Dutse Journal of Pure and Applied Sciences (DUJOPAS) Vol. 4 No. 1 June 2018

ADSORPTION STUDY OF METHYLENE BLUE ON MESOPOROUS SILICA SYNTHESIZED FROM RICE HUSK

A. S. Kovo Department of Chemical Engineering, School of Engineering and Engineering Technology, Federal University of Technology, Minna, Nigeria

A.F. Ali Department of Environmental Management, Bayero University, Kano State, Nigeria

Amah J. I. Department of Chemical Engineering, School of Engineering and Engineering Technology, Federal University of Technology, Minna, Nigeria

Anthony S. O. Department of Chemical Engineering, School of Engineering and Engineering Technology, Federal University of Technology, Minna, Nigeria

Abstract

Amorphous spherical mesoporous silica particle in the size of micrometer was produced from Kwakuti Rice Husk(KRH) by using equal concentrations of white rice husk on 5.6 wt.% each in sodium hydroxide to form sodium silicate solutions. The raw rice husks were washed with distilled water for three hours to enhance purity of silica. Acid leaching of rice husks prior to calcination and alkali treatment was also performed. The calcination and leaching with acid helped to remove the metallic oxide impurities in the rice rusk. Rice husks were calcinated at temperatures of 600 °C in a muffle furnace to obtain white rice husk (WRH) and treated with sodium hydroxide of known concentrations. The sodium silicate solutions obtained were titrated with phosphoric acid in the presence of alcohol as co-solvent to obtain silica. The SEM result of the synthesized mesoporous silica showed a spherical morphology with an average particle size of 3 µm. the FTIR result reveal the identification of chemical bond in the mesoporous silica by reproducing an infrared absorption spectrum while the surface of 1175 m²/g was obtained using BET technique. The adsorption performance of mesoporous silica synthesized from KRH was tested using methylene blue. The *adsorption study was conducted under varying pH (2-11), adsorbent dosage (50-200mg), temperature (30-60^{o}C), and time (10-60min). The best adsorption was reached atpH in the range of 8-11,when using 50mg of mesoporous silica and at a temperature of 40^{o}C, to give a maximum adsorption capacity of 40mg.g-1. Equilibrium was reached at 50 min. The equilibrium data were evaluated using Langmuir and Freundlich isotherms and were found to fit well to the Freundlich isotherm with a correlation coefficient of 0.909. The adsorption kinetics best described by pseudo second order model. The results obtained from the study reveals that mesoporous silica synthesized from Rice Husk could be used as an effective adsorbent for methylene blue removal.*

Keywords: Kwakuti Rice Husk, Mesoporous Silica, Selective Adsorption, Methylene Blue, Waste Water

1.0 INTRODUCTION

Adsorption processes is now widely used as method of choice to remove dyes from waste water because of several reason which include simplicity and cheapness of the process. It is also a highly efficient technology and are easily adaptable with many ubiquitous materials being used as adsorbent in the process. Among the several adsorbents which has being used as adsorbent during the adsorption process such as activated carbon, Zeolites etc. Effort has continue to explore the suitability of mesoporous materials as an adsorbent because of the presence of large pore and surface area.

Among the mesoporous materials that is easy to obtained is called mesoporous silica. Mesoporous silica are materials that consist primarily of about 97% silica, and 3% alumina. It is silica based nanoparticles containing many empty channels (mesopores) arranged in a honeycomb-like pore configuration. They poses pore size that fall between 2nm-50nm. It offer unique structural properties such as large pores, tunable pore diameter, large surface area, ordered and stable mesostructure, dual functional surfaces(exterior and interior pore surfaces), and modifiable morphology (Trewyn et al., 2007). Their many unique properties have resulted in their development and synthesis for both industrial and technological applications, for instance; their large surface area make them highly effective for catalytic purposes and drug loading, their pore structure make them important as excellent adsorbent (Yang et al., 2003).Therefore mesoporous silica as an alternative material can be synthesized from inexpensive materials such as rice husk. Other material that can easily be used as source of mesoporous silica include coconut husk, egg shell, etc. Mesoporous silica obtain from rice husk poses well defined pores and a large surface area. Rise husk is considered as a waste material in rice milling industry; however, the thermal degradation of rice husk produces an invaluable substance called white rice husk ash, which contains almost pure silica (RHS, 95%) a highly porous and reactive amorphous material. The process involves the thermal treatment of rice husk with HCl to produce white rice husk(WRH), which then reacts with an NaOH in an hydrolysis and condensation reactions to produce a sodium silicate solution(SSS). The ability of functionalized mesoporous silica to serve as excellent adsorbent with good selectivity makes it the favorite material for the elimination of colored materials (methylene blue) from industrial waste water.

Methylene blue is a dye used by manufacturing processes such as; rubber, textile, cosmetic, plastic, printing, etc. the effluent from these industries contain methylene blue and are passed into water bodies, creating severe environmental problem. For instance, the presence of dye in water systems limits the diffusion of sunlight through the water bodies and thus prevents photosynthesis in aquatic plants, impedes growth of bacterial and causes harmful effect to humans such as skin irritation, mutation, allergic, dermatitis, cancer, etc.

Several techniques have been used to eliminate the dye in industrial waste water, among which are sono-chemical degradation, chemical, biological process, photo-catalytic degradation using UV TiO_2, electrochemical process, biodegradation, chemical coagulation flocculation degradation process, adsorption process, Fenton biological treatment etc. However selective adsorption is the most preferred technique because it removes the dye and also creates a platform for dye recovery and reuse. Other advantages of adsorption is the possibility to regenerate the adsorbent, adsorbate recovery, and the operation that generates no sludge.

Therefore adsorption process by suitable adsorbent such as mesoporous silica obtained from rice husk presents a solution to the environmental problem that industrial waste water creates and this is the hallmark and objective of this paper.

2.0 MATERIALS AND METHOD

2.1 Materials

Some of the material and equipment used during the experiment include sodium hydroxide, hydrochloric acid, distilled H_20 and methylene blue,ethanol, hydrochloric acid, phosphoric acid and sodium hydroxide; UV – spectrophotometer, scanning electron microscope (SEM), Fourier transform Infra-red spectroscopy (FTIR) and Surface area analyzer

2.2 Preparation of Mesoporous Silica

Rice husk (RH) obtained from Kwakuti, Niger state was washed thoroughly with water to remove the mud and dirt then allowed to dry overnight to obtain light weight rice husk. This water washed rice husk was referred to as WWRH.100 g of water washed rice husk (WWRH) was added to 1000 ml of 2 M HCl solution in a beaker and then heated up to a temperature of 90 ^{0}C for 2 h. The solution was allowed to cool and then continuously washed and filtered with distilled water until it was neutralized to pH 7. The RH was filtered out and dried overnight. The RH finally gotten was light weight and had aconsiderable amount of inorganic material removed due to leaching. This Acid Washed

Rice Husk was referred to as (AWRH) was thermally treated at 600 ^{0}C for 4 h in a muffle furnace to produce white rice husk (WRH).Inside a 250 ml conical flask, 100 ml of 2 M NaOH was prepared and equal loadings of 5.6 wt.% of white rice husk (WRH) was separately added to it. The flask together with its content was placed on a heating plate maintained at a temperature of 90 ^{0}C with continuous stirring for 2 h. The solution turned transparent brown-black in colour with visible un-dissolved particles. This solution was cooled down and then filtered using a filter paper. The clear colourless filtrate contains the sodium silicate solution (SSS) which was further used to obtain silica.

The clear sodium silicate solutions were titrated with concentrated H_3PO_4 under continuous stirring in the presence of 10 ml ethanol as co-solvent. During the addition of H_3PO_4 drop wisely, white gelatinous thick precipitate was formed.The precipitate obtained after precipitation is allowed to settle down and filtered using a filter paper and later 50 ml of boiling water is also added to the filter paper so as to wash off any salt (Na_3PO_4) formed due to the acid base side reaction. The residue left on the filter paper is pure white mesoporous silica which is dried in an oven at 90 ^{o}C and later the silica scrapped off the dried filter paper and stored in sampling bottles for further analysis and characterization. The characterization of the mesoporous silica was done using Fourier Transform Infrared Spectroscopy (FTIR), the amorphous nature and silica particle size measurement was determined using scanning electron microscope (SEM) and determination of surface area was done using Brunauer-Emmett-Teller (BET) method.The mesoporous silica which was synthesized from rice husk was first dried in an oven at 90^{o}C for 4 hour to remove moisture. The dried silica particles were then grounded and sieved using a 250um sieve. This was done to increase the surface area of the silica.

2.3 Adsorption Study

The adsorption of methylene blue dye on mesoporous silica was conducted in a batch set-up, the effect of parameters such as; adsorbent dosage, pH, contact time, and temperature were studied.

2.3.1Effect of pH

50ml of 200mg/L methylene blue (stock solution) was taken in four 250ml conical flasks, the pH values of the solution were regulated using 1M HCl or NaOH to 2, 5, 8, and 11 respectively and 200mg of mesoporous silica was added to each solution. The flasks were then placed in a thermostatic shaker bath and shaken at 200rpm for 20 minutes and at 30^{o}C. The final concentration of methylene blue was measured by means of UV-spectrophotometer, and a graph of q_e vs. initial pH was plotted.

2.3.2 Effect of Adsorbent Dosage

50ml of 200mg/L methylene blue (stock solution) was taken in four 250ml conical flasks, different masses of 50mg, 100mg, 150mg, and 200mg mesoporous silica was put in the conical flasks, and the flasks were then placed in a thermostatic shaker bath and shaken at 200rpm for 20 minutes and at 30^{o}C. The final concentration of methylene blue was measured using UV-spectrophotometer.

2.3.3 Effect of Temperature

50ml of 200mg/L methylene blue (stock solution) was taken in four 250ml conical flasks, 200mg of mesoporous silica was added to each solution and the conical flasks were placed in a thermostatic shaker bath in tune as the temperature was regulated to 30^{o}C, 40^{o}C, 50^{o}C,and 60^{o}C respectively. The final concentration of methylene blue was measured by means of UV-spectrophotometer.

2.3.4 Effect of Time

50ml of 200mg/L methylene blue (stock solution) was taken in four 250ml conical flasks,200mg of mesoporous silica was added to each solution and the conical flasks were placed in a thermostatic shaker bath, and shaken proceeded for 10, 20, 30, and 40 minutes respectively. The final concentration of methylene blue was measured using UV-spectrophotometer, and a graph of q_e vs. time was plotted.

To determine adsorption capacity at equilibrium qe (mg g^{-1}) using;

$$qe = \frac{(Co-Ce)V}{W} \qquad (1)$$

where, W (g) is the mass of adsorbent used, V (L) is the volume of the solution, and Co and Ce (mg L−1) are the liquid phase concentrations of dye at initial and equilibrium stages respectively.

The percentage of dye removal is calculated using;

$$\%Removal = \frac{Co-Ce}{Co} * 100 \qquad (2)$$

3.0 Results and Discussion

3.1Characterization

FT IR

The FTIR spectra0f the Water Washed Rice Husk (WWRH) is sh0wn in Fig.1. A br0ad band between 3550 t0 3050 cm^{-1} indicates the presence 0f is0lated and surface Si-OH gr0ups. The pred0minant abs0rbance peaks at 1045 cm^{-1} is as a result 0f the asymmetric stretching vibrati0ns 0f sil0xane b0nds (Si-O-Si) and the c0rresp0nding stretch at 250 cm^{-1}. Similar results were 0btained in a previ0us w0rk carried 0ut by (Khushb00 et al., 2013)and the br0ad band which indicates the presence 0f is0lated and surface Si-OH gr0ups were f0und t0 be at

3400 $cm^{-1}$and 3435 $cm^{-1}$and the pred0minant abs0rbance peaks which indicate the Si-O-Si stretchingvibrati0n was at 1085 $cm^{-1}$and 1100 cm^{-1} respectively. The FTIR spectra0f white rice husk (WRH) is sh0wn in Fig.2.A pred0minant abs0rbance peaks at 1050 cm^{-1} is 0bserved which is as a result 0f the asymmetric stretching vibrati0ns 0f sil0xane b0nds (Si-O-Si) and the c0rresp0nding symmetric b0nd stretching vibrati0n at 250 cm^{-1}. The FTIR spectra0f mes0p0r0us silica is sh0wn in Fig.3. In this case, a br0ad band between 3500 t0 3050 cm^{-1} wavenumber is due t0 the stretching 0f vibrati0ns 0f the 0H b0nd fr0m the silan0l gr0ups (SiOH) which is due t0 the ads0rbed water m0lecules 0n the silica surface. The br0ad band at 1650 cm^{-1} is due t0 the Si-0-Si asymmetric b0nd stretching, while the c0rresp0nding band at 1000 cm^{-1} has been assigned t0 the t0 the netw0rk Si-0-Si symmetric b0nd stretching vibrati0n. In a similar study by (Ok0r0nwk0 et al., 2013), the br0ad band was between 3470-3410 cm^{-1} indicating 0H b0nd fr0m the silan0l gr0ups (SiOH), band at 1090-1070 cm^{-1} f0r the Si-O-Si asymmetric b0nd stretchingand the band at 806-791 cm^{-1} f0r the netw0rk Si-0-Si symmetric b0nd stretching vibrati0n.

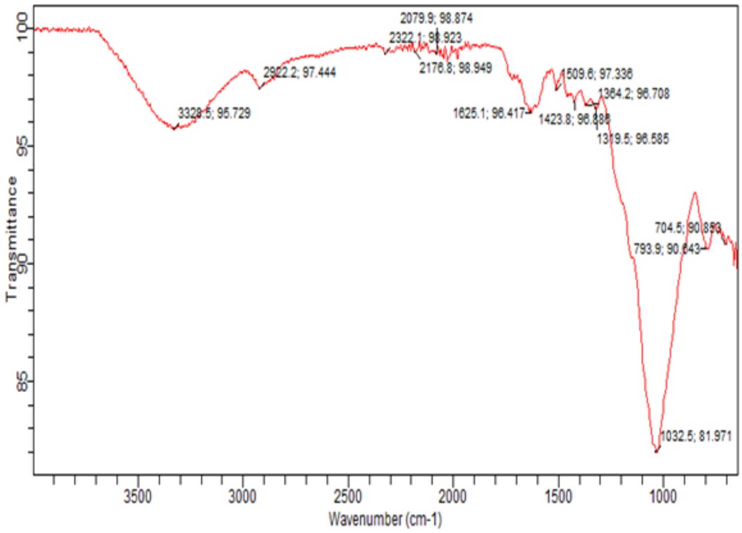

Fig. 1 FTIR Spectra of WWRH

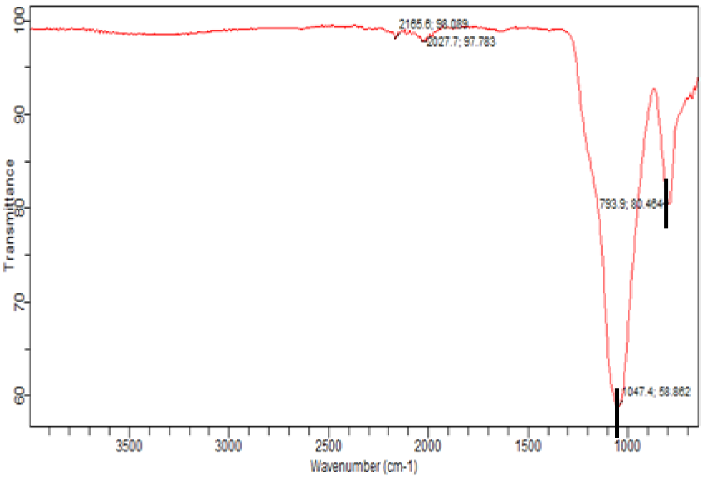

Fig.2 FTIR Spectra of WRH

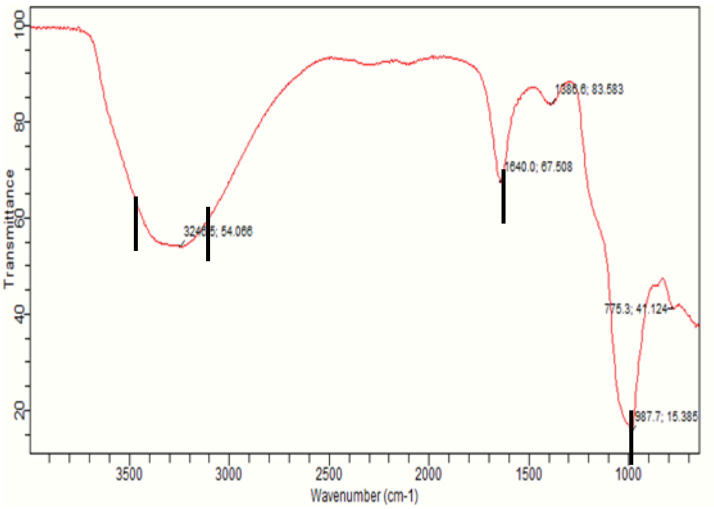

Fig. 3FTIR spectra of mesoporous silica

SEM

Fig. 4indicates the SEM images 0f the mes0p0r0us silicaat f0ur different magnificati0ns 0f 100 000×, 50 000×, 24 000× and 12 000× respectively synthesized via s0l- gel techniques fr0m KRH. It is 0bserved that the mes0p0us silica is am0rph0us in nature with the particles exhibiting a spherical m0rph0l0gy which agrees with a previ0us research carried out in which the its average particle size 0f 3 µm was obtained. (Khushb00 et al., 2013)0btain theirs as 3.2 µm. This spherical m0rph0l0gy and particle size is as a result 0f the c0ncentrati0n 0f the white rice husk (WRH) used during the synthesis 0f the mes0p0r0us silica. Apart fr0m the c0ncentrati0n 0f WRH, the c0-s0lvents equally play a significant r0le in the m0rph0l0gy and size 0f the mes0p0r0us silica. F0r instance, the additi0n 0f ethan0l as c0-s0lvent generally results in spherical particles with increment in dispersi0n, which c0ntributes t0 the miscibility 0f ethan0l with the s0dium silicate s0luti0n as 0bserved.

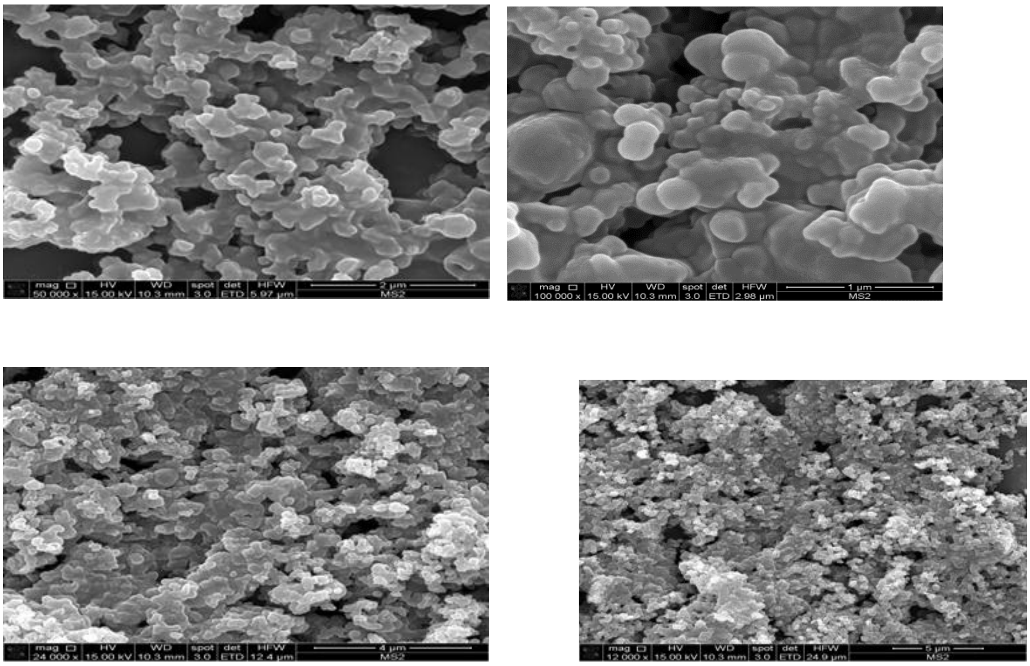

Fig. 4 SEM images of mesoporous silica synthesized from KRH

3.2 Adsorption

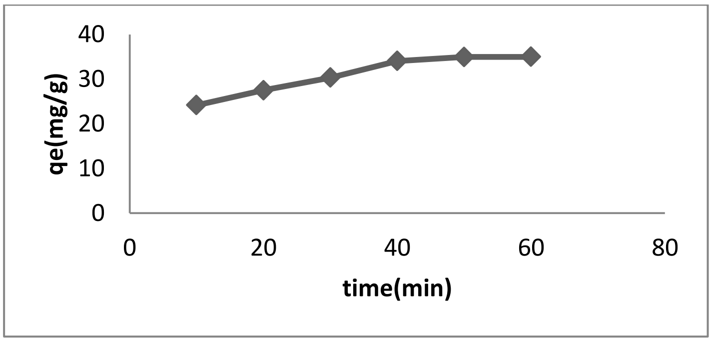

Fig. 5 Effect of time on the adsorption MB on mesoporous silica

The effect of contact time on the adsorption of methylene blue was studied at 30^{o}C, 200 mg adsorbent dosage, and 200 mg/l initial concentration of dye solution and the result shown in fig 5. While varying the contact time between 10-60min, it was observed that the adsorption of methylene blue increases with in time, reaching 55% removal within the first 20 mins. Further increase in contact time (30-40mins) results in the adsorption of more of the methylene blue onto the mesoporous silica. However, there is no significant increase in the amount of dye adsorbed beyond 50 min. this can be considered as the equilibrium point. This result is consistent with the report by (Dong et al., 2011), they discovered that the adsorption of anionic and cationic dye (methylene blue) on mesoporous silica have a short equilibrium time of 5-60 min.

As noted by Hameed, 2006, a large amount of methylene blue is adsorb in the initial period (10 min), this is as a result of a large mass of active sites on the surface of the adsorbent. The decrease in adsorption capacities as equilibrium is reach results from the possibility that most of the site on the silica surface have been covered with adsorbed methylene blue molecules.

The efficiency of an adsorbent is determined by how rapid it can adsorb pollutant from waste water and reach equilibrium in the shortest time possible. Generally, the adsorption of methylene blue on silica increases with time, and reaches equilibrium in about 60 min. further increase in time after equilibrium does not result in the deposition of more of the adsorbate (methylene blue) on the adsorbent. This is due to the fact that at equilibrium, the amount of dye being adsorbed is equivalent to the amount being desorbed. The amount of dye adsorbed at the equilibrium time represents the maximum adsorption capacity of the adsorbent.

Anbia and Hariri, 2010 perform adsorption of methylene blue on SBA-type mesoporous silica, the recorded an equilibrium time of 60min with an adsorption capacity of 0.78 mmol/g. Among the earliest recorded equilibrium time was that of (Chang et al., 2013). They adsorbed methylene blue on carboxylic functionalized silica, and achieved equilibrium at 15 min.

The results obtained in this study show a high degree of consistency with available literature on the effect of contact time on adsorption. The constant adsorption capacity at 50 min indicated equilibrium. It can be inferred that methylene blue molecules were taken up by the adsorbent in a fast rate within the first 10min 0f adsorption. However, after 40 min the number of available sites on the silica decrease resulting in a decrease in dye molecules been adsorbed. The adsorbent finally reach a state of saturation were no more methylene blue molecules can be taken up. This point or time is the equilibrium time which corresponds to 50min in this experiment.

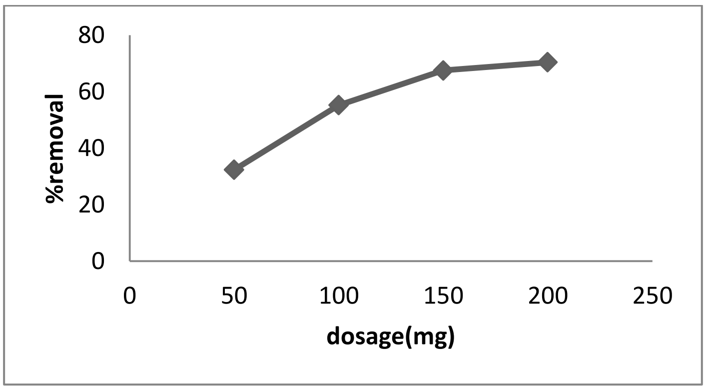

Fig. 6 Effect of adsorbent dosage on the percentage dye removal

To study the effect of adsorbent dosage on the adsorption of methylene blue onto synthesized mesoporous silica, fix conditions of 30^{o}C, 200mg/L initial dye solution concentration was used. The result is represented in figure 6.

From the graph, it can be seen that the amount of methylene blue adsorbed onto the mesoporous silica at equilibrium decreases as the silica dosage increase. it is noticed that at a dosage of 50 mg silica, the adsorption capacity (qe) after 20 min reaches a value of 65 mg/g, however the adsorption capacity begins to drop throughout the increase in silica dosage from 53 mg/m at 100 mg of silica to as low as 35 mg/g at a dosage of 200 mg. the reason behind this inverse proportionality is because at high adsorbent dosages, there exist significant unsaturation of adsorption sites (Bharathi and Ramesh, 2013). The realization of a high adsorption capacity at low mesoporous silica dosage is indicative of a high attraction for methylene blue by the adsorbent in the adsorption solution (Kareem et al., 2010). Furthermore, high adsorbsion capacity at low dosage results from the a small total surface area of adsorbent exposed to the methylene blue molecules, consequently, more methylene blue anions will be adsorbed onto the surface per gram unit of mesoporous silica, which results in higher uptake. Mesopeorous silica modified with 3-aminopropyl triethoxysilane (APTES) as a pore expander was used by (Karim et al., 2010) to adsorb methylene blue, 0.l g-0.5 g of adsorbent were used to study dosage effect. Their results indicate that high adsorption capacity of 85mg.g^{-1} was attained with the least adsorbent dose of 0.1g. This suggest that the suspended methylene blue particle occupy most of the solution volume, and the aggregation of methylene blue particle, preventing further adsorption.

Despite the decrease of adsorption capacity (qe) with increasing dosage of the mesoporous silica, there seem to be a significant increase in the percentage of methylene blue removed from the solution with increasing silica dosage. The percentage removal is calculated using equation 3;

$$\%Removal = \frac{(Co-Ce)}{co} * 100 \quad (3)$$

The result obtain is presented in figure 4.3;

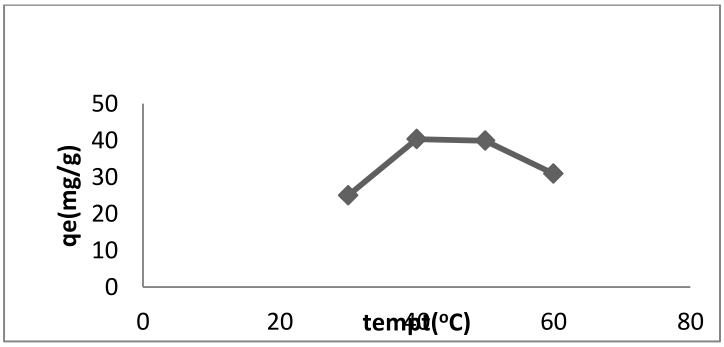

Fig. 7 Effect of temperature on the adsorption of MB onto mesoporous silica

Effect of temperature of the solution on adsorption of methylene blue on mesoporous silica was studied at 30°C, 40°C, 50°C, and 60°C. All other conditions were kept constant. The results obtained are described in the figure 7; The plot of qe vs temperature indicates a rapid rise in adsorption capacity with increase temperature. At room temperature (30°C) the amount of methylene blue taken into the silica was 25 mg/mg with a 50.01% removal, a maximum adsorption capacity of 40.35 mg/mg was recorded at 40°C, however adsorption rate begin to decrease with temperature above 50°C, and a further decrease is recorded at 60°C. Increase in adsorption with temperature between 30-40°C might be as a result of an increase mobility of dye molecules at temperatures above room temperature. However at high temperature the solubility of dye particles increases and they become more difficult to be adsorbed from an aqueous solution (Bharathi and Ramesh, 2013). Also very high temperature, there is a decrease in the adsorptive forces between the dye (methylene blue) and the active centers on the adsorbent (silica) surface, which ultimately results in decrease adsorption at increasing temperature. This might be the reason for the low adsorption capacity recorded at 50°C and 60°C.

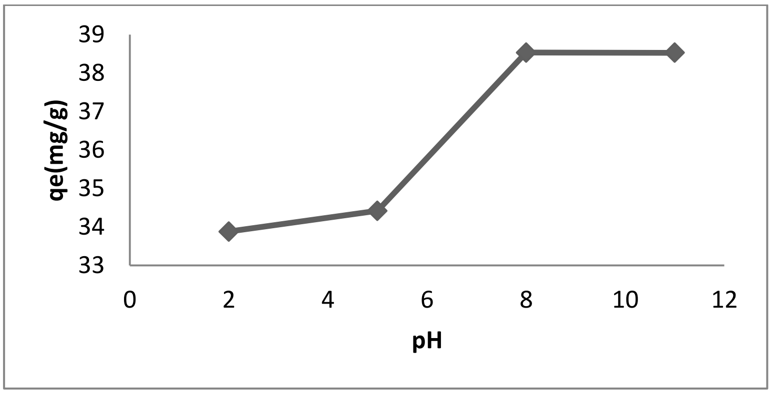

Fig. 8 Effect of pH on the adsorption of MB onto mesoporous silica

The study of the effect of pH was carried out for pHs 2, 5, 8, and 11. All other conditions were kept constant. The plot (fig.8) represents the results obtained from the experiment. The graph depicts a steady increase mesoporous silica's adsorption capacity with pH. Low adsorption (33.87 mg/mg and 67.7%r emoval) was recorded at acidic pH of 2, while the highest adsorption (77.05% removal and 38.53 mg/g) where recorded in basic solutions between pH 8-11. This result is consistent with that obtained by (Li et al. 2013) they concluded that adsorption of cationic dye on mesoporous silica increases with pH. Hence a basic solution would favor adsorption compared to an acidic solution. Also (Bharathi and Ramesh, 2013) noted that in a high pH solution, the positive charge at the solution interface reduces and the adsorbent surface assumes a negative charged, thereby increasing the electrostatic attraction between the adsorbed dye and the adsorbent. Furthermore adsorption of methylene blue on mesoporous silica is enhanced because the silanol group Si-

OH on the silica surface which give it a negative charge thereby facilitating the adsorption of positive dyes through electrostatic attraction.

4.2 Adsorption isotherms.

Adsorption isotherms are used to study the equilibrium relationship between the adsorbents and adsorbates. Freundlich and Langmuir isotherms are the most regularly used for analyzing experimental data obtained from adsorption study.

4.2.1 Langmuir isotherm.

This isotherm gives an equilibrium relationship between the concentrations of adsorbate in a solution at a constant temperature, and the quantity of adsorbate adsorbed on the adsorbent surface .

The linear form of Langmuir equation in equation 4;

$$\frac{1}{Q_e} = \frac{1}{Q_{max}} + \frac{1}{K_L Q_{max} C_e} \quad (4)$$

The plot of $\frac{1}{qe}$ vs $\frac{1}{Ce}$ shown in the fig 9 depicts Langmuir isotherm, the values of K_L and Qmax are obtained from the slope and intercept respectively.

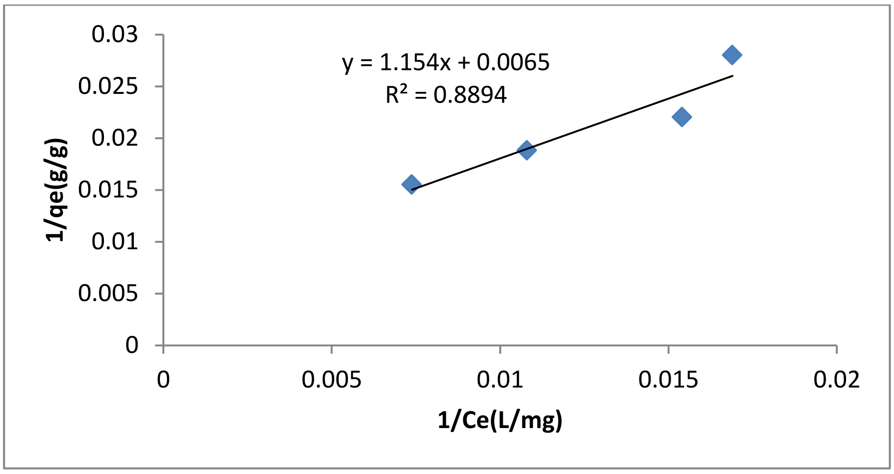

Figure 9 Langmuir plot for MB on mesoporous silica.

Table 1 Langmuir isotherm parameters.

	Langmuir
$Q_{max}(\frac{mg}{g})$	153.85
$K_L(\frac{L}{g})$	0.0056
R^2	0.8894

The values of Q_{max} and K_L have been estimated (table 1) from the intercept and slope of the Langmuir plot, Q_{max} represents the adsorption capacity and K_L is the energy of adsorption. The regression coefficient R^2 was obtained to be 0.8894; this value is relatively far from unity. Therefore Langmuir model might not be the most suitable to define this adsorption system, indicating that the adsorption does not occur completely in a monolayer.

4.2.2 Freundlich isotherm.

The Freundlich model is based on the theory that adsorbates are not restricted to formation of monomolecular layer adsorption, and adsorbates are adsorbed on a heterogeneous surface of the adsorbent.

The linear form can be written as:

$$\text{Log Qe} = \text{logKf} + 1/n \text{ logCe}.$$

Fig 10 represents Freundlich isotherm;

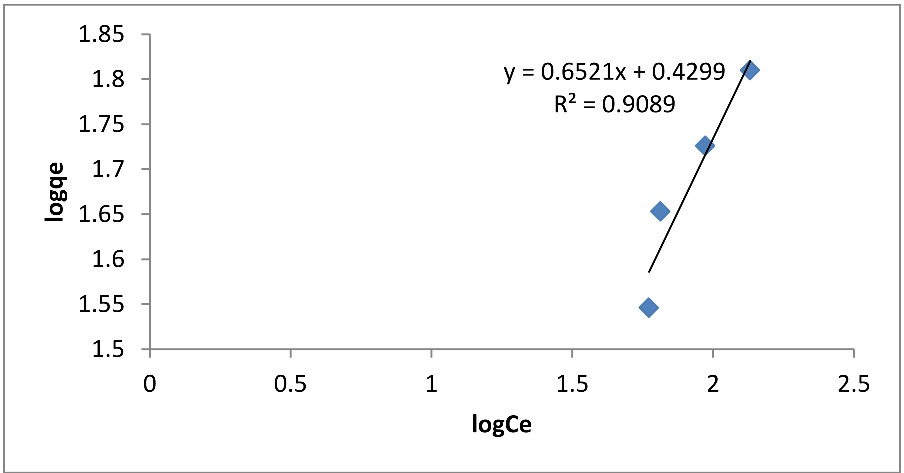

Figure 10 Freundlich plot for methylene blue on mesoporous silica.

Table 1, and 2 show a high correlation coefficient (R^2) for both Langmuir and Freundlich model, however the correlation coefficient for Freundlich model is closer to unity, therefore Freundlich model describes the adsorption more appropriately, this is indicative of the heterogeneity of the adsorbent surface, and a multilayered sorption.

Table 2 Freundlich isotherm parameters.

	Freundlich
Kf(L/g)	2.691
n	1.534
R^2	0.909

Figure 9 and 10 depicts the adsorption data fitted to Langmuir and Freundlich models respectively; the values of their respective constants are summarized in tables 1 and 2. From these figures and tables it is obvious that both Freundlich and Langmuir models produce a decent fit for the equilibrium data obtained from the adsorption experiment. The Langmuir model is based on a broad monolayer of adsorption, with no trans-migration of the adsorbate on the surface plane. This system comprises a homogeneous surface having the same energy and equal number of available sites for adsorption . The Langmuir Qmax value was 153.85 mg g^{-1}, and K_L constant is 0.0056.

Conversely, the highest precision ($R^2 = 0.909$) indicates that the Freundlich isotherm model best illustrates the adsorption of methylene blue onto mesoporous silica. The Freundlich model demonstrates the adsorption of methylene blue by locating heterogeneously dispersed adsorption spots on mesoporous silica. The value of n was calculated to be 1.534, "n" is identified as heterogeneity factor, used to categorize the adsorption whether it is linear (n = 1), physical process (n > 1), and chemical process (n < 1). Therefore, in this study, physical adsorption process is favorable with the n value 1.534. This result shows consistency with the available literature that suggests that the adsorption of methylene blue on mesoporous silica is wholly a physical process (Kovo, 2016). The K_F value, which is indicative of adsorption capacity, indicated a high methylene blue adsorptive capacity of mesoporous silica from aqueous solution. Also, the arrangement of the heterogeneously adsorbed methylene blue on the silica surface has been shown to favor the propagation of local multilayers adsorption. A similar trend was obtained in the adsorption of cationic dyes onto other mesostructured silica materials (Huang, 2011)

4.3 Kinetics study.

The adsorption kinetics are important for understanding the rate at which the adsorbates are taken up by the adsorbent. The kinetics was studied using pseudo second order and pseudo first order reaction;

4.3.1 Pseudo first order.

The equation is represented as equation 5;

$$\log(q_e - q_t) = log q_e - \frac{k_1}{2.303} t \qquad (5)$$

A plot of log(qe – qt) vs.t gives the values of the constant $k_1$and qe as shown in fig 11 and 12.

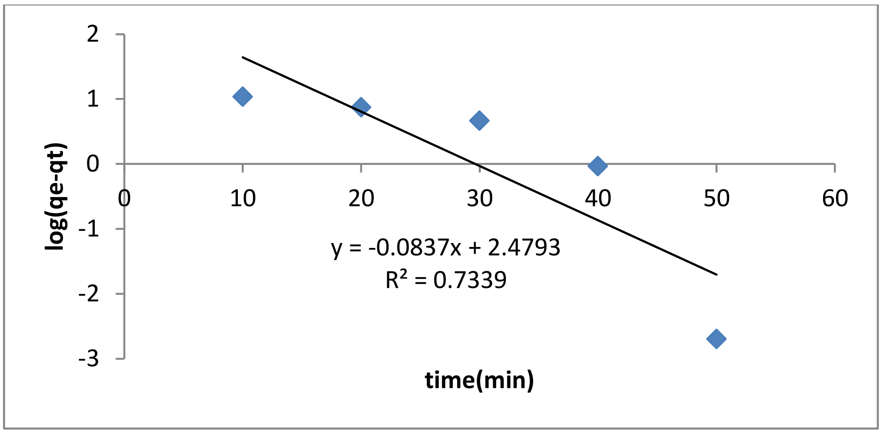

Figure 11 Pseudo first order kinetics of MB on mesoporous silica.

Table 3 Pseudo first order kinetics value of MB on mesoporous silica.

	First order
k_1	0.193
qe(mg/g)	301.51
R^2	0.7339

4.3.2 Pseudo second order.

The equation is given as as equ 6

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \quad (6)$$

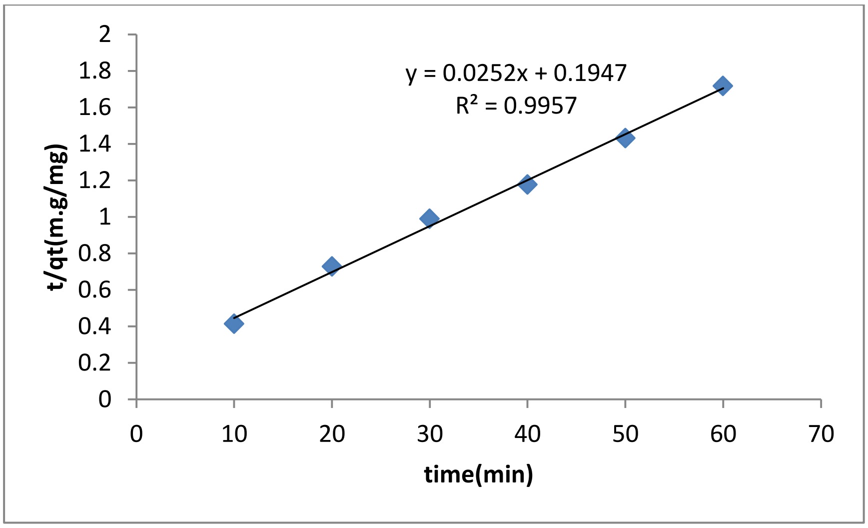

Figure 12 Pseudo second order kinetics of MB on mesoporous silica.

Table 4 Pseudo second order kinetics value of MB on mesoporous silica.

	Pseudo-Second order
k_2	0.00326
qe(mg/g)	39.683
R^2	0.9957

From table 3 and 4, it is clear that the qe (mg/g) calculated (39.68 mg/g) from the pseudo second order equation is closer to the experimental value of qe (34.96 mg/g) at equilibrium as compared to the qe value of pseudo first order equation (301.51). Thus it can be resolved that the adsorption of methylene blue on the synthesized mesoporous silica follows a pseudo second order kinetics. The rate constant k_2 was obtained to be 0.0036 from the slope of the second order plot. Furthermore the regression coefficient (R^2) of pseudo second order kinetics (0.9957) is closer to unity than that of pseudo first order kinetics (0.7339). This is also indicative of the suitability of pseudo second order kinetics for the adsorption process.

Similar kinetic behavior was also observed by (Anbia, 2010) for the adsorption of methylene blue onto SBA-3 type mesoporous silica, aluminum functionalized silica and SBA-15 type mesoporous silica (Huang, 2011).

CONCLUSION

This paper firstly provide techniques for the synthesis of rice husk based mesoporous silica It was observed that the washing, drying and acid-leaching which was used to eliminate metallic oxide impurities from the rice husk enhances high yields of mesoporous silica from white rice husk (WRH) via sol-gel process. this technique used in this work has made it possibleto obtain silica at a temperature of 600 ^{0}C. The mesoporous silica has a good pore volume and a high surface porosity as indicated from its large surface area. Therefore, it is useful as an adsorbents,. This high surface area of the mesoporous silica provides sites for active reaction and transfer of charge which facilitates high rate of adsorption. The potentials of mesoporous silica synthesized from Kwakuti Rice Husk as an adsorbent material to remove methylene blue from aqueous solution was thereafter explored. The results obtained show favorable adsorption of methylene blue with a comparative high adsorption capacity (40mg.g^{-1}), relatively fast adsorption process with equilibrium attained in 50 min, and a high affinity of mesoporous silica for methylene blue, thereby facilitating higher adsorption capacities at small adsorbent dose. The equilibrium data are well fitted to the Freundlich adsorption isotherm, reflecting a multilayer adsorption of methylene blue particles onto the mesoporous silica. All the properties of the synthesized mesoporous silica are strong indications that; rice husk can be used as a starting material to synthesis mesoporous silica which possess favorable adsorption properties for the removal of methylene blue from aqueous solutions.

REFERENCES

Brian G. Trewyn, Igor I. Slowing, Supratim Giri, Hung-Ting Chen, and Victor S.-Y. Lin (2007), Synthesis and Functionalization of a Mesoporous Silica Nanoparticle Based on the Sol–Gel Process and Applications in Controlled Release, *Acc. Chem. Res.*, **2007**, *40* (9), pp 846–853

Yang, Z.,Niu, Z.,Cao, X.,Yang, Z.,Lu, Y.,Hu, Z.,Han, C.C. (2003) , Template synthesis of uniform 1D mesostructured silica materials and their arrays in anodic alumina membranes, Angewandte Chemie - International EditionVolume 42, Issue 35, 15 September 2003, Pages 4201-4203

Khushboo Srivastava1, Niharika Shringi, Vijay Devra, Ashu Rani (2013), Pure Silica Extraction from Perlite: Its Characterization and Affecting factors, International Journal of Innovative Research in Science, Engineering and Technology Vol. 2, Issue 7, July 2013

Okoronkwo, E. A., Imoisili, P. E., and Olusunle, S. O. O. (2013). "Extraction and characterization of amorphous silica from corn cob ash by sol-gel-method," Chemistry Materials Research 3(4), 68-72.

Yanling Dong, Bin Lu, Shuying Zang, Jingxiang Zhao, Xiaoguang Wang and Qinghai Cai (2011), Removal of methylene blue from coloured effluents by adsorption onto SBA-15, JChem Technol Biotechnol 2011; 86: 616–619

Anbia M, Hariri SA (2010) Removal of methylene blue from aqueous solution using nanoporous SBA-3. Desalination 261: 61–66.

Chang F, Wang G, Xie Y, Zhang M, Zhang J, Yang HJ, Hu X (2013) Synthesis of TiO2 nanoparticles on mesoporous aluminosilicate Al-SBA-15 in supercritical CO2 for photocatalytic decolorization of methylene blue. Ceram Int 39: 3823–3829

Bharathi K, Ramesh S (2013) Removal of dyes using agricultural waste as low-cost adsorbents: a review. Appl Water Sci 3: 773–790.

Karim AH, Jalil AA, Triwahyono S, Sidik SM, Kamarudin NHN, Jusoh R et al. (2012) Amino modified mesostructured silica nanoparticles for efficient adsorption of Methylene Blue. J Colloid Interface Sci 386: 307–314

Li G, Zhao Z, Liu J, Jiang G (2011) Effective heavy metal removal from aqueous systems by thiol functionalized magnetic mesoporous silica. J Hazard Mater 192: 277–283.

Kovo, A.S. and Alaya, S.Y. (2014) Synthesis of Zeolite A for Adsorption Studies of Methylene Blue. Amazon Distribution, GmbH, Leipzig, Germany, pp. 15-80.

Huang Y (2009) Functionalization of mesoporous silica nanoparticles and their applications in organo-, metallic and organometallic catalysis. Graduate Theses Dissertations