J. Chem. Soc. Nigeria, Vol. 49, No. 3, pp 470 - 486 [2024]

ISOTHERMAL AND KINETIC STUDIES ON THE ADSORPTION OF CATIONIC (MB) AND ANIONIC DYE (MO) BY OIL SEED RESIDUE OF *Guizotia scabra*

P. A. Chomo, K. O. Ijege and V. A. Rwuaan

Department of Applied Chemistry, College of Science and Technology, Kaduna Polytechnic-Nigeria
Corresponding Author: chomopam@gmail.com; +234(0)8065752561

ABSTRACT

Agricultural products are not only beneficial to man for food, its waste or residue is seen to be helpful in the chemical circle in producing low cost adsorbents. This research is aimed at studying the isothermal and kinetic mechanism on the adsorption of methylene Blue (MB) and methyl orange (MO) which are cationic and anionic dyes respectively by the residue of the oil seed of *Guizotia scabra*. The sample was impregnated with Phosphoric acid and carbonized at 450^{O}C for 45minutes. UV /visible spectrophotometer was used to obtain the absorbance of the dyes. Series of experiments were conducted, the results revealed the effect of contact time, adsorbent dosage, pH, and initial dye concentration. The percentage removal of adsorbate of MB ranged from 82.58 to 98.37% while MO was 69.85 to 96.14% for adsorbent dose that varied from 0.05 to 0.20g.The percentage removal of MB ranged from 10.86 to 21.03% while MO was 43.70% to 72.96% for contact time that varied from 10 to 40 minutes. The percentage removal of MB ranged from 91.72 to 99.36% while MO was 24.76% to 9.90% for change in pH from 2 to 11. The percentage removal for MB ranged from 39.21 to 99.48% while MO was 87.62 to 73.41% for dye initial concentrations varied from 10 to 40mg/L. Equilibrium parameter analyzed found that Langmuir and Freundlich isotherm fit for all material but Langmuir fit better for M.B (R^2=0.9997) than for MO. Freundlich fit better for MB (R^2=0.9583) than for MO (R^2=0.8319). The adsorption kinetics study shows MB (R^2 = 0.9979) fit better for pseudo - first- order kinetics mechanism than MO (R^2=0.8602) and MO (R^2=0.995) fit better for pseudo-second–order kinetics mechanism than MB ((R^2=0.7405).

Keywords: *Guizotia scabra*, Isotherm, Kinetics, Adsorption, Methylene Blue, Methyl Orange

INTRODUCTION

Adsorption is one of the most common methods used in wastewater treatment because it is economical, effective and simple in design. However, the adsorption process is influenced by the nature of the adsorbate and its substituent groups. The presence and concentration of surface functional groups play an important role in the adsorption capacity and the removal mechanism of the adsorbate [1, 2]. It is estimated that approximately 40,000 tonnes of dyes out of roughly 450,000 tonnes in total production are not used but discharged into wastewaters. A large variety of dyestuffs is available under the

ISSN 0795 - 22066

categories of acid, basic, reactive, direct, disperse, sulphur and metallic dyes [3]. Dyes are synthetic aromatic compounds, which have various functional groups [4]. Some dyes and their degradation products may be carcinogens and toxic, and consequently their treatment cannot depend on biodegradation alone [5, 6]. The main purpose of this research is to evaluate the isothermal and kinetic mechanism of adsorption on the oil seed residue of *Guizotia scabra* of cationic dye, Methylene blue (MB) and an anionic dye, methyl orange from aqueous solutions. The effects of contact time, initial dye concentration, adsorbent dosage and pH of the solutions were studied.

MATERIALS AND METHODS

Preparation of Adsorbate

One gram of both methylene blue [cationic dye, chemical formula: $C_{16}H_{18}ClN_3S.3H_2O$, molecular mass = 373.90 g/mol], and methyl orange [anionic dye, chemical formula: $C_{32}H_{22}N_6Na_2O_6S_2$, molecular mass = 696.7 g/mol analytical grade were accurately weighed and dissolved in 1000cm^3 volumetric flask to serve as stock standard solutions.

Preparation of Adsorbent.

The sample was washed with distilled water to remove impurities from the sample and it was air dried for 5 days, the sample was grounded with blender to obtain a fine size, soxhlet apparatus was used to extract the oil from the sample to get residue. 5g of the sample was weighed and placed into four (4) different crucibles and it was impregnated with 50cm^{3}concentrated Phosphoric acid (H_3PO_4) and placed in the oven at a temperature of 110^{0}c for 2hours, and it was placed into a dessicator to cool.

The carbonization was performed in a muffle furnace for 45minutes at 450c and it was then allowed to cool in a desiccator. The activated carbon was washed with distilled water until the pH became neutral [7].

Adsorption Studies

The adsorptive properties of *Guizotia scabra* Residue (GSR) were investigated at varied adsorption times, initial dye concentrations, initial pH, and adsorbent dosage to determine its kinetics, isotherm, and optimal adsorption conditions. Every batch adsorption run was done at room temperature. GSR were dispersed in a certain volume of dye solution (V) and agitated (150 rpm) at a specified time (t). Synthetic MB solutions were prepared by dissolving the dye powder in distilled water (DW) at desired initial concentration (C_o). Samples were filtered from the solution to determine the concentration at time t (C_t) or until equilibrium dye concentration (C_e) was reached. Dye removal efficiency (% RE, Eq. 1) [8] and equilibrium adsorption capacities (Eq. (2)) [9] were determined considering the

ISSN 0795 - 22066

mass of GSR (m) dispersed into the dye solution.

$$RE = \frac{Co-Ce}{Co} \text{ x } 100\ \% \text{ ----------1}$$

$$q_e = \frac{Co-Ce}{m} \text{ x } V \text{ ----------2}$$

Adsorption kinetic studies were conducted by using dye solutions with C_o = 40 mg L^{-1} and then measuring the dye uptake (q_t) of GSR at varied t until equilibrium was attained (Eq. 3) [8]. Adsorption isotherm was carried out at C_o = 5-200 mg L^{-1}, whereas the investigation of the effect of GSR loading at S/L = 5-20 g

L^{-1} with C_o = 40 mg L^{-1}. Adsorption at different initial pH was done using dye solutions with C_o = 40 mg L^{-1} and initial pH were adjusted to the desired value by using pure NaOH and HCl (0.1 M) solutions.

$$q_t = \frac{Co-Ct}{m} \text{ x } v \text{ ----------3}$$

Effect of Contact Time on Methylene Blue (Mb) and Methyl Orange (MO)

0.05g of the activated carbon was weighed into four different conical flashes, 50ml of the methylene blue and methyl orange was added. The conical flask was corked and shaken with a mechanical shaker at different time ranging from 10 to 40 minutes. The filtrates were analyzed using a uv/visible spectrophotometer at a wave length of 664nm and 460nm [10].

Effect of Absorbent Dose on Methylene Blue (MB) and Methyl Orange (MO)

0.05g, 0.1g, 0.15, 0.2g of the activated carbon was weighed into four different conical flasks respectively, 50ml of the dyes methylene blue and methyl orange was added, the conical flask was corked and shaken with a vibrator for 30minutes. The filtrates were analyzed using a uv/visible spectrophotometer at a wave length of 664nm and 460nm [11].

Effect of Initial Dye Concentration of Methylene Blue (Mb) and Methyl Orange (MO)

A dye concentration ranging from (10-40ppm) was prepared. 50ml of each of the dye concentration was added to each of the conical flask containing 0.05g of the activated carbon and it was corked and shaken with a vibrator for 30minutes, the filtrates was analyzed using a uv/visible spectrophotometer at a wave length of 664nm and 440nm [12].

Effect of pH

0.5g of the adsorbent was weighed into four different conical flask containing 50ml of the dye solution, and it was made up to pH of 2,6,9 and 11 with the use of HCl and NaOH and the pH was checked with the use of pH meter. The conical flask was shaken with a vibrator for 30minute and it was analyzed using a UV/Visible spectrophotometer at a wavelength of 664 and 460 [13].

The concentration of the anionic and cationic dyes in a known volume of the supernatant was

ISSN 0795 - 22066

determined spectrophotometrically. The amount of the dyes adsorbed on the GSR was thus determined. Adsorption of the dyes on GSR was determined in terms of equilibrium concentration (C_e), percentage Removal *RE* %, Adsorption Capacity q_e and the equilibrium concentration (C_e) was determined.

RESULTS AND DISCUSSION

Characterization of G. scabra Adsorbent

FTIR Analysis

Table 1 revealed the FTIR result showing the stretching vibration band at around 879.65cm^{-1} may be due to C-Cl stretching vibration. The bands around 1073.4cm^{-1} and 1177cm^{-1} are due to C-N stretch and the stretching vibration at 1565cm^{-1} is due to C-N symmetric stretching vibration and also the stretching vibration at 3153cm^{-1} is due to C-H stretch functional group respectively. A similar result was presented by [14, 15,16].This indicate the possible involvement of physical forces, such as hydrogen bonding, vander waals and covalent chemical bonds in the adsorption process [17].

Table 1. Suspected functional groups in *G. scabra* Adsorbent

Peaks (cm^{-1})	Bonds	Functional group
879.65	C-Cl stretch	Alkyl halides
1073.4	C-N stretch	Aliphatic amines
1177	C-N stretch	Aliphatic amines
1565	N-O symmetric stretch	Nitro compounds
3153	C-H stretch	Aromatic

Scanning Electron Microscopy (SEM) Analysis

Scanning Electron Microscopy (SEM) showed the granulometric structure of *Guizotia scabra* seed oil residue and active carbon. The surface morphology of the sample showed clearly that *Guizotia scabra* seed oil residue were properly developed rough and uneven, it is seen to be more porous compared to the parent material. The availability of pores and internal surface area is for effective adsorbent [18]. The pores and internal surface area provided a good surface for methylene blue and methyl orange.

ISSN 0795 - 22066

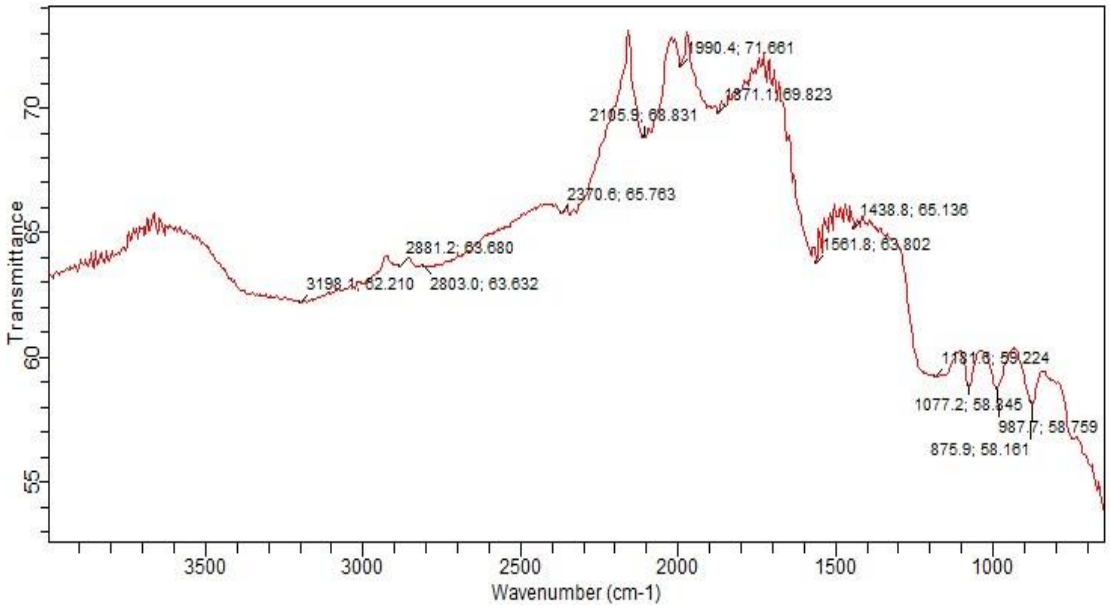

Fig. 1 FTIR of *G. scabra* Adsorbent

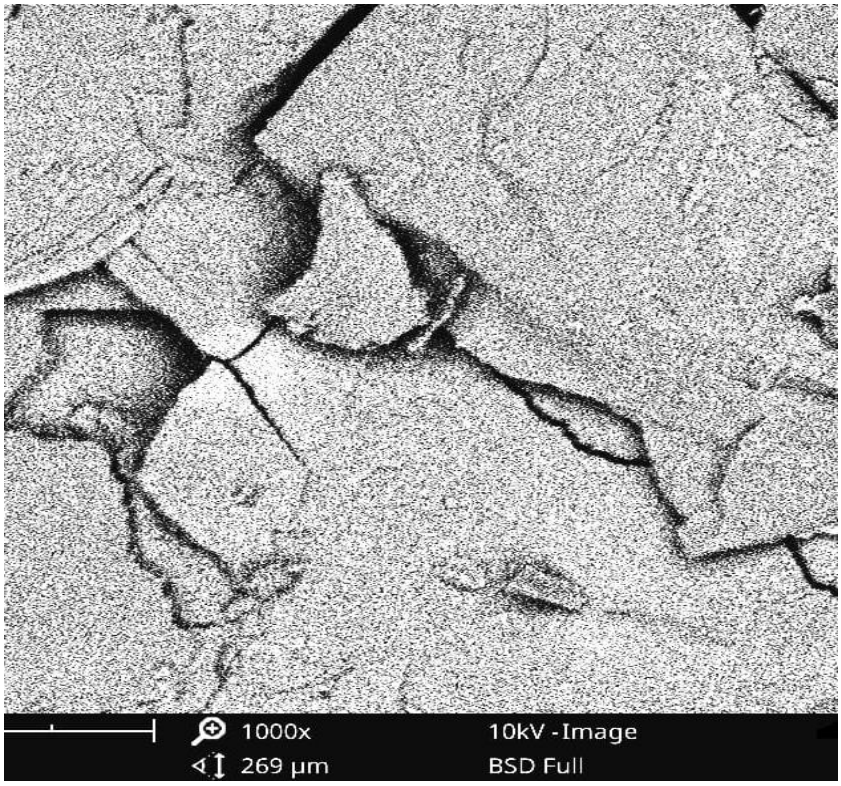

Fig. 2 SEM before activation

ISSN 0795 - 22066

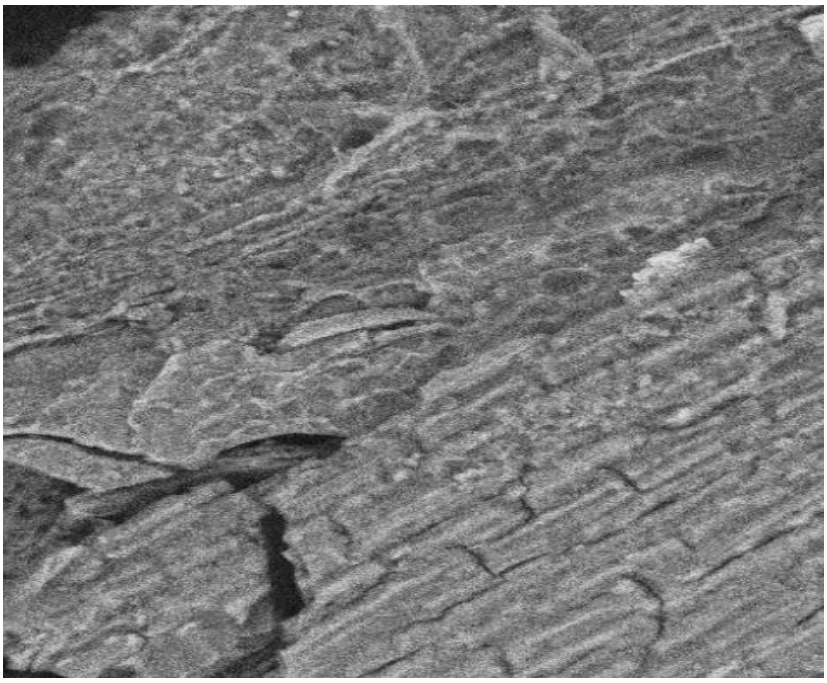

Fig. 3 SEM after activation

Adsorption Studies

Fig. 4 revealed the effect of adsorbent dose on adsorption of methylene blue (MB) [λ_{max} = 665 nm] and methyl orange (MO). The experiment were carried out with adsorbent dose varied from 0.05 to 0.2g. the percentage removal varied from 82.58% to 98.37% for methylene blue and 69.85% to 96.14% for methyl orange. The percent removal increases with increase in the adsorbent dose for both dyes. The increase in removal of dyes with adsorbent dose is due to the introduction of more binding sites for adsorption. Similar, results were reported by the other researchers [19, 20].

Fig. 5 showed the effect of contact time in the adsorption of MB and MO. The percentage removal ranges from 10.86% to 21.03% for MB and ranges from 43.70% to 72.96% for MO. It is observed that the percentage removal of the dyes increases rapidly with an increase in contact time initially, and thereafter, beyond a contact time of about 20 min for MB there was decrease in adsorption site this is credited to the face that while 40mins for MO, there was noticeable adsorption with increase in time. This could be due to greater pore size and a strong attraction between the adsorbent and the

ISSN 0795 - 22066

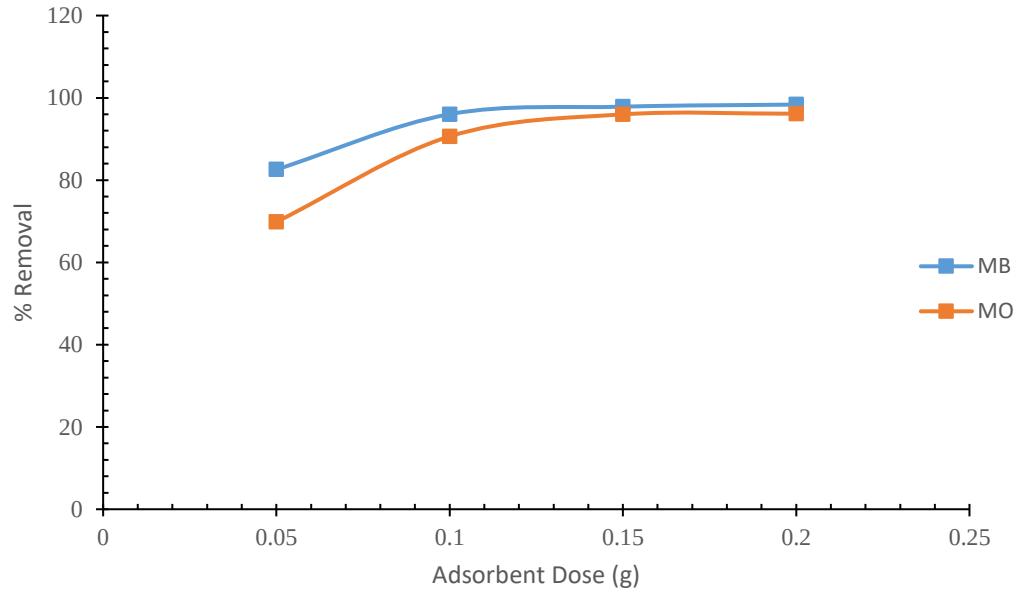

Fig.4 Effect of adsorbent dose on the adsorption of MB and MO

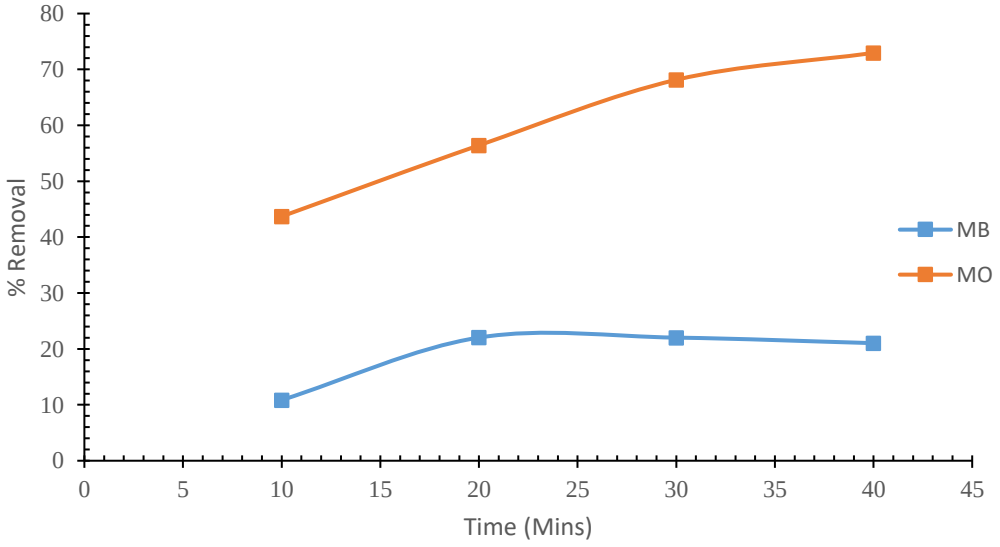

Fig. 5 Effect of Contact time on the adsorption of MB and MO

Fig.6 showed the effect of pH on the adsorption of MB and MO. The pH of the experiment was varied from 2 to 11. Percentage removal of MB was in the range of 91.72% to 99.36% while MO was in the range of 24.76% to 9.90%. Methylene blue is

ISSN 0795 - 22066

cationic, at lower pH value, low removal was observed which was due to the high concentration of H^+ ions that resulted in repulsion and hence cause the reduced bio sorption [21]. However, at higher pH values, maximum removal was observed. The reason for increased in removal efficiency at alkaline pH is due to the availability of more negatively charged surface which caused decrease in repulsion between the positively charged dye molecule and the biosorbent [22]. In the case of anionic dye (MO), adsorption is greater at lower pH. It may be due to the increased positive charges on the surface of adsorbent that attracts the functional groups of a dye carrying negative charge [23].

Fig.7 revealed the effect of initial concentrations of dyes (MB and MO) adsorbed. The effect of concentration of dyes (10 to 40 mg L^{-1}) have been also tested with constant dose of adsorbent (0.05g). The removal of dyes increased from 39.21% to 99.48% in case of methylene blue, this show that the adsorption of MO on *Guizotia scabra* seed oil residue increases spontaneously with increasing sorbate concentration till 20mgL^{-1} and then become constant onward [23] while methyl orange decreased from 87.62% to 73.41%. These results indicated that the adsorption of dyes are much dependent on concentration of solution. These observations are in close agreement with that reported by [24,25, 26] for removal decreases with increase initial concentration of dyes in the case of MO.

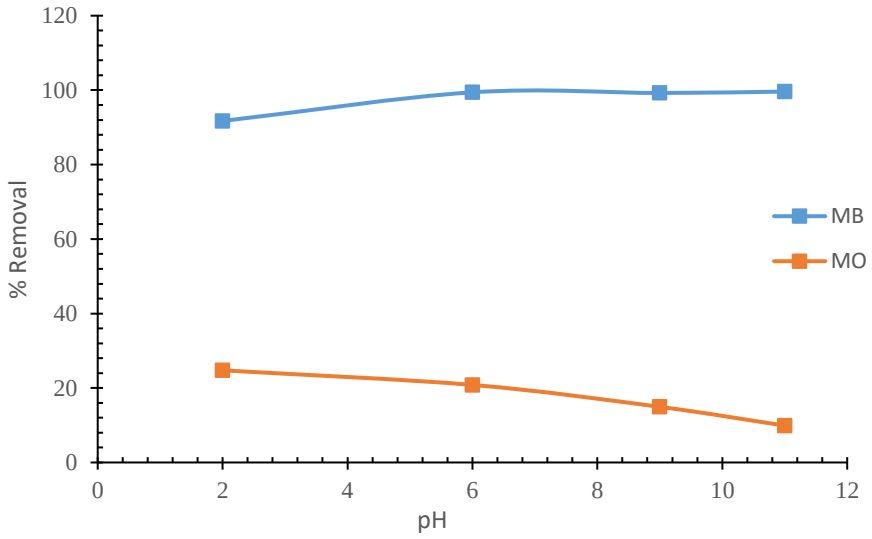

Fig.6 Effect of pH on the adsorption of MB and MO

ISSN 0795 - 22066

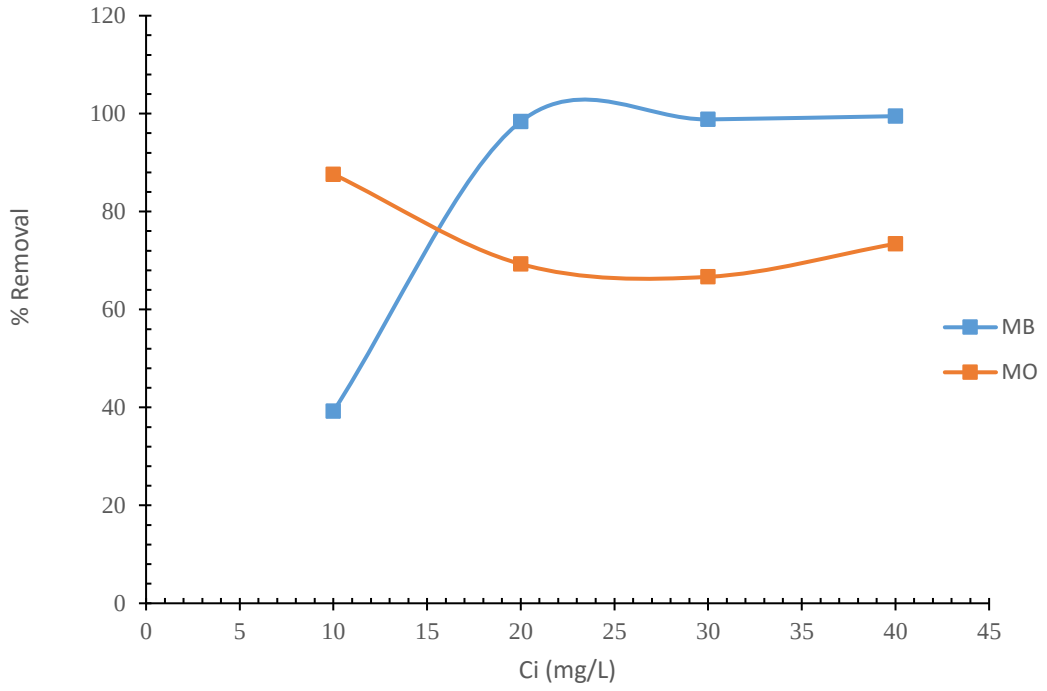

Fig.7 Effect of initial Dye concentration on the adsorption of MB and MO

Adsorption Isotherm

Fig. 8 and 9 revealed the isotherm models (Langmuir and Freundlich) in the adsorption process. It can be seen that the regression correlation coefficient (R^2) of the Langmuir equation for MB (R^2 = 0.9997) and (R^2 = 0.6259) for MO. The MB is more linear when compared with that of MO. Freundlich equation (R^2 = 0.9583) for M.B while MO has (R^2 = 0.8319), again the MB is more linear when compared with that of MO in this case. This implies that the adsorption isotherm data are well fitted by the Langmuir isotherm. The monolayer adsorption capacity, according to the Langmuir isotherm, was found to be 3.749 mg/g for MO and -0.743mg/g at 30ºC. The fact that the Langmuir isotherm fits the experimental data very well in the case of M.B may be due to the homogeneous distribution of active sites on the adsorbent surface because application of the Langmuir equation involves the assumption that the surface is homogeneous [27]. Also, it could be due to the cationic properties of the dye that is attracted to the surface of the adsorbent.

The value 1/n gives an indication on the validity of the adsorption of adsorbent-adsorbate system. A value 1/n between 0 and 1 that indicates a favorable adsorption [28,29]. In addition to that, this also indicates that the adsorption capacity increases, and further,

ISSN 0795 - 22066

adsorption sites appear. When 1/n > 1, the adsorption is not favorable, the adsorption connections become weak and the adsorption capacity decreases. From our result, it showed that 1/n for MO was 2.13 indicated that adsorption was not favorable and 1/n of MO was -1.5 for MB, this indicated a favorable adsorption. This result is similar to the report by [30]. The modeling of the adsorption isotherm of the MB shows that it obeys Freundlich law, which implies heterogeneity of surface. In addition, there is a good correlation coefficient (R^2 = 0.992) and adsorption is favorable (0 < 1/n < 1).

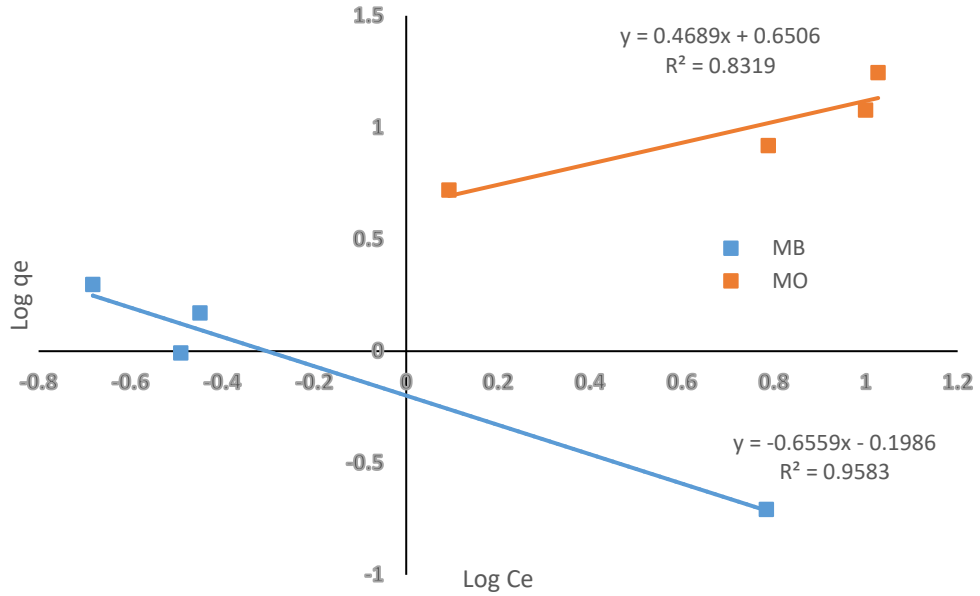

Fig. 8 Freundlich Isotherm for the adsorption of MB and MO on *G. scabra* Adsorbent

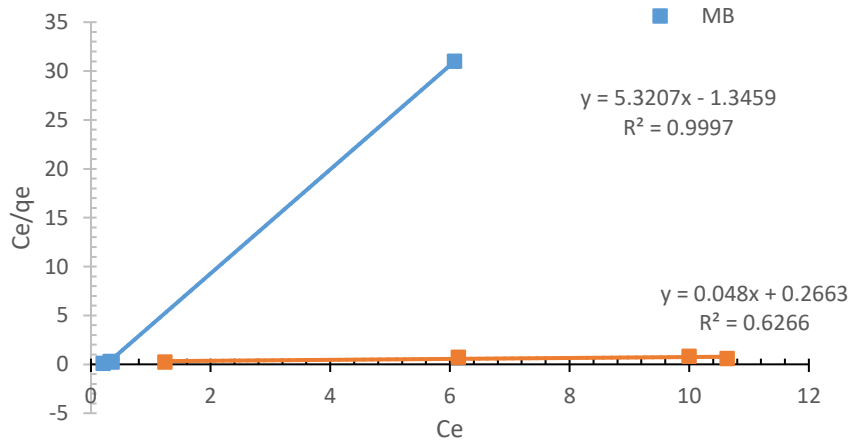

Fig. 9 Langmuir isotherm for the adsorption of MB and MO on *G. scabra* Adsorbent

ISSN 0795 - 22066

Table 3 revealed the values of the pseudo first and pseudo second-rate constants for the removal of both dyes. Pseudo-First-Order Kinetic Model assumed that the adsorption is controlled by the diffusion step, the single layer adsorption completed through boundary diffusion is mainly described, which is expressed as follows $\frac{dq}{dt}_t = k_1 q_e - q_t$ [31].

Table 2. Langmuir and Freundlich constant

Freundlich Isotherm						Langmuir Isotherm					
MB			MO			MB			MO		
K_F	1/n	R^2	K_F	1/n	R^2	q_m	K_L	R^2	q_m	K_L	R^2
0.78	2.13	0.9583	4.47	0.47	0.8319	-0.74	5.56	0.9997	3.75	-0.25	0.6259

Table 3. Pseudo–first- order and pseudo- second – order kinetic constant

Pseudo-first- order				Pseudo-second-order			
MB		MO		MB		MO	
K_1	R^2	K_1	R^2	K_2	R^2	K_2	R^2
0.0045	0.9583	0.4689	0.8319	0.00111	0.9997	0.0005	0.6259

ISSN 0795 - 22066

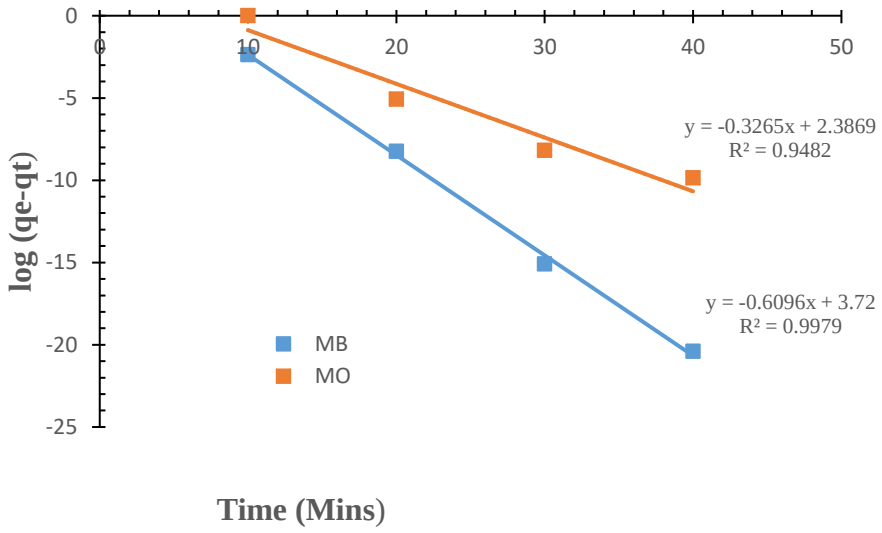

Fig. 10 Pseudo- First- order for the adsorption of MB and MO on *G. scabra* Adsorbent

Pseudo-Second-Order Kinetic Model assumed that the adsorption is affected by the chemical adsorption rate, involving electron sharing or electron transfer between the adsorbent and the

adsorbate. Results showed MB (R^2 = 0.9979 has a better linear fitting than MO (R^2 = 0.8602), indicating that the kinetic adsorption data of MB obeyed pseudo first order than MO. Kinetic adsorption data of MO (R^2 = 0.995) obey pseudo second order due to the closeness of the correlation coefficient of 1 than MB (0.7405). The initial stage of adsorption can be described by both the pseudo-first-order kinetic and the pseudo-second-order kinetic models. In comparison, the pseudo-second-order kinetic model can well fit the whole adsorption process including the second half adsorption [32] .

ISSN 0795 - 22066

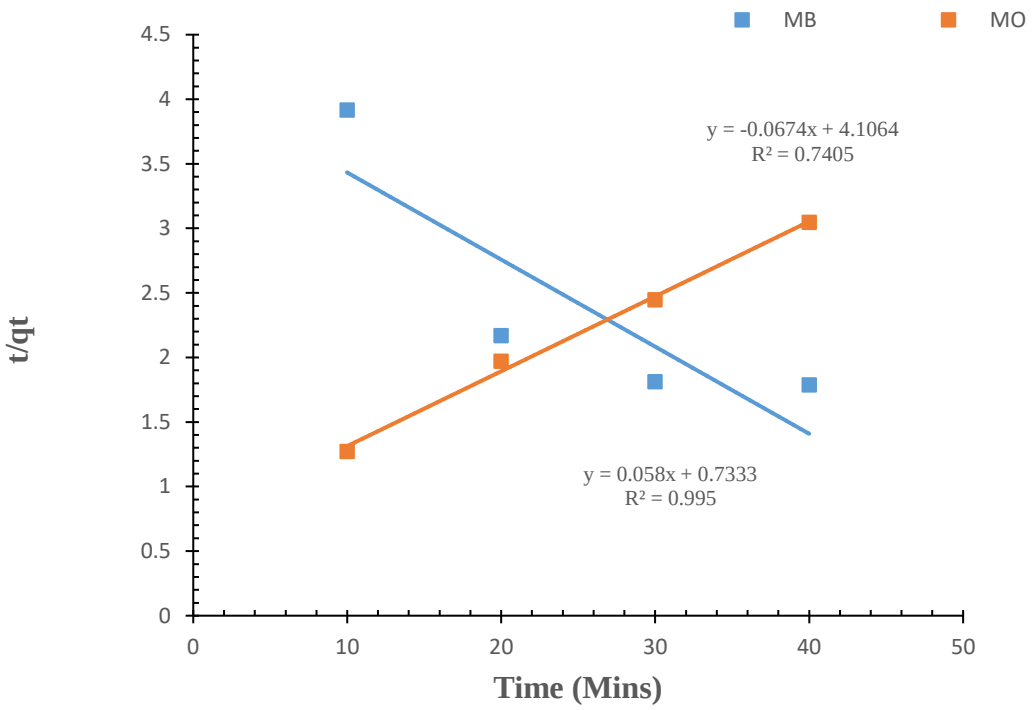

Fig. 11 Pseudo - second –order for the adsorption of MB and MO on *G. scabra* Adsorbent

CONCLUSION

The investigation showed that the *Guizotia scabra* seed oil residue was a promising precursor to be used in the preparation of the activated carbon for the removal of methylene blue and methyl orange from aqueous solution. amines, alkyl halide and alkyne. The equilibrium data was fitted to Langmuir isotherm than the Freundlich. The kinetic adsorption data for methylene blue obeyed the pseudo first order, while the methyl orange obeyed the pseudo second order. SEM study showed that the activated carbon was porous with well-developed pores. The functional groups present in the derived activated carbon were aromatics, aliphatic amines, alkyl halide and alkyne. The equilibrium data was fitted to Langmuir isotherm than the Freundlich. The kinetic adsorption data for methylene blue obeyed the pseudo first order, while the methyl orange obeyed the pseudo second order

ISSN 0795 - 22066

REFERENCES

[1] Lahaye, J. (1998). The chemistry of carbon surfaces. *Fuel*, 77(6), 543-57

[2] Yenisoy-Karakas, S., Aygun, A., Gunes, M. & Tahtasakal, E. (2004). Physical and chemical characteristics of polymer-based spherical activated carbon and its ability to adsorb organics. *Carbon*, 42, 477–484.

[3] Marsh, H. & Rodríguez-Reinoso, F. (2006). *Activated carbon*. Amsterdam: Elsevier.

[4] Noroozi, B., Sorial, G. A., Bahrami, H. & Arami, M. (2007). Equilibrium and kinetic adsorption study of a cationic dye by a natural adsorbentSilkworm pupa. *J. Haz. Mater.*, B139, 167–174.

[5] Reife, A. (1993). Dyes, environmental chemistry. In Kirk-

[6] Pagga, U. & Braun, D. (1986). The degradation of dye stuffs: part II. Behaviour of dyestuffs in aerobic biodegradation tests. *Chemosphere*, 154, 79–489.

[7] Suarez-garcia, F., Matinez-Alonso, A.J., and Tascon, T.M.D. (2002). Pyrolysis of Apple pulp; chemical activation wuith phosphoric acid, *Journal of Analytical and Applied Pyrolysis* 63, 283-301

[8] Choi, H.J., & Yu, S.W. (2019). Biosorption of methylene blue from aqueous solution by agricultural bioadsorbent corncob. *Environ. Eng. Res*.;24:99-106.

[9] Tezcan, U, Ates F. Low-cost adsorbent prepared from poplar sawdust for removal of disperse

[10] El-sayed, G.O., Yehia, M.M., and Asaad, A.A. (2014). Assessment of Activated Carbon prepared from conrncob by Chemical activation with Phosphoric acid, *Journal of Environmental Management*, 166, 116-123.

[11] Sharma, Y.C. and Uma, A.C. (2010). Optimization of parameters for adsorption of methylene blue on low-cost activated carbon. *Journal of Chemical Engineering*, 55, 435-439

[12] Mohd-Salleh, M.A., Mahmoud, D.K., Abdul, A. (2011). Cationic and anionic dye adsorption by agricultural solid waster: a comprehensive review, desalination 280, 1-13

[13] Amin, N.K. (2008). Removal or Reactive dye from Aqueous Solutions by adsorption onto activated Carbons prepared from Sugar Cane baqasse pith. Desalination. *Journal of Chemical Society of Nigeria*, 223, 152-161.

[14] Kumari, H. J., Krishnamoorthy, P., Arumugam, T. K., Radhakrishnan, S., Vasudevan, D. (2017). An efficient removal of crystal violet dye from waste water by adsorption onto TLAC/Chitosan composite: A novel low cost adsorbent – *International Journal of Biological Macromolecules* 96: 324–333.

[15] Setthaya, N., Chindaprasirt, P., Yin, S., Pimraksa, K. (2017). TiO2-zeolite photocatalysts made of metakaolin and rice husk ash for removal of methylene blue dye– Powder Technology 313: 417–426

ISSN 0795 - 22066

[16] Armin, K., Pouya, H., Mazaher, A., Rouholah, Z., and Ali, M (2017). "Equilibrium, Thermodynamics, and Kinetic Sorption Studies for the Removal of Coomassie Brilliant Blue on Wheat Bran as a Low-Cost Adsorbent". *Journal of water supply, research and technology*. Vol. 23(1), 1–13.

[17] Alzaydien, A.S. (2015). Adsorption behavior of methyl orange onto wheat bran. The role of surface and pH. *Journal of Chemistry*. 31, 643-651

[18] Rao, M.M., Ramesh, A., Rao, G.P.C., Seshaiah, K. (2006). Removal of copper and cadmium from the aqueous solutions by activated carbon prepared from Ceiba pentandra hulls. *Journal of Hazardous materials.* 129, 123–129

[19] Namasivayam, C.. and Yamuna, R.T. (2003), Utilizing biogas residual slurry for dye adsorption, Amer. Dyestuff Rep. Aug, 235-239.

[20] Sarioglu, R., and Atay, Y. (2016). "Chromium adsorption and Cr (VI) reduction to trivalent chromium in aqeous solutions by soya cake." *Journal of Hazardous Materials* 94, 49-61.

[21] Saeed, A., and Sharif, M.I. (2010). Application potential of grapefruit peel as dye sobent: kinetics, equilibrium and mechanism of crystal violet adsorption. *Journal of Hazard Mater*ial, 179, 564–572.

[22] Ahmed MJ, Okoye PU, Hummadi EH, Hameed BH.(2019. High-performance porous biochar from the pyrolysis of natural and renewable seaweed (Gelidiella acerosa) and its application for the adsorption of methylene blue. *Bioresour. Technol*.; 278:159-164.

[23] Sadia, A., Muhammad, I.D., Atta, R., Imran, Q., and Ijaz, U. (2012). Equilibrium, Thermodynamics, and Kinetic Adorption Studies for the Removal of Coomassie Brilliant Blue on Wheat Bran as a Low-Cost Adsorbent. *Journal of Applied Chemistry*. Pp 30-37

[24] Verma V.K. and Mishra A.K. (2005). Dye removal by Sawdust based adsorbent, Pollution Research, 24 (1), 97-99.

[25] Garg, V.K. Gupta, R., Yadav, B., and Kumar, R. (2003). Removal of acid dyes by low cost adsorbent, *Journal of Chemical* Engineering, 89, 121-124.

[26] Gupta G.S. Prasad G. and Singh V.N. (2002). Removal of Chrome dye from water by fly ash, *International Journal of Biological Macromolecules*, 15, 98-103

[27] Azraa, A., Jain, K., Tong, K.S., Rozaini, C.A., and Tan, L.S (2012). Equilibrium, Kinetic and Thermodynamic Studies on the Adsorption of Direct Dye onto a Novel Green Adsorbent Developed from Uncaria Gambir Extract. *Journal of physical science*. Vol. 23. pp:1-13

[28] Gammoudi, S., Srasra, N.F., and Srasra, E. (2011). Adsorptive Removal of Dyes from Aqueous Solution by KMnO4-Modified Rice Husk and Rice Straw Engineering Geology 124-119 129.

[29] Moussavi, G.H. and Khosravi, R (2011). Chemical Engineering Research and Design 89: 2182-2189

[30] Ouardi, M., Armin, K., Pouya, H., Mazaher, A., Rouholah, Z., and Ali, M. (2017).

ISSN 0795 - 22066

Equilibrium, Thermodynamics, and Kinetic Sorption Studies for the Removal of
Coomassie Brilliant Blue on Wheat Bran as a Low-Cost Adsorbent. *Science World*
Journal. Vol 14:1-2

[31] Langmunir, I. (1916). Research Laboratory of the General Electrical Company 2221

[32] Xiaodong, L., and Yunjin, L. (2019). Adsorptive Removal of Dyes from Aqueous Solution by KMnO4-Modified Rice Husk and Rice Straw. *Iranian journal of environmental health and engineering*. pp: 8-9

ISSN 0795 - 22066