Removal of Eosin yellow dye from aqueous solution using oil bean seed shells based activated carbons: Equilibrium, Kinetics and thermodynamics studies

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Abstract

Biosorption potentials of acid (OBAC) and salt (OBSC) activated carbons from pentaclethra Macrophylla (PMAC) shells for the removal of eosin yellow from aqueous solution were investigated. The adsorbents were characterized by Fourier transform infrared (FTIR) spectroscopy, and the absorbance measured with UV spectrophotometer. The effects of particle size (75-85mm), adsorbent dosage (0.5-4.0g), initial pH of solution (2-10), eosin yellow concentration (50-500mg/l), temperature (30^0C-60^0C) and contact time (3-150 min) were studied. The percent eosin yellow uptake was found to increase with increase in adsorbent dosage and contact time and decreased with increase in particle size, initial eosin yellow concentration and temperature. Optimum adsorption of eosin yellow was observed at pH 8. The biosorption equilibrium data were well represented by Langmuir, Freundlich, Dubinin-Radushkevich, Temkin models. Kinetic data obtained fitted the pseudo-second-order model very well with high correlation coefficient. The calculated thermodynamic parameters (ΔG, ΔH and ΔS) indicated that adsorption of eosin yellow onto OBAC and OBSC was endothermic, spontaneous and feasible in the temperature range studied. Results of this work showed that PMAC could be used as low cost adsorbents for the removal of eosin yellow from aqueous wastewater.

Keywords: Adsorbents, Eosin yellow, Kinetics, Isotherm and Thermodynamics studies

1.   INTRODUCTION:

With economic and technological development, water pollution is a common problem worldwide. Water pollution has become more and more serious, especially regarding dye ions. Dye ions; mainly from dyeing industries have become serious threats to human beings and the aquatic ecosystem, due to their toxicity and persistence after being released into the natural water. Adsorption processes which produce good quality effluents that are low in concentration of dissolved organic compounds, such as dyes are rapidly gaining importance as treatment processes. Widespread contamination of soil and groundwater by synthetic organic chemicals (e.g., dyes) has been recognized as an issue of growing importance in recent years. Among them, textile industry ranks first in the usage of dyes for colouration of fiber (Garg et al., 2003).Most of these compounds are potential or known human carcinogens and are of considerable health concern, even at low concentrations. For this reason, the fate and transportation of these compounds has been the subject of much research.

Methods for decolourization have therefore become important in recent years. In principle, decolourization is possible with one or more of the following methods: adsorption, precipitation, chemical degradation, photo degradation and biodegradation. The purification of waste waters contaminated by hazardous pollutants of inorganic and organic nature is among the serious problems of conservation, especially when such toxic materials, e.g. dyes, contaminating the environment even in insignificant concentrations, are involved. The elimination of such pollutants from aqueous solutions is an important problem not only from a technical but also from an economic point of view. Decolouration in drinking water may be due to the presence of coloured organic substances or highly coloured industrial wastes, of which pulp, paper and textile wastes are most common. Highly coloured, polluted water will frequently have an associated objectionable taste, but the degree to which this association is causative is not known. Synthetic dyes represent a relatively large group of organic chemicals which are encountered in practically all spheres of our daily life. It is therefore possible that such chemicals have undesirable effects not only on the environment, but also on humans. In order to minimize the possible damage to people and the environment arising from the production and application of dyes, several studies have been conducted around the world. A number of researchers have used various adsorbent prepared from local materials for the removal of textile dyes from aqueous solutions .The development of sorbents of different types is carried out by many research and commercial institutions. Active carbon, for example, is known as an effective sorbent of toxic materials from water solution. Its sorbent

characteristics are regenerable by thermal desorption; however, a significant part of the sorbent is lost in each desorption cycle. This is the main reason for low economical efficiency in its application. Therefore, the interest in the development of sorbents of specific African oil bean shell has significantly increased in recent years.

Eosin yellow (EY) is an acidic dye where on dissolution, the sodium ion enters the aqueous solution ensuring the negatively charged oxygen group provides the dye with an overall negative charge. Analytical grade eosin dye (99.99% purity) used in this study was supplied by Merck and used without further purification. The negative charge of the dye should repel that of ionic adsorbent. Eosin yellow is selected as a model compound for evaluating the potential of activated carbon prepared from African oil bean shell to remove dye from aqueous solution. Eosin yellow (EY) is most commonly used for colouring among all other dyes of its category. Eosin yellow (EY) is an important acid dye widely used for printing calico, dyeing, printing cotton and tannin, indicating oxidation-reduction, and dyeing leather, and in purified zinc free form, it is used as an antiseptic and for other medicinal purpose but can have various harmful effects. The dye causes eye burns, which may be responsible for permanent injury to the eyes of human and animals. If swallowed or inhaled can cause chronic effect like cancer, the dye cause irritation to the gastrointestinal tract with symptoms of nausea, vomiting, and diarrhea. It may cause methemoglobinemia, cyanosis, convulsions, tachycardia, and dyspnea, if inhaled. It is likely to cause irritation to the skin (Senthilkumaar et al., 2005; Ghosh et al., 2002).

Oil bean seed (*Pentaclethra macrophylla*) belongs to the leguminous family mimosa cease found mostly in tropical Africa which leads to recent worldwide attention. This is because of their high nutrient potentials, especially with regard to solving the prevalent protein energy malnutrition (PEM) in less developed parts of the world(Enujiugha and Akanbi, 2005).These seeds are eaten in the form of salad (Chilaka et al., 2005), across different African countries. Although the seeds retained their whitish colour after processing, they eventually undergo browning during soaking and fermentation (Njoku and Okemadu, 2003). Jood et al. (2006) observed that these browning reactions cause loss of nutritive value in food products. Oil seeds (groundnut, soybean, palm kernel, cotton seed, olive, locust bean, melon seed, conophor nut, castor oil bean, African oil bean, sunflower seed, sesame seed, linseed,) are the second most valuable commodity in the world trade today. African oil bean is cultivated in forest areas, with about eight flat glossy brown edible seed per pod. The pods explode at

maturity and disperse the seeds. The raw seed is a potential source of protein, energy and fatty acids (Enujiugha and Agbede, 2000).

2. MATERIAL AND METHODS:

Material Sourcing and Pretreatment

The *PentaclethraMacrophylla* shells were sourced from agricultural wastes at Eke Awka market, Awka, Anambra state. The oil bean shell were collected in large quantity, cleaned, oven dried (105^0C) for 3 hours and kept for carbonization.

Figure 1: *PentaclethraMacrophylla* Benth pod with leaves

Figure 2: African oil bean seed

Each of the 10grams of the oil bean shell sample were first carbonized at four different temperatures, 150^0C, 200^0C, 300^0C, 400^0C for 30, 60, 90 and 150 minutes.

After the thermal activation process, mineral activation was achieved by soaking different samples of the product for 24hours in 1M solution Sulfuric acid and potassium chloride at an impregnation ratio of 2:1 w/w solution of solvent to carbon. The chemically activated carbon produced was further washed with distilled water to bring the pH to neutral level after which it was dried in an oven at 120^oC before separation into different particle sizes.

2.1 Characterization of Oil Bean Shell

Determination of Specific Surface Area (Sears, 1956).

The specific surface area of the activated carbon was estimated using sears' method by agitating 1.5g of the estimated carbon sample in 100ml of diluted hydrochloric acid of a pH = 3. Then a 30g of sodium chloride was added with stirring and the volume was made up to 150 with deionized water. The solution was titrated with 0.1M NaOH and the volume V, needed to raise the pH from 4 to 9 was then recorded. The surface area according to this method was calculated by the following equation.

$$S \left(\frac{m^2}{g}\right) = 32V \tag{1}$$

Where V = volume of sodium hydroxide required to raise the pH of the sample from 4 to 9.

Determination of pH

2g of activated carbon was weighed using a weighing balance and put in round bottom flask containing $20cm^3$ of distilled water. The solution was heated to its boiling point with an attached condenser for 15 minutes. The solution was filtered and the pH measured at 50°C.

Determination of Bulk Density (Alexeyer, 1998)

A specific gravity bottle was weighed on a weighing balance and recorded as W_1; sample of activated carbon produced was placed inside the specific gravity bottle and tapped to ensure compartment until the sample occupies a known volume. Weight of specific gravity bottle and sample is recorded as W_2

The bulk density is calculated as below:

$$bulk\ density\ \frac{g}{mL} = \frac{W_2 - W_1}{Volume} \tag{2}$$

Determination of the Free Moisture Content

The moisture content of the activated carbon was determined by placing 2g of it in a known weight of evaporating dish and labeled W_1.The sample were placed in the drying oven for 2 hours at 105°C. After drying, the drying oven was allowed to cool for sometimes and the dried sample was collected with the help of a hand trowel, placed in a desiccator and allowed

to cool. The dried sample was reweighed in a weighing balance and labeled w_2. The moisture content of the sample was calculated using the relationship.

$$percentage\ moisture\ content = \frac{W_1 - W_2}{W_1} \times 100 \tag{3}$$

Where W_1 = Weight of sample before drying,

W_2 = Weight of sample after drying.

Determination of Iodine Number/Content

The iodine number/content was determined using the sodium thiosulphate volumetric method. The amount of iodine adsorbed from aqueous solution was estimated by titrating a blank with standard thiosulphate solution and starch indicator compared with titrating against iodine containing 2g of the sample (activated carbon). Typically 2g of activated carbon was weighed into a centrifuge tube which was added 25ml of 0.lM iodine solution. The tube was immediately stopped and shaken for 10mins then centrifuged at 1000rmp for 5mins.

A 20ml of aliquot of supernatant liquid was pipette into a conical flask and the residual amount of iodine determined by titrating with standard thiosulphate solution in which starch was used as an indicator. Blank determination was carried out without the activated carbon sample. The iodine number is given by the relationship

$$I\left(\frac{mg}{g}\right) = \frac{(B-S) \times VM \times 126.91}{B \times W} \tag{4}$$

Where,

B and S = volumes of thiosulphate solution required for blank and sample titrations respectively.

W = the mass of the activated carbon sample

M = concentration (mol /L) of the iodine solute 126.91 = atomic mass of iodine.

Determination of Ash Content (Dara, 1991)

The crucible was measured using the mettle balance and the weight recorded. 2g of sample (activated carbon was weighed into the crucible and the weight of the sample and the crucible was obtained. The sample was placed in the oven and dried at 110^oC then burned in a muffle furnace at 650^oC for 4 hours in the presence of air. The ash content was calculated from the residue left after carbon combustion.

$$\%ash\ content = (weight\ of\ ash \times 100)/(weight\ of\ sample)$$

$$weight\ of\ ash = (weight\ of\ crucible + weight\ of\ ash) - (weight\ of\ crucible) \qquad (5)$$

3. BATCH ADSORPTION EXPERIMENT

This entails the study of various parameters on adsorption capacity of the activated carbon produced. The activated carbon and 50mg/l Eosin yellow dye stock solution was used in the adsorption study. The batch adsorption experiments were carried out using 0.5g adsorbents and 50ml of 50mg/l Eosin yellow dye solution in 250ml stoppered conical flasks on a temperature controlled water bath shaker set at 120 rpm. The initial concentration was taken as 100mg/l because below and after this initial concentration taken, the percentage removal was very high and same was observed during the calibration of the dye. The effects of adsorbents dosage, pH, contact time, initial dye concentration and adsorbent particle size on adsorption of Eosin yellow dye onto OBAC and OBSC were investigated. Preliminary investigations showed that the concentration of dye remained constant after 60 minutes of contact with 0.5g of OBAC and OBSC. The allowed contact time for equilibrium study was 120 min.

The effect of adsorbent dosages on dye removal from solution was investigated by varying the amount of OBAC and OBSC from 0.5 to 4.0g. The effect of pH was investigated by adjusting the pH of the solution over a range of 2-10. The pH was adjusted by adding a few drops of diluted 1.0M NaOH or 1.0M H_2SO_4 before each experiment. The pH was measured by using a pH meter. The effects of contact time and kinetics on adsorption of dye were determined at different time intervals over the time range 3-150 minutes. Temperature effects on dye uptake by OBAC and OBSC were studied by varying the temperature between 30°C and 60°C. Similarly, the effect of adsorbent particle size on dye sorption on the adsorbents was investigated at particle size range 75- 850 micrometers.

At the end of each experiment, the adsorbent solution mixture was centrifuged and the supernatant was analyzed for dye using a UV spectrophotometer. The amount of EY dye sorbed onto OBAC and OBSC at time t, q_t, at equilibrium, q_e, percent EY dye adsorbed at time t, $\%q_t$ and at equilibrium $\%q_e$ were computed using equations (6), (7), (8) and (9), respectively.

$$q_t = \frac{(C_0 - C_t)}{W} V \qquad\qquad (6)$$

$$q_e = \frac{(C_0 - C_e)}{W} V \qquad\qquad (7)$$

$$\%q_t = \frac{(C_o - C_t)}{C_o} \; X \; \frac{100}{1} \qquad\qquad (8)$$

$$\%q_e = \frac{(C_o - C_e)}{C_o} \; X \; \frac{100}{1} \qquad\qquad (9)$$

Where C_o, C_t, and C_e are the initial concentrations, concentration at time t, and the concentration at equilibrium, respectively. V and W are the volume of the solution (l) and weight of carbon(g), respectively. The batch experiments were carried out in triplicate and the negative controls (with no adsorbents) were simultaneously carried out to ensure adsorption was by the adsorbents and not by the container. The values reported were the average of the three values.

4. RESULTS AND DISCUSSION
4.1 Characterization of adsorbents

4.1.1 Proximate Analysis

The characteristics result of the two adsorbents used in the present study was listed in table 1. The surface area of OBAC (954.56m^2/g) was larger than that of OBSC (889.84m^2/g). The larger specific surface area of OBAC may mean that OBAC was covered with more adsorption sites (Purattanasin and Sariem, 2015). The iodine numbers for OBAC and OBSC were 764.53 and 715.07m^2/g, respectively. The iodine number is a measure of surface area, activity level and microspore content of activated carbon, higher iodine number indicates high degree of activation. Iodine number is also the fundamental parameter for characterizing the performance of an activated carbon as it provides a good approximation of the entire surface available for the adsorption of the lower molecular compounds especially the microporosity (Nemchi et al, 2012). The relatively high surface area of the OBAC and the OBSC may be due to the removal of most of the volatile matter during carbonization and oxidation process which leaves the adsorbents more porous and hence larger surface area. These values confirm the linear relationship between iodine number and surface area.

The bulk density of the activated carbon was 0.2785g/ml which is very low, and this may be attributed to the material lightness. Lower bulk density enhances the trapping of impurities inside the porous structure. The pH of the activated carbon was found to be 5.7 and 8.6

which may be due to acidic and alkalinity substances used during activation. Also, the moisture content was found to be 3.63% and 3.61% which is quite low and therefore acceptable, since high moisture content will dilute the action of the carbon and necessitates utilizing some extra load of carbon (Thangamani et al., 2007). Ash content generally gives an idea about inorganic constituents associated with carbon (Bansal et al., 2002). High ash content is undesirable for activated carbon since it reduces the mechanical strength of carbon and affects adsorptive capacity. The ash content was found to be 5.87 and 3.76% for OBAC and OBSC respectively, which is very low, thereby increasing the fixed carbon content.

Table 1: Physicochemical properties of OBAC and OBSC

Property	OBAC	OBSC
Ash content (%)	5.87	3.76
Surface area (m^2/g)	954.56	889.84
Bulk density (g/cm^2)	0.43	0.59
Iodine number (mg/g)	764.53	715.07
Moisture content (%)	3.63	3.61
pH	5.7	8.6

4.1.2 Instrumental Analysis
Fourier transform infra-red

The Fourier transform infra-red (FTIR) spectroscopic analysis were utilize to identify the functional groups present in the neutral, acid and salt activated carbon produced from African oil bean shells which could possibly influence their adsorption ability. The FTIR wavelength bands of acid and salt activated oil bean shell were shown in figure 1 and figure 2 respectively. However, some peaks were observed at each graph of the analysis which confirms the presence of functional groups on the neutral, acid and salt activated carbon surfaces respectively. The acid activated carbon spectrum showed characteristics peaks at 693.95cm^{-1}, 817.79 cm^{-1}, 1005.52 cm^{-1}, 1395.78 cm^{-1}, 1621.907 but the highest its highest peak was 3680.51cm^{-1} which showed the presence of C-Cl stretch in Alkyl Halide, C-H stretch in Alkane, C=H stretch in Alkenes, C-O stretch in Ether, C-N stretch in primarily Amine, N-H bonding in Amine and C=O stretch in carbonyl respectively. Similarly, the salt activated oil bean shell showed its highest peak at 810.40 cm^{-1}, and other characteristic peak were at bands 1031.02 cm^{-1} , 1174.35 cm^{-1} , 1305.18 cm^{-1} , 1369.04 cm^{-1} ,1369.04 and other

which showed the presence of C-Cl stretch in Alkyl Halide, , C-H stretch in Amine, H-bonded in Alcohol, C-N stretch in Amine, C=O stretch in Alkenes and C=O stretch in Anhydride respectively.
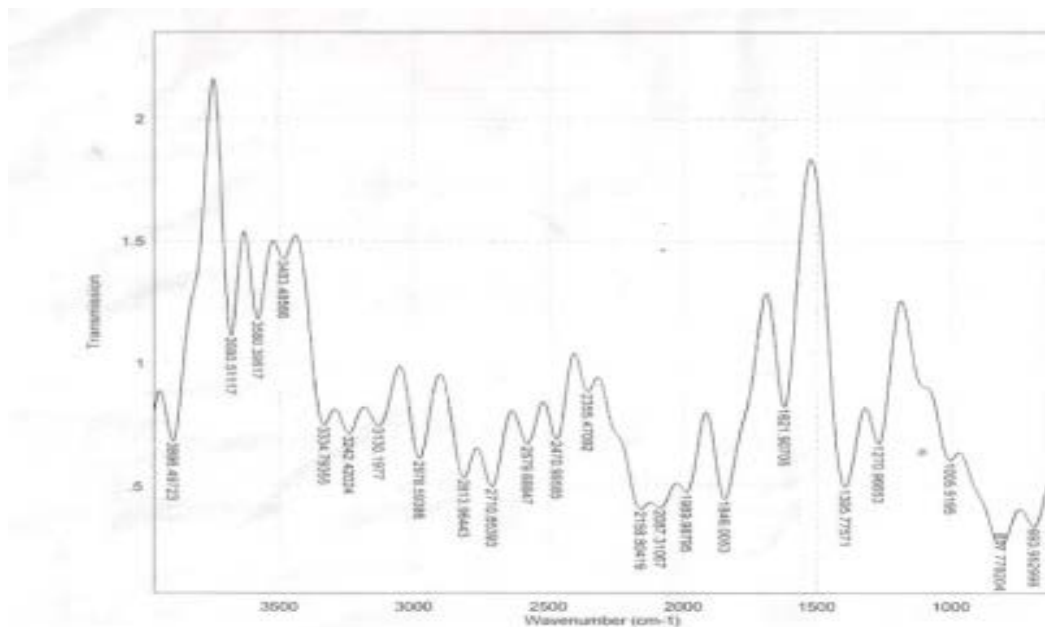

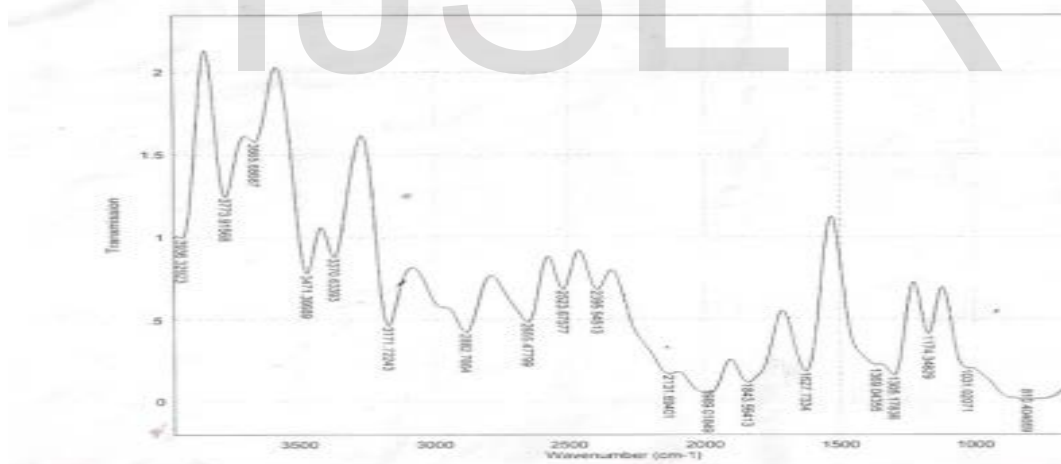Figure 1: Fourier transform infrared spectra of acid activated oil bean carbon

Figure 2: Fourier transform infrared spectra of salt activated oil bean carbon

3.3   Batch Adsorption study

3.3.1   Effect of Initial Eosin Yellow Dye Concentration

From figure 3.5, adsorption percentage removal shows a decreasing trend, from 89.80% to 49.98% as the initial eosin dye concentration was increased from 50mg/l to 500mg/l

respectively. The percentage removal was showed to be higher on acid activated oil bean carbon than when using salt activated carbon. At lower concentration (50mg/l), all eosin yellow dye present in the adsorption medium could interact with binding sites on the surface of adsorbent so higher adsorption yields were obtained. At higher concentrations, lower adsorption yield were observed because of the saturation of the adsorption sites (Sathishkumar et al., 2007).
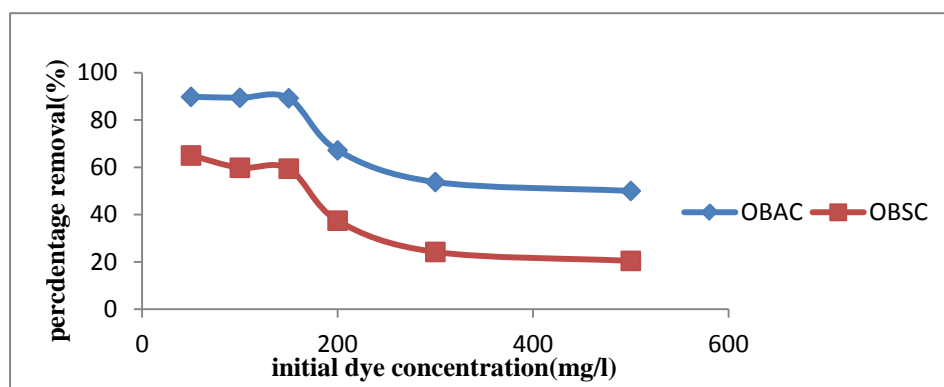
Figure 3.5: Effect of initial concentration of Eosin yellow dye using OBAC and OBSC.

3.3.2 Effect of particle size

The effect of particle size on the percentage removal of eosin yellow dye adsorbed was given in figure 3.6, which was investigated with the range of 75microns to 850micron meter particle size; 75micronmeter which is the lowest particle size gave the highest percentage removal which was considered as the optimum particle size for the experiment while 850micronmeter which is the highest particle size gave the lowest percentage removal. It was also shown that there was an insignificant decrease from 150 micrometer and a sharp drop from 600micronmeter. The percentage removal was showed to be higher on acid activated oil bean carbon than when using salt activated carbon. This proved that the particle size of the oil bean shells activated carbon is inversely proportional to the amount of eosin yellow dye removed, and is in agreement with (Kannan et al , 2008)., as they reported that the amount of eosin yellow adsorbed increases with the decrease in particle size. This is due to the increase in the availability of the surface area with increase in pores of the adsorbent.
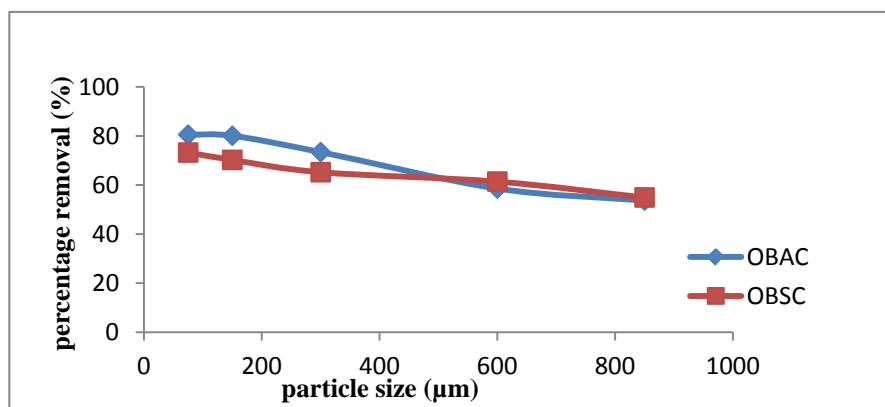
Figure 3.6: Effect of particle size on the extent of removal of Eosin yellow dye using OBAC and OBSC

3.3.3: Effect of initial pH on removal of eosin yellow dye

Figure 3.7 shows the effect of pH on dye removal at different initial solution of pH using an initial dye concentration of 50mg/L and adsorbent dosage of 0.5. From 3.7, it was observed that the removal of eosin yellow dye increased with the increased of pH from 2 to 10. But was noted that at pH of 8 gave the highest percentage removal but decreased at pH of 10. The percentage removal was showed to be higher on acid activated oil bean carbon than when using salt activated carbon. Lower adsorption of eosin yellow dye at lower pH is probably due to the presence of H^+ ions competing with the cations groups on the dye for adsorption sites. As surface charge density decreases with an increase in the solution pH, the electrostatic repulsion between the positively charged eosin yellow dye and the surface of the activated carbon is lowered, this may result in an increase in the rate of adsorption. The solution pH is one of the most important factors that control the sorption of dyes on sorbent materials. The initial pH influences the kinetics of sorption because the proton concentration decreases when the initial pH increases, and then the dye molecules have more chance to react with the active sites on the surface of the activated carbon because of a lower proton competition. (Olugbenga et al., 2013). Since pH 8 gave the highest percentage removal of eosin yellow dye from aqueous solution, it was then selected as the optimum pH for all further experiment.
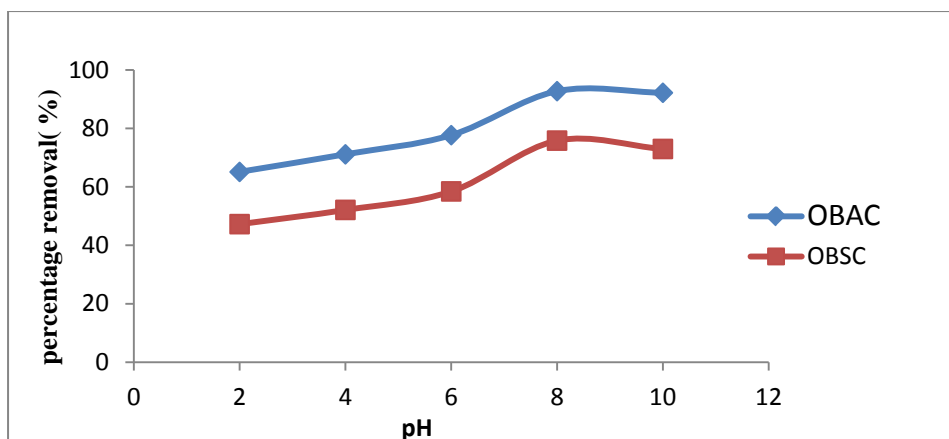
Figure 3.7: Effect of pH on the extent of removal of Eosin yellow dye using OBAC and OBSC

3.3.4: Effect of adsorbent dosage

Adsorbent dosage is an important parameter because this determines the capacity of an adsorbent for a given initial concentration of the adsorbate at the operating conditions. The effect of adsorbent dosage on the adsorption of eosin yellow dye onto activated carbon was presented in figure 3.8. The percentage of eosin yellow dye removed increased as the adsorbent dosage was increased over the range 0.5–4.0 and percentage removal obtained was from 70.95 to 97.15% for OBAC respectively. The percentage removal was showed to be higher on acid activated oil bean carbon than when using salt activated carbon. Increase in adsorption with adsorbent dosage could be attributed to increased surface area and availability of more adsorption sites. This observation was consistent with Langmuir hypothesis of an increasing competition among adsorbent particles for an organic substance with increasing number of adsorbent particles per unit volume.
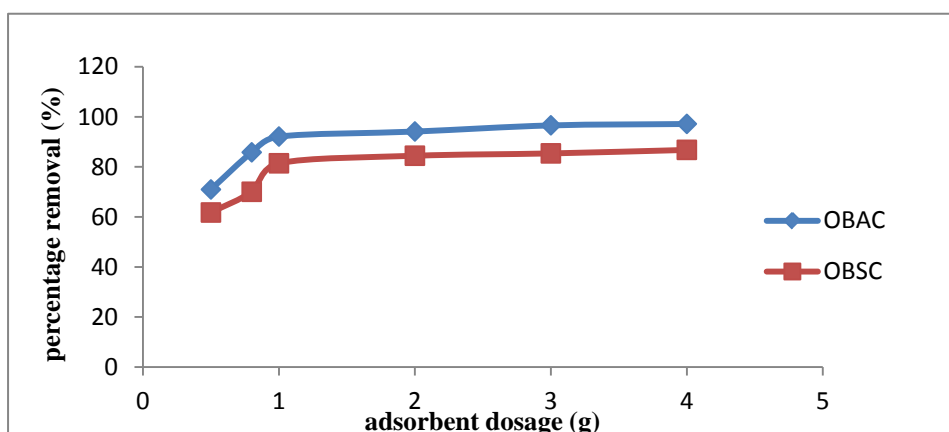
Figure 3.8: Effect of adsorbent dosage on the extent of removal of Eosin yellow dye using OBAC and OBSC

3.3.5: Effect of contact time

The effect of contact time on the adsorption of eosin yellow dye was presented in figure 3.9. The extent of dye removal by activated carbon increased with the increased of contact time. The removal of eosin yellow by adsorption using activated carbon was found to gradually increase until equilibrium was reached at 120 minutes. At equilibrium, the amount of eosin dye desorbed from the adsorbent was equal to those adsorbed onto it, i.e. they are in a state of dynamic equilibrium; hence an indication of the maximum adsorption capacity of the adsorbent at the experimental conditions. The percentage removal was showed to be higher on acid activated oil bean carbon than when using salt activated carbon. With increase in agitation time, the external mass transfer coefficient increases, resulting in quicker adsorption of the eosin dye molecules by the adsorbents. (Olugbenga et al., 2013).
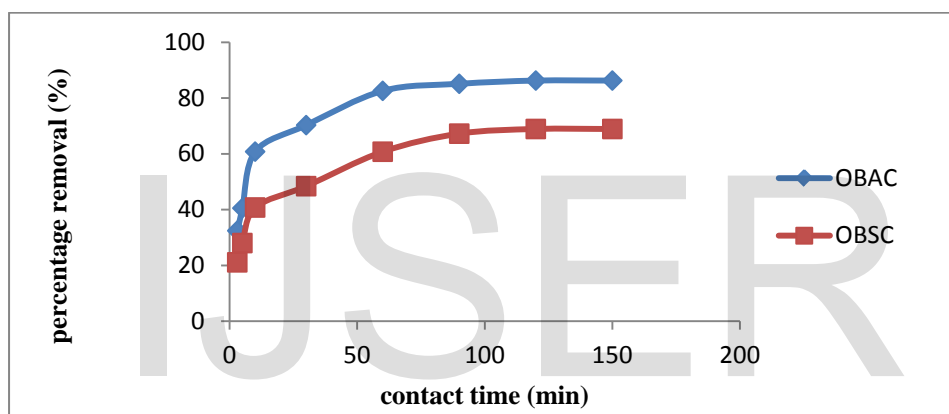
Figure 3.9: Effect of contact time on the extent of removal of Eosin yellow dye using OBAC and OBSC.

3.3.6: Effect of temperature on removal of eosin yellow dye

Temperature has an important effect on the process of adsorption. The percentage of eosin yellow dye adsorption was studied as a function of temperature in the range of $30^{o}C$ - $60^{o}C$. The results obtained are presented in figure 3.10, which showed that as the temperature increases, the percentage removal of the eosin yellow dye decreases. The maximum percentage removal (93.52%) was at $30^{o}C$ which made it an optimum temperature for further experiments in this work. The percentage removal was showed to be higher on acid activated oil bean carbon than when using salt activated carbon. The decrease in percentage of adsorption with the increase in temperature may be due to desorption caused by an increase in the available thermal energy. Higher temperature induces higher mobility of the adsorbate

causing desorption. Then the quantity of adsorption was found to increase as the temperature decreased meaning that the process is exothermic in nature (Ghassan, 2010).
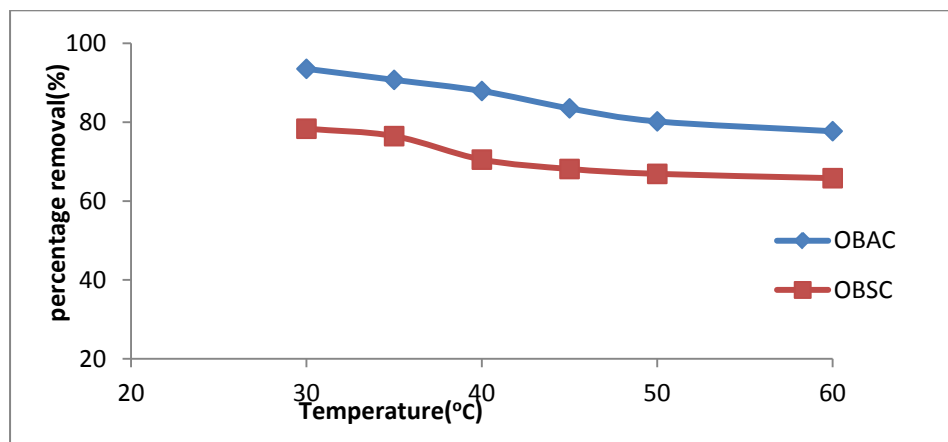

Figure 3.10: Effect of temperature on the extent of removal of Eosin yellow dye using OBAC and OBSC

3.4 Adsorption Kinetics.

Adsorption kinetics was investigated for better understanding of the dynamics of adsorption of eosin dye onto the two activated (acid and salt) oil bean shell in order to obtain predictive models that allow estimations of the amount of eosin dye adsorbed with respect to time. Adsorption kinetics models were used to check adsorptive behavior of the process.

3.4.1: Pseudo First Order kinetic model.

Both of pseudo-first order and pseudo-second order models were used to predict the kinetic data of eosin yellow dye adsorption on oil bean shell activated carbon. The kinetic experimental data and the models fit using eosin yellow dye for adsorption onto the acid and salt activated carbon were shown in figure 3.11 and figure 3.12 respectively. The pseudo-first order and pseudo-second order parameters were summarized in Table 2.
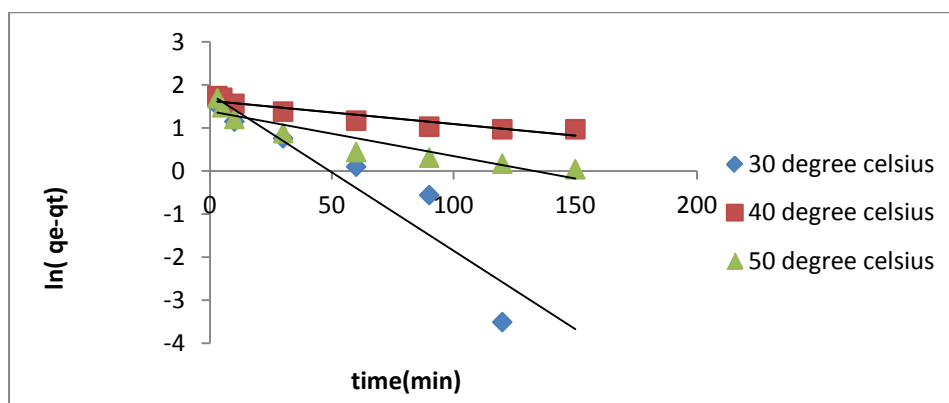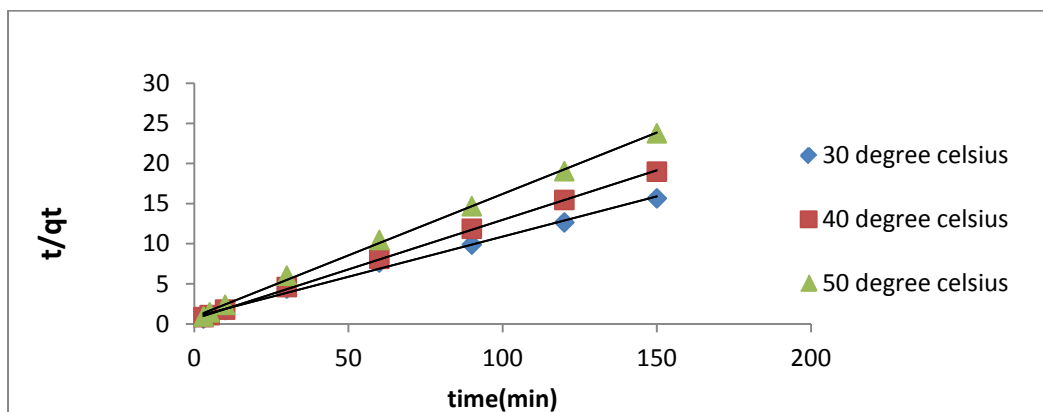

Figure 3.11: A plot of pseudo first order for adsorption kinetics of Eosin yellow dye on OBAC using different temperatures.
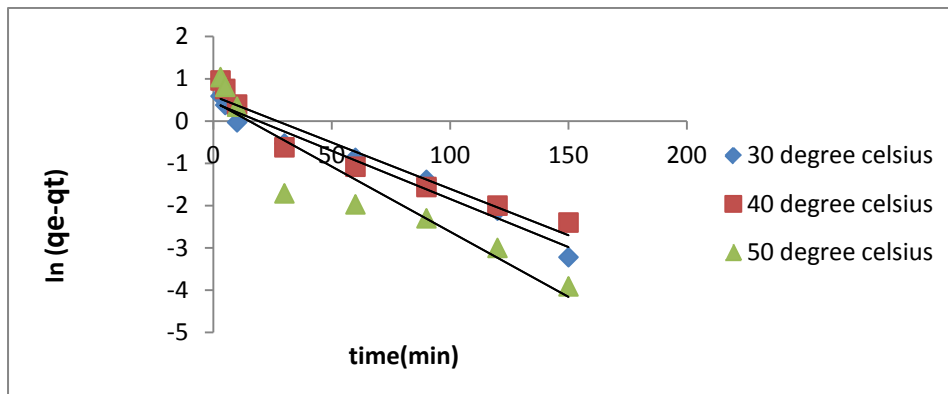
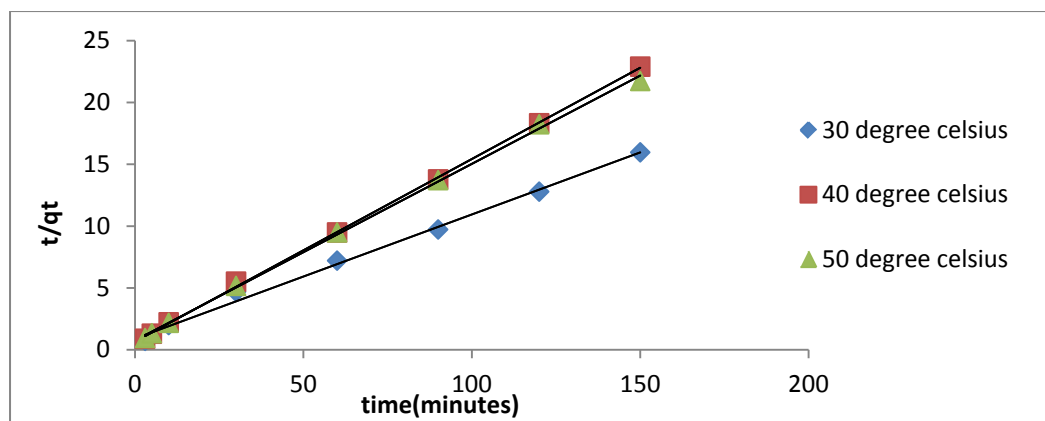Figure 3.12: A plot of pseudo first order for adsorption kinetics of Eosin yellow dye
on OBSC using different temperatures

3.4.2: Pseudo-Second Order kinetic model

From the values of R^2 for both models, it can be seen that pseudo-second order model gave better correlation than the pseudo first order. For pseudo-second order, the R^2 value obtained were 0.994 and 0.955 at 30°C using OBAC and OBSC respectively which are very high and this indicated that the adsorption of eosin yellow dye onto oil bean shell activated carbon obeyed the pseudo-second order kinetic model. The better applicability of pseudo-second order rather than pseudo-first kinetic model on the adsorption of eosin yellow dye was also reported by (Olugbenga et al., 2013).

Figure 3.13: A plot of pseudo second order for adsorption kinetics of Eosin yellow dye on OBAC using different temperatures.

Figure 3.14: A plot of pseudo second order for adsorption kinetics of Eosin yellow dye on OBSC using different temperatures.

Table 2. Comparison of pseudo first and second order kinetic models rate constants, experimental and calculated qe values obtained at different temperature

| Adsorbent	Pseudo first order model				Pseudo second order model		
	Temp (^{o}C)	K_1 (1/min)	q_e cal. (mg/g)	R^2	K_2 (g/mg/min)	q_e cal. (mg/g)	R^2
OBAC	30	0.36	5.98	0.889	0.01	10.00	0.994
	40	0.02	4.00	0.874	0.02	8.13	0.999
	50	0.02	5.10	0.880	0.03	6.54	0.998
OBSC	30	0.51	1.54	0.972	0.01	10.00	0.995
	40	0.05	1.80	0.928	0.03	6.80	0.999
	50	0.07	1.59	0.885	0.03	7.04	0.999

3.5   Adsorption Isotherm

3.5.1: Langmuir isotherm: The experimental equilibrium adsorption data was analyzed using Langmuir adsorption isotherm model. As shown in figure 3.16, the experimental data conforms to langmuir isotherm.
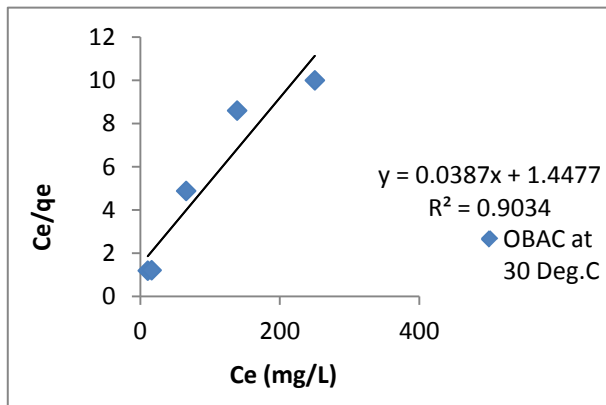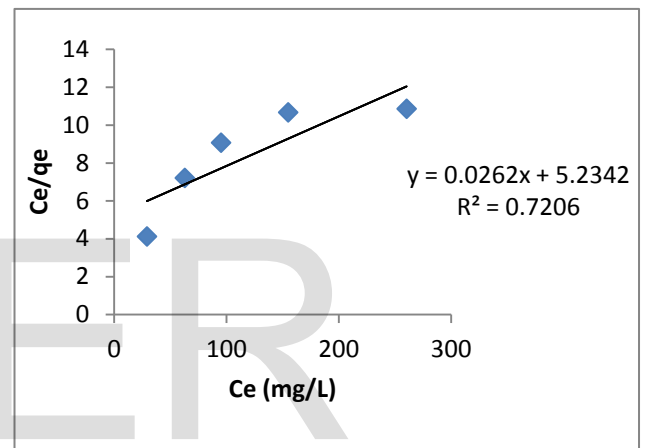
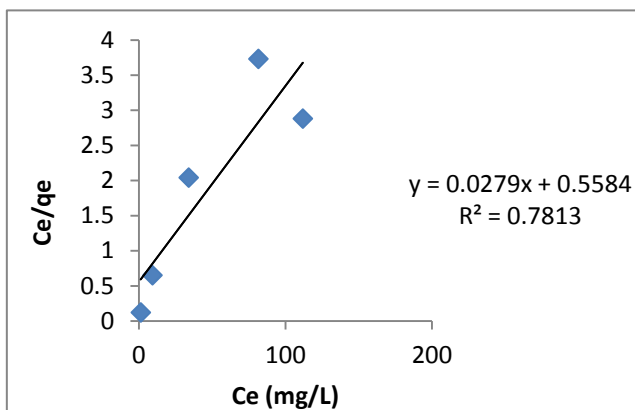3.15: Langmuir adsorption isotherm plot of Eosin yellow dye on OBAC at 30^0C
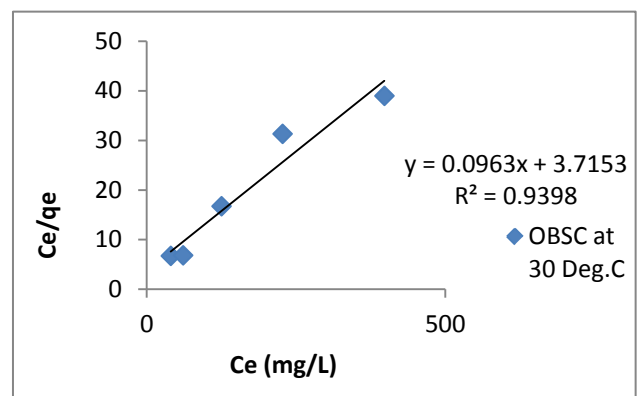
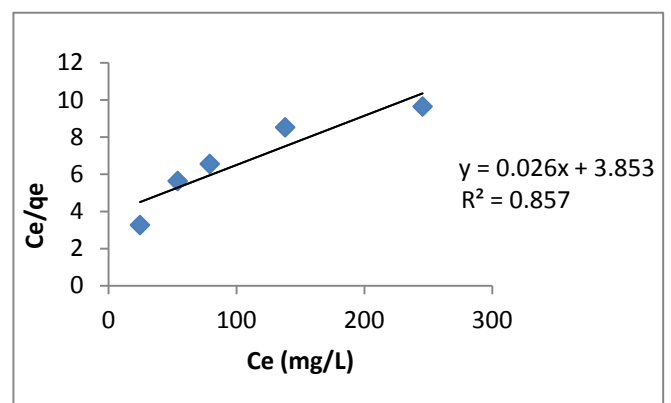3.16: Langmuir adsorption isotherm plot of Eosin yellow dye on OBAC at 30^0C
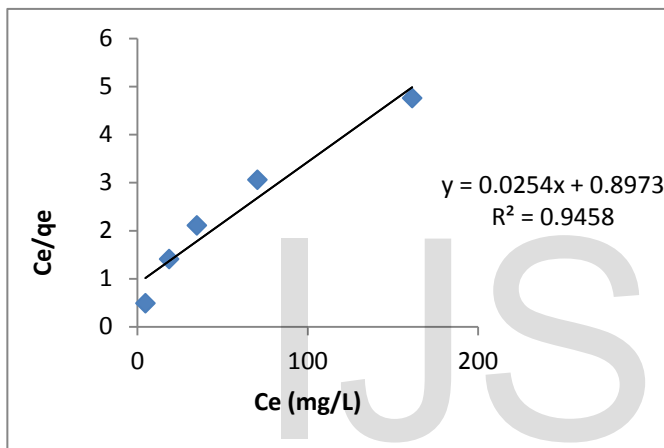
3.17: Langmuir adsorption isotherm plot of Eosin yellow dye on OBAC at 40^0C

3.18: Langmuir adsorption isotherm plot of Eosin yellow dye on OBSC at 40^0C
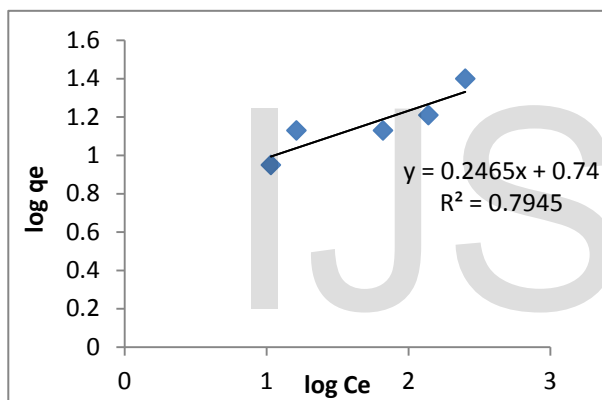

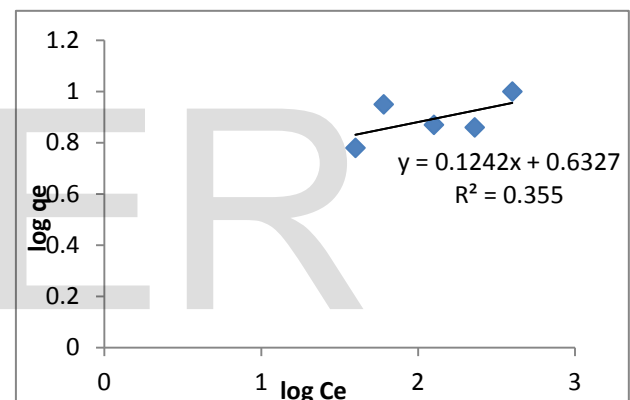3.19: Langmuir adsorption isotherm plot of Eosin yellow dye on OBAC at 50^0C

3.20: Langmuir adsorption isotherm plot of Eosin yellow dye on OBSC at 50^0C
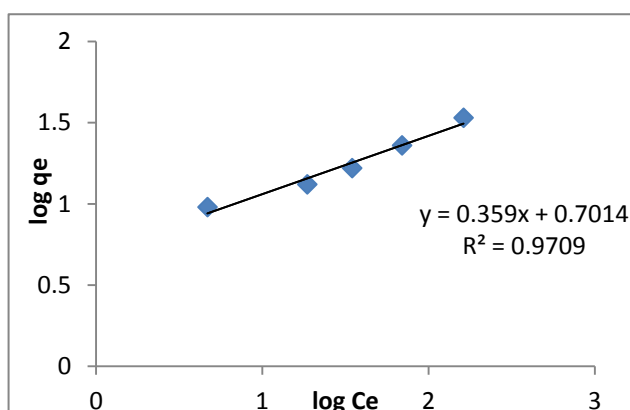
3.5.2 Freundlich isotherm:

From figure 3.21 to 3.21 for Freundlich isotherm plots, the experimental data showed a poor agreement with the isotherm model due to the R^2 value at 30^0C for both OBAC and OBSC which does not lie in the acceptable range ($0.9 < R^2 < 1.0$), but the model fitted well by the adjustment of temperature at 40^0C and 50^0C for both samples with the regression coefficients closed to 1. The intensity of adsorption (n) was obtained from the slope. On the other hand, the results suggested that eosin yellow dye was favourably adsorbed by the activated carbon since the value of the intensity of adsorption (n) was greater than unity (n >1) as shown in Table 3. From the intercept, the Freundlich bisorption constant was noted to be 5.50 L/mg and 4.29 L/mg onto OBAC and OBSC at 30^oC respectively.
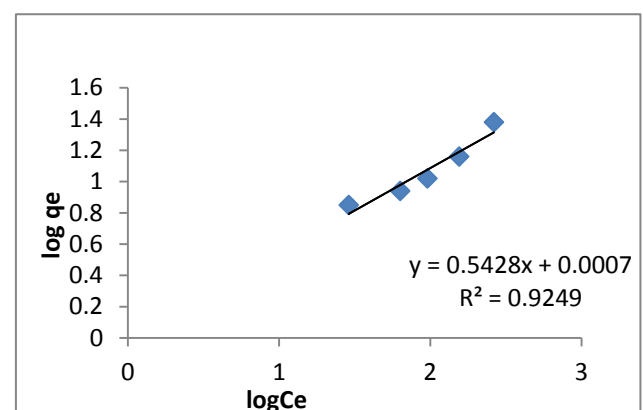

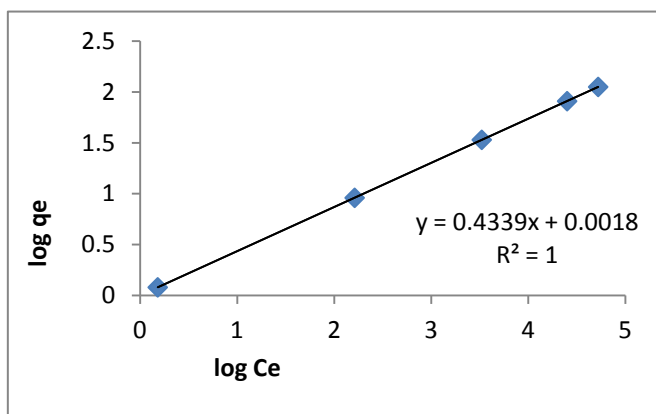3.21: Freundlich adsorption isotherm plot of Eosin yellow dye on OBAC at 30^0C

3.22: Freundlich adsorption isotherm plot of Eosin yellow dye on OBSC at 30^0C

3.23: Freundlich adsorption isotherm plot of Eosin yellow dye on OBAC at 40^0C

3.24: Freundlich adsorption isotherm plot of Eosin yellow dye on OBSC at 40^0C

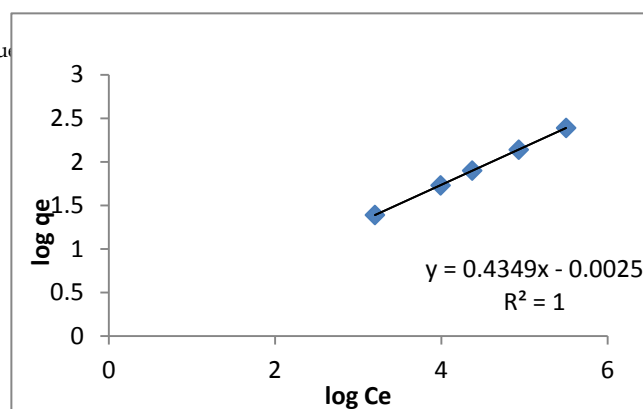3.25: Freundlich adsorption isotherm plot of Eosin yellow dye on OBAC at 50^0C

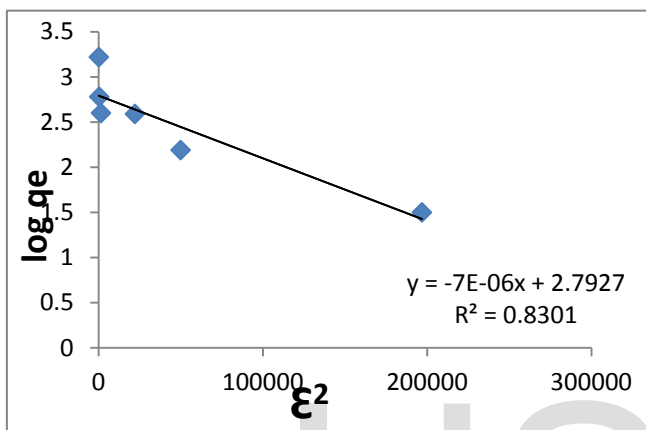3.26: Freundlich adsorption isotherm plot of Eosin yellow dye on OBSC at 50^0C

Table 3: Comparison of Langmuir and Freundlich constants and correlations for adsorption of eosin yellow dye onto OBAC and OBSC

| Langmuir isotherm model						Freundlish isotherm model		
Adsorbent	Temp (^{o}C)	b (L/mg)	q_o (mg/g)	R_L	R^2	K_F	n	R^2
OBAC	30	0.026	26.32	0.27	0.903	5.50	4.07	0.794
	40	0.028	40.00	0.26	0.945	5.02	2.79	0.970
	50	0.048	37.04	0.17	0.781	1.00	1.00	1.00
OBSC	30	0.026	10.42	0.27	0.939	4.29	8.06	0.355
	40	0.005	38.46	0.67	0.720	1.00	1.85	0.924
	50	0.007	38.46	0.59	0.857	1.00	1	1.00

From Table 3, the maximum adsorption capacity of eosin yellow dye (q_o) was obtained to be 26.32 mg/g from the slope at 30^oC for oil bean acid activated carbon (OBAC) and 10.42 mg/g for oil bean salt activated carbon (OBSC) respectively. The Langmuir equilibrium constant (b) was calculated from the intercept of the linear plot to be 0.026 L/mg for both (OBAC) and (OBSC) at 30^oC respectively. The Langmuir adsorption constant called separation factor or equilibrium parameter (R_L) indicates the shape of the isotherm to be either irreversible ($R_L = 0$), favourable ($0< R_L<1$) or linear ($R_L=1$) or unfavourable ($R_L>1$) (Malik 2004), moreover, R_L obtained was 0.27 for both OBAC and OBSC at 30^oC suggesting that Langmuir isotherm model was favoured at the concentration studied. Also, from (Table 3), the correlation coefficient (R^2) obtained was 0.903 and 0.939 at 30^oC onto OBAC and OBSC respectively. Since the value of correlation coefficient lies in the acceptable range ($R^2>0.90$). Therefore, the experimental data fitted well into the Langmuir isotherm model. (Jaynes and Boyd, 1991). This eventually indicates that the homogenous nature of the activated carbon surface and each dye molecule on activated carbon adsorption surface has equal adsorption activation energy. The result also showed the formation of monolayer coverage of dye molecule at the outer surface of activated carbon.

3.5.3 Dubinin-Radushkevich

From the plots of Dubinin-Radushkevich adsorption isotherm displayed in figures 3.27 and 3.28 for OBAC and OBSC respectively, it was shown that the constant such as q_s, and K_{ad} were determined. From the linear plot of DRK model, q_s was determined to be 16.31mg/g, the mean free energy, E= 0.27KJ/mol indicating a physio-sorption process (Dada et al., 2012) and the R^2 =0.830 and 0.863 for OBAC and OBSC, which was still low to compared to Langmuir isotherm
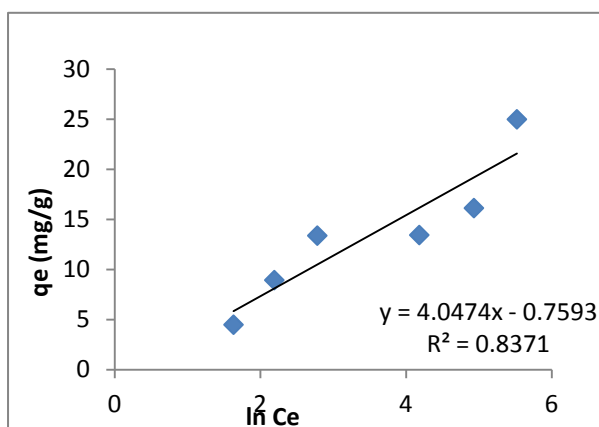

3.27: Dubinin-Radushkevich adsorption isotherm plot of Eosin yellow dye on OBSC at 30^0C
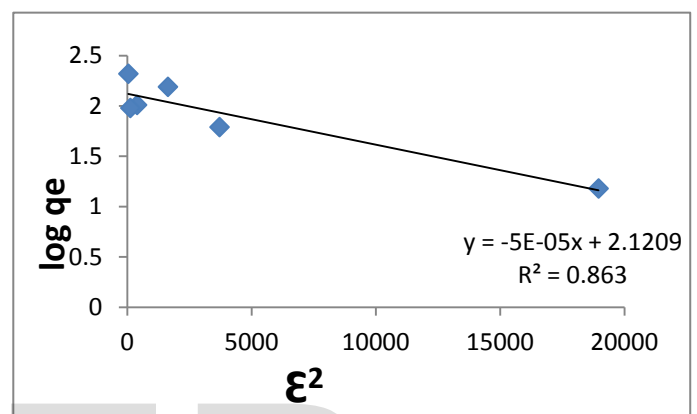

3.28: Dubinin-Radushkevich adsorption isotherm plot of Eosin yellow dye on OBSC at 30^0C

3.5.3: Temkin Isotherm

From the Temkin plot shown in figure 3.29 to 3.30, the following values were estimated: A_T = 0.83 L/g, B = 612J/mol ,which is an indication of the heat of sorption indicating a physical adsorption process and the R^2 = 0.837 and 0.669 for OBAC and OBSC respectively, which was still low to compare to Langmuir isotherm. Hence, Temkin isotherm model does not fit the experimental data.

3.29: Temkin adsorption isotherm plot of Eosin yellow dye on OBAC at 30^0C
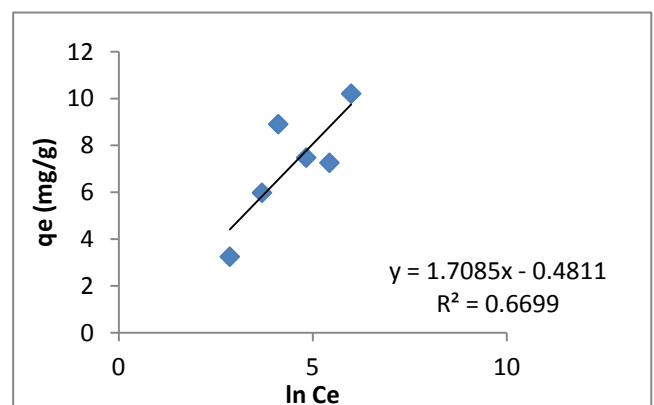
3.30: Temkin adsorption isotherm plot of Eosin yellow dye on OBSC at 30^0C

3.6: Thermodynamic study

3.6.1 Change in Enthalpy

Thermodynamic parameters ΔH^o, ΔS^o, ΔG^o were determined to investigate the feasibility, spontaneity and the nature of the reaction. This was achieved by Van't Hoff's plot of $\ln \frac{q_e}{c_e}$ against $\frac{1}{T}$ (figure 3.31 and figure 3.32) from Gibbs-Helmholtz equation $\ln(\frac{q_e}{C_e}) = -\Delta \frac{H^o}{RT} + \frac{\Delta S^o}{R}$. From the slope, change in enthalpy (ΔH^o) was -27.02KJ/mol which indicates that the reaction process is exothermic, this confirmed that the percentage of adsorption decreases as the temperature increases due to the desorption caused by an increase in the available thermal energy showing that is exothermic process. (Ghassan, 2010).

3.6.2 Change in Entropy

From figure 3.31and 3.32 respectively, the change in entropy (ΔS^o) were obtained to be -80.23KJ/mol and -50.74KJ/mol from intercept both onto OBAC and OBSC respectively. The negative values of ΔS^o confirmed the decreased randomness at the solid-liquid interface during adsorption (Mogaddasi et al.,2010).

3.6.3 Change in Free Gibbs Energy

Change in Gibbs free energies were obtained from $\Delta G^o = \Delta H^o - T \Delta S^o$ which were -2.71KJ/mol and -0.40KJ/mol at 30°C onto OBAC and OBSC respectively. The negative and small values of ΔG^o values confirmed the spontaneous nature and feasibility of the adsorption process (Olugbenga et al., 2013).
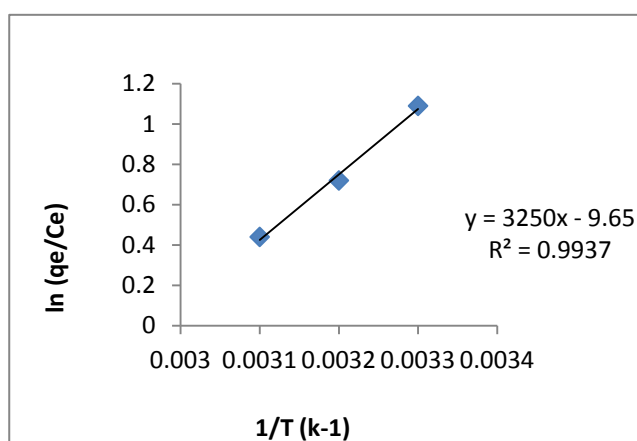

Figure 3.31: Van't Hoff plot of adsorption of
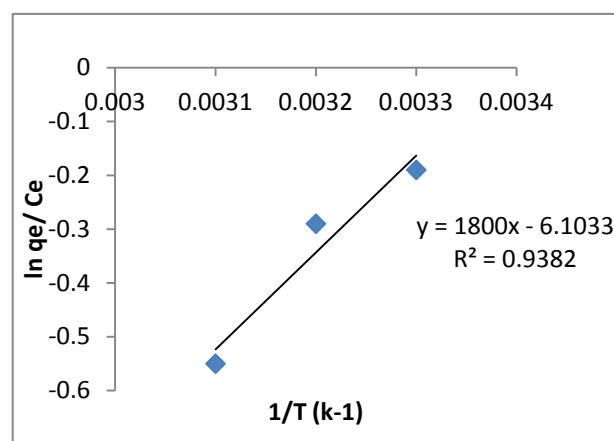
Eosin yellow dye onto OBAC

Figure 3.32: Van't Hoff plot of adsorption of

Eosin yellow dye onto OBSC

4.0   CONCLUSION

The activated carbon was produced from oil bean shells using sulphuric acid and potassium chloride as a chemical activation agent. The percentage removal of eosin yellow dye onto produced oil bean acid activated carbon was concluded to have the highest value than the carbon produced from salt activation. This was as a result of high available of microscopic pores and area created on the adsorbent by the strong acid which enhanced the adsorption rate process. From the experimental results, it was found that percentage of EY dye adsorbed vary with initial solution pH, initial concentration of the EY, temperature, particle size, contact time and adsorbent dosage onto OBAC and OBSC. The adsorption equilibrium data was studied but found to fit the Langmuir isotherm ($R^2 > 0.90$) at 30°C. The Pseudo-second order kinetic model was found to be more favorable ($R^2 > 0.90$) at 30°C. The thermodynamic study gave negative values of ΔH^o at 30°C which indicated that the reaction process was exothermic. The negative values of ΔS^o confirmed the decreased randomness at the solid-liquid interface during adsorption and also the negative and small values of ΔG^o values confirmed the spontaneous nature and feasibility of the adsorption process. The adsorption data suggest that activated carbon produced from oil bean shell could be used as an alternative adsorbent rather than commercial activated carbon. Moreover, it may be useful for designing and fabrication of an economically cheap treatment process using batch or stirred tank flow reactors for the removal of EY dye.

NORMENCLATURE:

OBAC: Oil Bean Acid Activated Carbon

OBSC: Oil Bean Salt Activated Carbon

EY: Eosin Yellow

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