Langmuir isotherm is defined as;

$$C_e/q_e = 1/K_L + KLC_e/QL \quad \text{.....(5)}$$

Where q_e is the adsorption capacity at equilibrium (mg/g), C_e is the equilibrium (residual) colour concentration in solution after adsorption (mg/l), K_L (mg/g) and Q_L (L/g) are Langmuir constants, R_L value can either shows unfavorable (R_L>1), linear (R_L=1), favorable (0<R_L<1), or irreversible (R_L=0) adsorption process.

Figures 4 and 5 respectively show Freundlich isotherm model of the colour adsorption and the isotherm constants and their correlation coefficient, R^2 are also listed in Table 1. A plot of lnq_e against lnC_e gives a straight line with a slope 1/n and an intercept of lnK_F. It was observed that from Table 1 and 2, the adsorption of the colour onto MC was found to closely fit Langmuir Isotherm model as the correlation coefficient calculated from Langmuir equation is greater than the one calculated from Freundlich equation, assuming homogenous surface layer coverage, that is once a dye occupied a site, no further adsorption could take place at the site while the colour adsorption onto MS closely fit Freundalich Isotherm as the correlation coefficient calculated from Freundlich equation is greater than the one calculated from Langmuir equation, suggesting heterogeneous nature of the MS and demonstrates the formation of multilayer coverage of the colour at the surface of the adsorbent. The separation factor (R_L) could not explain adsorption favorability on MC due to its negative value while it is unfavorable on MS due to $R_{L\ value}$ >1; however, the heterogeneity factors from Freundlich equation (n) (Table 1) with values less than 1 suggests chemosorption process.

Table 1: Freundlich Isotherm Constants and R^2 for Colour Adsorption onto MC and MS

Adsorbent	1/n	n	K_F(mg/g)	R^2
MC	1.0403	0.9613	0.1789	0.0963
MS	1.424	0.7022	0.2262	0.9737

Table 2: Langmuir Isotherm Constants and R^2 for Colour Adsorption onto MC and MS

Adsorbent	K_L	Q_L	R_L	R^2
MC	-26.9718	0.0936	-1.328	0.4712
MS	-7.6869	0.0394	1.9984	0.6536

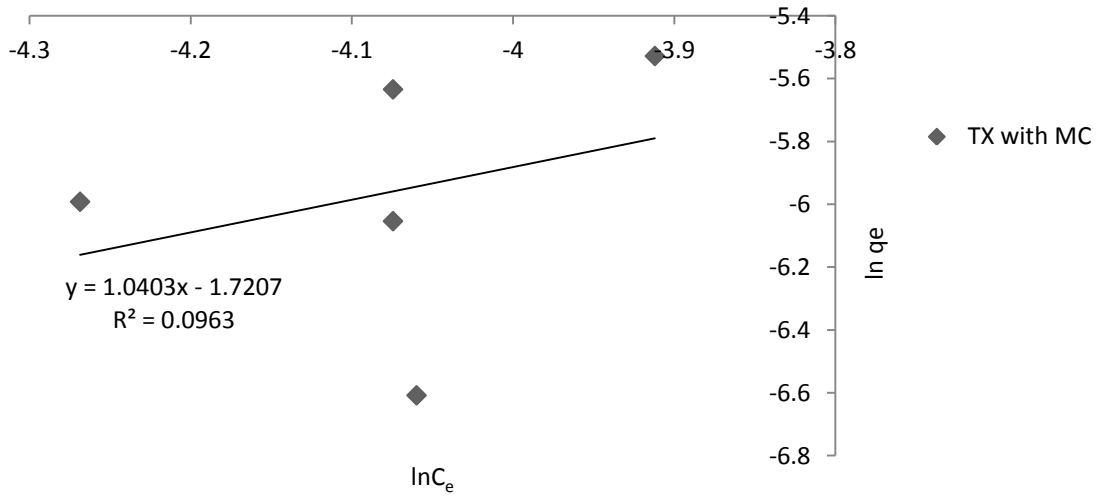

Fig. 4; Freundlich Isotherm for Colour Adsorption onto Maize Cob

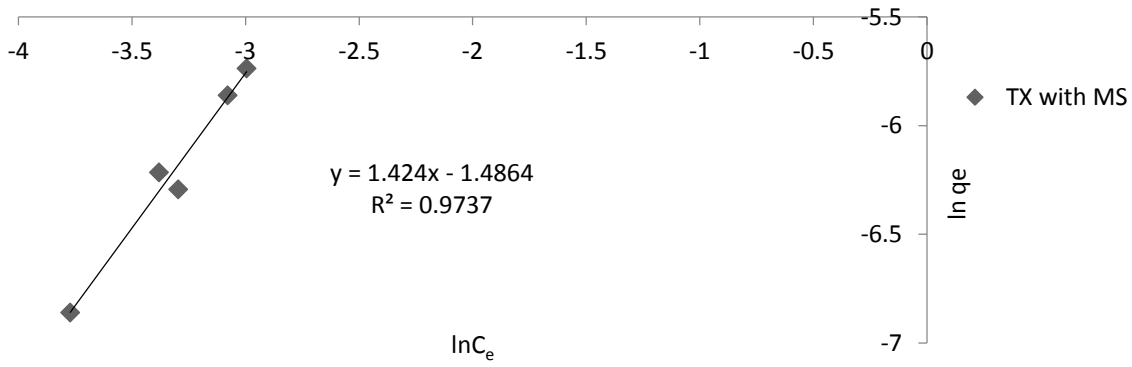

Fig. 5: Freundlich Isotherm for Colour Adsorption onto Mahogany Shells

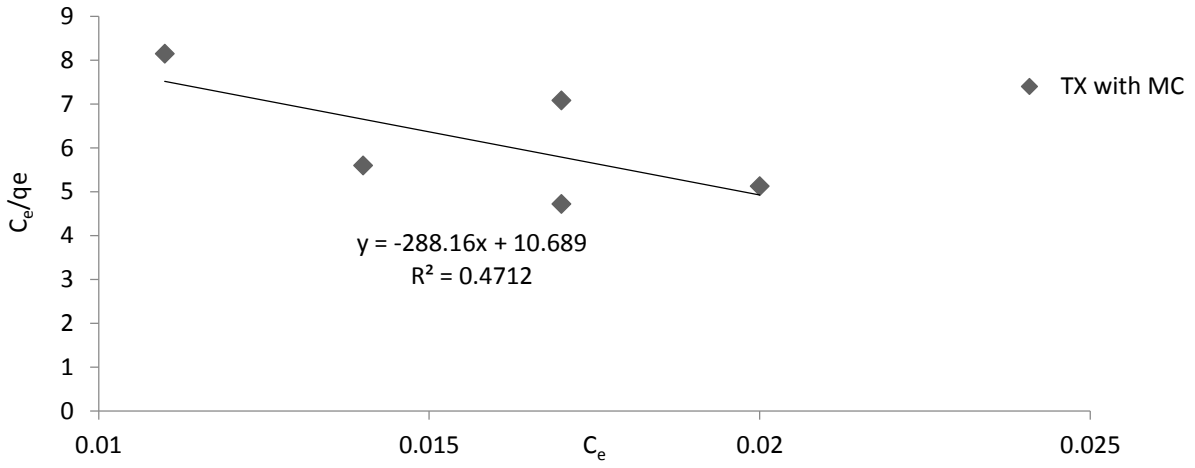

Fig. 6: Langmuir Isotherm for Colour Adsorption onto Maize Cob

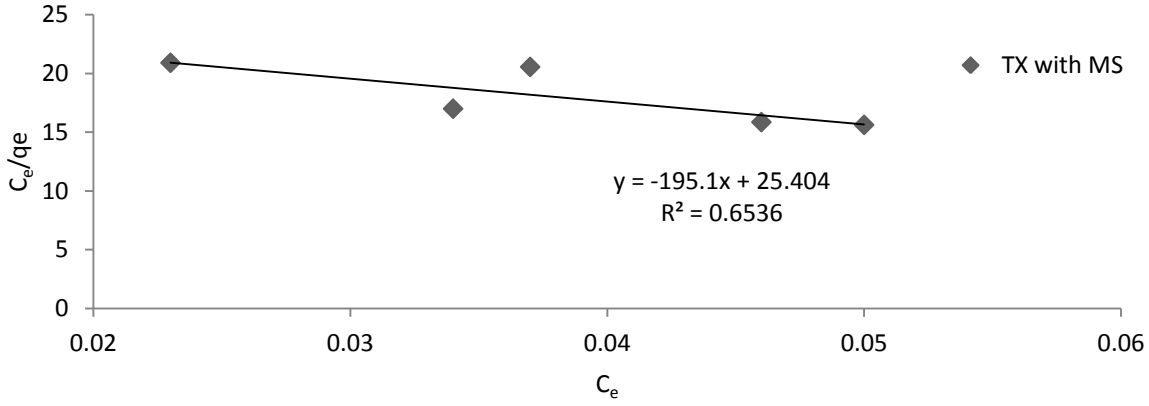

Fig. 7: Langmuir Isotherm for Colour Adsorption onto Mahogany Shell

CONCLUSION

Activated carbon from Maize Cob and Mahogany Seed Shells were used to treat textile wastewaters. These adsorbents were found to have a colour adsorption capacity. Factors such as contact time, adsorbent dose and concentration were monitored and influence the adsorption process using these materials. It was found that the colour was optimally adsorbed at 2g for both adsorbents where MC having recorded the highest colour removal efficiency with 86% and also at shorter time of 25 minutes compared to MS which record 73% at 30 minutes.

Freundlich and Langmuir isotherm models were used for the mathematical description of colour adsorption equilibrium onto the adsorbents and the result obtained from the study of the adsorption isotherm showed that the adsorption equilibrium data onto MC was closely fitted to the Langmuir model whereas for MS was closely fitted to Freunlich model. Hence, adsorption of the colour onto MC and MS is observed to be a chemosorption adsorption process.

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