International Journal of Research and Review
Vol. 9; Issue: 10; October 2022
Website: www.ijrrjournal.com
Research Paper *E-ISSN: 2349-9788; P-ISSN: 2454-2237*

Adsorption of Methylene Blue on MnO_2-Modified Activated Carbon Prepared from Cocoa Pod Shells

Akissi Lydie Chantal Koffi[1], Djamatché Paul Valéry Akesse[1], Amadou Kouyate[1], Bini Kouamé Dongui[1], Kouassi Binjamin Yao[2]

[1]Laboratory for Environmental Science and Technology, Jean Lorougnon Guede University, Daloa, Côte d'Ivoire, BP 150 Daloa, Côte d'Ivoire
[2]Laboratory of Industrial Processes, Synthesis, Environment and New Energies (LAPISEN) ; Institut National Polytechnique Houphouët-Boigny, BP 1313 Yamoussoukro, Côte d'Ivoire

Corresponding Author: Akissi Lydie Chantal Koffi

DOI: https://doi.org/10.52403/ijrr.20221006

ABSTRACT

This study focused on the preparation of activated carbon modified with manganese oxides, in order to apply it to the removal of methylene blue in aqueous solution. Activated carbon (AC) was elaborated from cocoa pod shells, which is a local biomass available in Côte d'Ivoire. This activated carbon was then modified with manganese oxides to give AC-MnO_2 in order to increase its performance in the removal of methylene blue in aqueous solution. The characterization of these activated carbons revealed their microporous structure with a specific surface of 890.64 m^2/g for AC and 732.3 m^2/g for AC-MnO_2. Kinetic study showed that the methylene blue elimination reaction is pseudo-second order with an equilibrium time of 60 min. Langmuir's model of a monolayer adsorption better reproduces the experimental adsorption isotherms with a maximum adsorption capacity of 222.22 mg/g with CA and 270.27 mg/g with AC-MnO_2.

Keywords: Adsorption, Activated carbon, cocoa pod shell, Methylene blue, manganese oxides

INTRODUCTION

Dye is a natural or synthetic material that adds a specific color to the material it is being applied to. Currently, synthetic dyes are used in a wide range of industries from commodity manufacturing such as textile manufacturing [1], food technology [2] and photoelectrochemical cells [3]. The presence of even very low concentrations in discharge effluents to the environment is worrying for both toxicological and esthetic reasons [4]. Methylene blue (MB) dye is widely used in the textile industry for dyeing cotton, wood, and leather, in addition to the pharmaceutical industries [5]. Methylene blue dye causes harmful effects on human health such as nausea, vomiting, heart rate increasing and eye/skin irritation [6-7].

Various processes were developed for the dye removal from the wastewater including adsorption and biosorption [8-9], chemical and electrochemical oxidation [10-11], membrane separation process [12], photodegradation [13]. The adsorption technique, which is based on the transfer of pollutants from the solution to the solid phase, is known as one of the efficient and general wastewater treatment method [14]. Activated carbon (AC) has been widely used as an adsorbent in the purification of aqueous media, gas/solid phase separation, catalysis, electrochemical processes, among others. Its surface characteristics, such as the extended range of porosity and high surface area, ease of separation, low operational cost and significant sorption affinity make activated carbon a versatile and preferred material for various applications [15-16].

In recent years, emphasis has been placed on preparing activated carbon with modified surfaces using different procedures to improve the potential of activated carbon for specific contaminants [17]. Impregnation with metal salts, which form an oxide surface coating on the carbon, is one of the most commonly used methods [18]. Manganese oxides commonly have a high affinity for many heavy metals and catalytic activity for many nutrient elements and organic contaminants [19]. The introduction of Manganese may cause the change in oxygen-containing functional groups to facilitate the adsorption [20].

In this study, activated carbon from cocoa pod shells was modified with potassium permanganate ($KMnO_4$) to further improve its efficiency, and its performance for methylene blue (MB) adsorption in aqueous solution was evaluated.

MATERIALS & METHODS

Adsorbents preparation

Activated carbon (AC) is prepared by the method of chemical activation with ortho phosphoric acid (H_3PO_4). 30 g of cocoa pods powder are impregnated in 300 mL of orthophosphoric acid solution (20%) for 24 h. After 24 h, the sample was then washed in distilled water until the sample was neutralized, filtrated and dried in the oven at 60 °C for 24 h. After drying, the sample is left at room temperature to cool for at least 30 mn before carbonization. The sample was heated in an electric oven with heating ramps 10 °C per min until 450 °C was maintained for 3 hours. The activated carbon (AC) obtained by this treatment were washed with distilled water, filtered and dried at 105 °C for 24 h.

To obtain AC-MnO_2, 3 g of cocoa pods activated carbon (AC) are impregnated in 100 mL of potassium permanganate ($KMnO_4$) solution at different concentrations: 0.05M; 0.075M; 0.1M. The mixture is weakly acidified with 2 or 3 drops of H_2SO_4. The mixture is stirred for 24 h. The brown color after the impregnation shows that the permanganate is reduced to oxide of manganese MnO_2. After 24 h, mixture is rinsed with distilled water to remove excess manganese oxides then is dried in an oven at a temperature of 105°C for 24 hours.

Material Characterization

The acidic and basic surface groups were determined according to the method of Boehm [21]. 0.5 g of activated carbon sample was placed in 50 mL of 0.1 N solutions of either sodium hydroxide or hydrochloric acid. The vials were shaken for 48 h, then 20 mL of each filtrate was pipetted, and the excess of base or acid was titrated with 0.1N HCl or 0.1N NaOH, as required. The numbers of acidic groups were calculated under the assumption that NaOH neutralizes all acidic groups (carboxylic, phenolic and lactonic groups) and HCl reacts with all basic groups.

Methylene blue index was calculated using the method of the European Center of Chemical Industry Federations (CEFIC, 1989) taken from [22]. The methylene blue index (MBI) is determined by evaluating the amount of methylene blue adsorbed from a solution of initially known concentration per gram of adsorbent (0.1 g of activated carbon), when being in contact for 40 min at room temperature (30 °C). The absorbance is measured by the molecular absorption spectrophotometer (UV-5200). and The MBI was determined as shown below.

$$MBI\ (mg/g) = \frac{V_{MB}.(C_i - C_f) * M}{m_{AC}} \quad (1)$$

where V_{MB} (L) is the total volume of methylene blue solution, Ci (mol/L) is the initial concentration of MB solution of, C_f (mol/L) is the final concentration MB solution, m_{AC} (g) is the mass of activated carbon in contact with MB solution.

Iodine index was carried out according to the AWWA B 600-78 standard taken from [23]. Iodine index involves titration of a known volume of iodine solution with a 0.1 N solution of sodium thiosulfate before and after adsorption on activated carbon. 20 mL of 0.1 N iodine solution was added to 0.05 g of activated carbon. The mixture was stirred

for 30 min at room temperature (30 °C) and centrifuged at 3000 rpm. Then 10 mL of the supernatant was titrated with a 0.1 N sodium thiosulfate solution. The iodine number I_2 (mg/g) is calculated as follows:

$$I_2 = \frac{25.4(20 - V_{th})}{m_{ac}} \qquad (2)$$

The specific surface area was calculated from the amount of adsorbed BM at maximum adsorption capacity according to

$$S_L = \frac{Q_m N_A S_{BM}}{M_{BM}} \qquad (3)$$

S_L: Specific surface area of Langmuir (m^2/g)
Q_m: Maximum adsorption capacity (mg/g)
N_A: Avogadro number ($6.022.10^{23} mol^{-1}$)
S_{BM}: Surface occupied by a molecule of methylene blue ($175.10^{-20} m^2$)
M_{BM}: Molecular Weight of methylene blue = 319.85 g/mol
The determination of the maximum adsorption capacity is done by applying the Langmuir model to the adsorption isotherms of methylene blue on activated carbon.

Batch adsorption experiments

Kinetic studies were used to investigate the effect of contact time and determine the kinetic parameters. The experiments were carried out in Erlenmeyer flasks (250 mL) by adding 0.05 g of prepared carbons (CA and CA-MnO_2 0.05M) with 100 mL of MB solution of 100 mg/L. The mixture was agitated with agitation speed of 120 rpm. At predetermined time intervals (0–100 min), activated carbon and solution were separated by centrifuging (SIGMA 2-16P) at 3000 rpm for 10 mn. MB concentration in the solution was measured at 665 nm using UV-visible spectrophotometer (UV-5200).

Equilibrium adsorption tests were performed in a set of Erlenmeyer flasks (250 mL) where 100 mL of methylene blue solutions with initial concentrations of 50–150 mg/L were prepared. An amount of 0.05 g of the activated carbon was added into each flask covered with glass stopper and the flasks were then placed in an isothermal water-bath shaker (the temperature is 30 ± 2°C) with agitation speed of 120 rpm to reach equilibrium. Finally, activated carbon and solution were separated by centrifuging (SIGMA 2-16P) at 3000 rpm for 10 mn. MB concentration in the solution was measured at 665 nm using UV-visible spectrophotometer (UV-5200).
The amount of MB adsorbed by the adsorbent (qe) and the percentage removal of MB (X) were calculated by using the following equations:

$$q_e(mg/g) = (C_o - C_e) \times \frac{V}{m} \qquad (4)$$

$$X\,(\%) = \frac{C_o - C_t}{C_o} \times 100 \qquad (5)$$

where Co and Ce (mg/L) are the concentrations of MB at initial and at equilibrium time t respectively. V (L) is the volume of the solution and m (g) is the mass of dry adsorbent used.

STATISTICAL ANALYSIS

The curve fittings of the data obtained were performed using Microcal Origin 8.0 software.

RESULT AND DISCUSSION

Characterization of AC and AC-MnO_2

Table 1 shows the physicochemical characteristics of activated carbon (AC) and modified activated carbon (AC-MnO_2).

Table 1. Physicochemical characteristics of AC and AC-MnO_2

Adsorbent	Iodine index (mg/g)	MBI (mg/g)	Total acidic (mmol/g)	Total basic mmol/g	S_L (m^2/g)
AC	1525.24	694.68	1.87	0.48	890.64
AC-MnO_2	1516.6	688.63	1.52	0.36	732.3

The iodine index was a measure of micropore content of the activated carbon by adsorption of iodine from solutions. It is used as an estimate of the total surface area. By comparing the value of the iodine index with that of the BM index of the two prepared adsorbent, we see that the two activated carbons have microporous structures. Table 1 shows also that the iodine and BM indices decrease when CA is

impregnated with $KMnO_4$.This could be explained by the occupation of the activated carbon pores by manganese oxides. As shown in Table 1, the two activated carbons prepared from cocoa pod shells have high specific surface areas (890.64 m^2/g for AC and 732.3 for AC-Mn m^2/g), indicating that they can be potential adsorbents. The modification of AC by $KMnO_4$ to obtain AC-MnO_2 causes a reduction in surface area. Boehm titration is applied to determine the concentration of acidic and basic functional groups in of AC and AC-MnO_2. The results show that both adsorbents appear to have more acidic than basic groups on their surfaces. Activated carbons are considered acidic. Therefore, it can be said that the impregnation with $KMnO_4$ changed the chemical environment of the activated carbon surface and made it more acidic.

Effect of $KMnO_4$ concentration on MB adsorption capacity

The concentration of potassium permanganate ($KMnO_4$) was varied from 0.05 to 0.1M in order to evaluate the effect of the amount of manganese oxides in the material on the abatement rate. The results are shown in figure 1.

Figure 1 shows that increasing the concentration of $KMnO_4$ has no effect on the adsorption rate of MB because the adsorption rate remains the same (98.89%) for the three modified activated carbons. On the other hand, it is observed that the adsorption rates of the impregnated activated carbons are higher than that of the activated carbon without impregnation in $KMnO_4$ (87.18%). This shows that the addition of $KMnO_4$ increased the adsorption properties of the activated carbon.

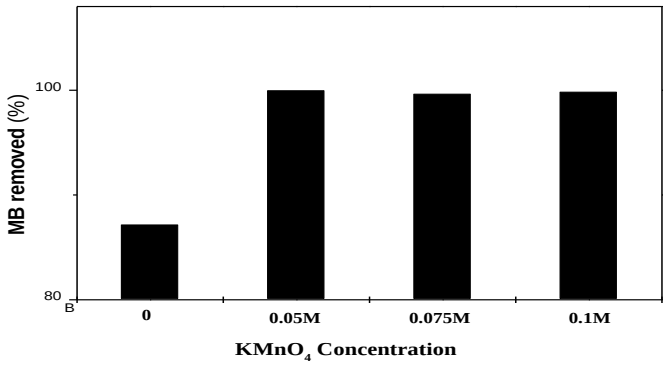

Figure 1: Effect of $KMnO_4$ concentration on MB adsorption capacity

Effect of Contact time

Contact time is an important factor affecting removal of dye in solution. The effect of contact time on the adsorption of MB on AC and AC-MnO_2 in solution were shown in figure 2.

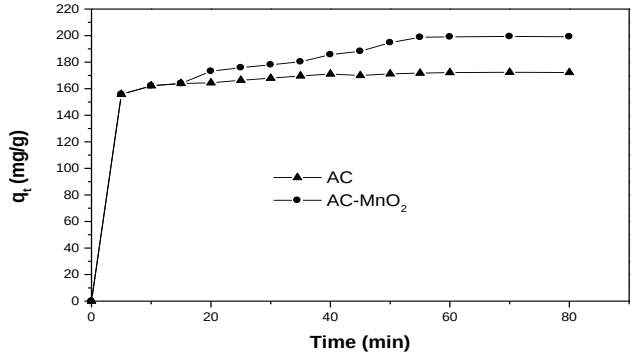

Figure 2: Effect of contact time on the adsorption of MB on AC and AC-MnO_2.

The result from the above graph shows that the removal of MB increases as adsorption time increases. It is deduced from the above graph that the adsorption capacity of MB increases with time to reach its maximum value after 60 minutes which constitutes the equilibrium time for the two studied activated carbons. The modification of the AC did not affect the equilibrium time, but it did affect the adsorption capacity. In fact, at 60 minutes, the quantity of BM adsorbed is 199.12 mg/g with AC-MnO_2 against 172.197 mg/g with AC.

We note for the two activated carbons, a rapid adsorption of MB in the first 10 minutes. This rapid adsorption phase is followed by a slow adsorption phase before reaching equilibrium. The rapid evolution of the adsorbed quantity of MB during the first minutes of contact could be explained by the rapid and significant occupation of the many sites available for the adsorption of the dye [24]. The slow adsorption phase is due to the fact that the sites are more and more occupied, thus becoming less and less available. It then follows from a diffusion of MB towards the less accessible sites slowing down the rate of adsorption.

Adsorption kinetics

Kinetics experiment is conducted to examine the mechanism that governs the adsorption of adsorbate onto the adsorbent surface [25]. This is important in describing the rate-determining step of the adsorption process [26]. In this study, pseudo-first order and pseudo-second order kinetics were considered in evaluating the experimental data. The pseudo-first order kinetic model, also known as the Lagergren equation [27], assumes that the rate-limiting mechanism of the adsorption process is physical adsorption. The linearized kinetic rate equation can be written as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (6)$$

where k_1 is the rate constant of pseudo-first order adsorption (1/min); q_e and q_t are the amount of MB adsorbed per gram of adsorbent (mg/g) at equilibrium and at any time respectively. A straight line for the plot of ln (qe - qt) versus t (figure 3) would give the first-order rate constant k_1 and equilibrium adsorption capacity qe, from the slope and intercept of the line.

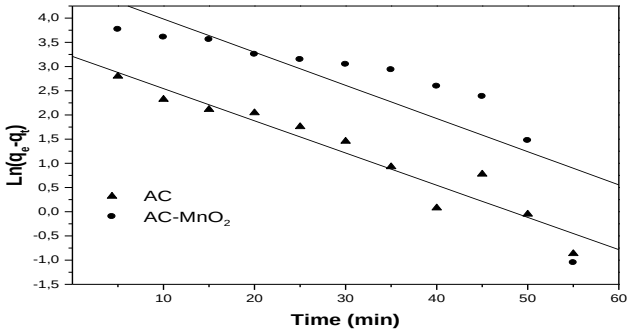

Figure 3: Pseudo-first order kinetics plots for MB adsorption on AC and AC-MnO_2.

The pseudo-second order kinetic model assumes that the rate-limiting mechanism of the adsorption process is chemisorption [28]. The linearized kinetic rate equation can be written as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e} t \qquad (7)$$

where k_2 (g/mg.min) is the rate constant of pseudo-second order adsorption. The plot of t/qt versus t (figure 4) would give the pseudo-second order rate constants k_2 and qe.

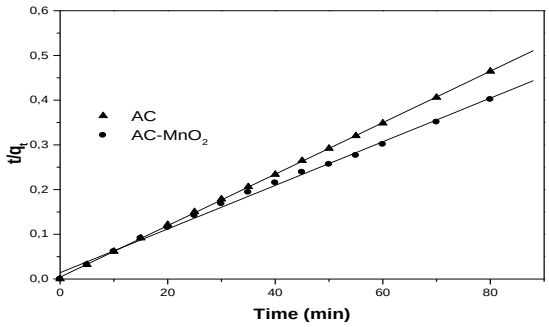

Figure 4: Pseudo-second order kinetics plots for MB adsorption on AC and AC-MnO_2.

The calculated kinetic parameters are given in Table 2.

Table 2: Parameters of two kinetic models for BM adsorption onto AC and AC-MnO_2

Model		Pseudo-first order			Pseudo-second order		
Adsorbent	**q_e exp (mg/g)**	**q_e cal (mg/g)**	**k_1 (1/min)**	**R^2**	**q_e cal (mg/g)**	**k_2 (g/mg min)**	**R^2**
AC	172.19	24.75	0.066	0.964	173.61	0.008	0.999
AC-MnO_2	199.12	106.38	0.068	0.825	204.9	0.002	0,998

Based on the fact that the model with the largest value of R^2 is the best fit [29], it appears that the pseudo-second order kinetic model better describes the experimental data than the pseudo-first order kinetic model for both adsorbents. This suggests that the rate-limiting mechanism of the adsorption process is chemisorption. The sorption process could be the formation of a covalent bond between the surface functional groups of the adsorbent and the adsorbate. Also, the evident gap between q_e cal and q_e exp show that the MB adsorption processes on AC and the AC-MnO_2 are not a pseudo-first order reaction. Table 2 shows that the q_e,cal values calculated from pseudo-second-order kinetic equation agreed well with the experimental data (q_e,exp).

Adsorption isotherms

Adsorption isotherms are important to describe the adsorption mechanism and to determine the maximum adsorption capacity and also to consider the feasibility of the application process. Langmuir and Freundlich equations were used to study the adsorption isotherms.

The Langmuir model is describing the monolayer adsorption onto a surface with a finite number of identical sites. Linear form of Langmuir isotherm is given by [30]:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{k_L \times q_{max}} \frac{1}{C_e} \qquad (8)$$

Where q_{max} (mg/g) is the maximum adsorption capacity and k_L is a constant factor related to the energy. The variations of 1/qe are plotted versus 1/Ce in Figure 5.

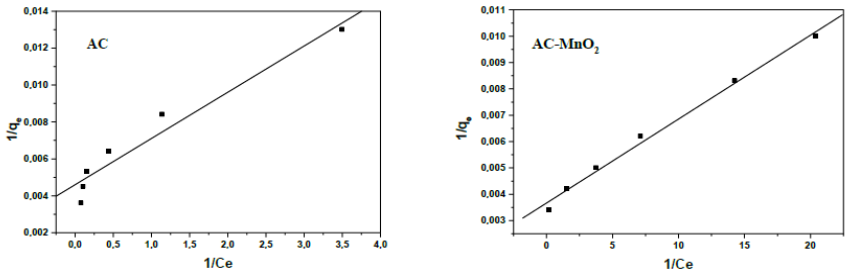

Figure 5: Langmuir isotherms of BM adsorption onto AC and AC-MnO_2 at 30 °C

The Freundlich model is based on the sorption onto a heterogeneous surface. The linear expression of Freundlich equation is as follow [31]:

$$\mathrm{Ln}q_e = \ln K_F + \left(\frac{1}{n}\right)\ln C_e \qquad (9)$$

Where K_F and n are the Freundlich constants, being indicators of adsorption capacity and adsorption intensity, respectively. Lnq_e versus LnCe is plotted in Figure 6.

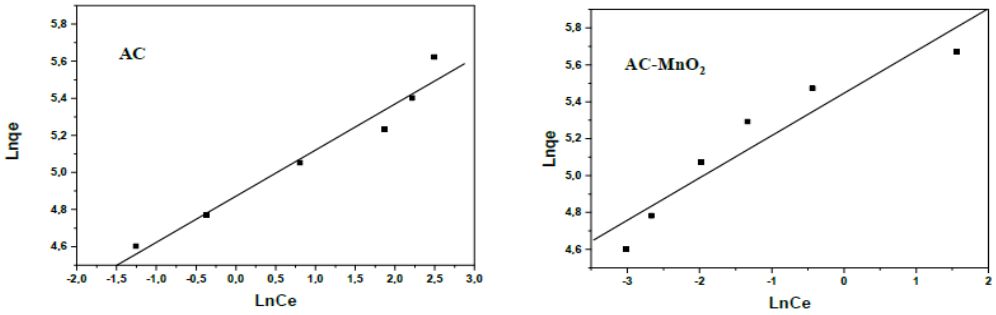

Figure 6: Freundlich isotherms of BM adsorption onto AC and AC-MnO_2 at 30 °C

The regression coefficients and model parameters for Langmuir and Freundlich isotherms are listed in Table 3.

Table 3: Isotherms models constants for MB adsorption onto AC and AC-MnO_2

	Langmuir			Freundlich		
Adsorbent	**q_{max} (mg/g)**	**k_L (L/mg)**	**R^2**	**1/n**	**K_F (mg/g)(mg/L)**	**R^2**
AC	222.22	1.80	0.973	0.25	130.720	0.958
AC-MnO_2	270.27	12.33	0.996	0.23	232.688	0.945

It is observed with both activated carbons that the correlation coefficients R^2 of Langmuir model are higher (0.973 for CA and 0.996 for CA-MnO_2) than those obtained with Freundlich model (0.958 for CA and 0.945 for CA-MnO_2) indicating that Langmuir model reproduces the experimental data better than Freundlich model. This result may be due to the homogeneous distribution of active sites on activated carbon surface, suggesting that MB adsorption on CA or CA-MnO_2 is of a uniform monolayer type with the same adsorption energies [32]. The maximum adsorption capacity obtained is 222.22 and 270.27 mg/g respectively for AC and AC-MnO_2. It increased with the modification of activated carbon with $KMnO_4$; this could be explained by the increase in number of oxygen containing functional groups of AC-MnO_2.

CONCLUSION

In this study, activated carbon (AC) made from cocoa pod shells was modified by impregnation in potassium permanganate solution for more efficient removal of methylene blue in aqueous solution. The adsorption kinetics data were found to be better described by the pseudo-second-order model. The equilibrium data of AC and AC-MnO_2 fit well with the Langmuir model, and the adsorption equilibrium can be reached after 60 min. The maximum adsorption capacity of methylene blue on AC-MnO_2 was 270.27mg/g, which was 22 % higher than that on unmodified AC (222.22 mg/g). Based on a favorable removal performance, AC-MnO_2 can be used as a promising adsorbent material to treat contaminated water with methylene blue.

Conflict of Interest: None

REFERENCES

1. Adegoke K.A., Bello O. S. Dye Sequestration Using Agricultural Wastes as Adsorbents. Water Resources and Industry. 2015;12: 8-24. https://doi.org/10.1016/j.wri.2015.09.002.
2. Ahmad M. A., Ahmad N., Bello O. S. Modified Durian Seed as Adsorbent for the

Removal of Methyl Red Dye from Aqueous Solutions. Applied Water Science. 2015; *5*: 407–423. https://doi.org/10.1007/s13201-014-0208-4.

3. Bello O. S., Owojuyigbe E. S., Babatunde M. A., Folaranmi F. E. Sustainable Conversion of Agro-Wastes into Useful Adsorbents. Applied Water Science**.** 2017; 7: 3561–3571. https://doi.org/10.1007/s13201-016-0494-0.
4. Tan I.A.W., Hameed B.H., Ahmad A.L. Equilibrium and Kinetic Studies on Basic Dye Adsorption by Oil Palm Fibre Activated Carbon. Chemical Engineering Journal. 2007; 127: 111–119. https://doi.org/10.1016/j.jhazmat.2008.01.034.
5. Brião G.V., Jahn S.L., Foletto E.L. Highly Efficient and Reusable Mesoporous Zeolite Synthetized from a Biopolymer for Cationic Dyes Adsorption. Colloids and Surfaces. 2018; 556: 43-50. https://doi.org/10.1080/16583655.2020.1736767.
6. Jawad A.H., Sabar S., Ishak A.B.M., Wilson L.D. Microwaveassisted Preparation of Mesoporous Activated Carbon from Coconut (Cocos Nucifera) Leaf by H_3PO_4 Activation for Methylene Blue Adsorption. Chemical Engineering Communications. 2017; 204: 1143–1156. https://doi.org/10.1080/00986445.2017.1347565.
7. Jawad A.H., Abdulhameed A.S. Mesoporous Iraqi Red Kaolin Clay as an Efficient Adsorbent for Methylene Blue Dye: Adsorption Kinetic, Isotherm and Mechanism Study. Surfaces and Interfaces. 2020; 18: 100422. https://doi.org/10.1016/j.surfin.2019.100422.
8. Wong S., Ghafar N.A., Ngadi N., Razmi F.A., Inuwa I.M., Mat R., Amin N.A.S. Effective Removal of Anionic Textile Dyes Using Adsorbent Synthesized from Coffee Waste. Scientific Reports. 2020; *10* (1): 2928. https://doi.org/10.1038/s41598-020-60021-6.
9. Yagub M. T., Sen T.K., Afroze S., Ang H.M. Dye and Its Removal from Aqueous Solution by Adsorption: A Review. Advances in Colloid and Interface Science. 2014; 209: 172–184. https://doi.org/10.1016/j.cis.2014.04.002.
10. Salem I.A. Activation of H_2O_2 by Amberlyst-15 Resin Supported with Copper (II)-Complexes towards Oxidation of Crystal Violet. Chemosphere. 2001; 44 (5): 1109–1119. https://doi.org/10.1016/s0045-6535(00)00478-1.
11. Singh S., Lo S.L, Srivastava V.C., Hiwarkar A.D. Comparative Study of Electrochemical Oxidation for Dye Degradation: Parametric Optimization and Mechanism Identification. Journal of Environmental Chemical Engineering. 2016; *4* (3): 2911–2921. https://doi.org/10.1016/j.jece.2016.05.036.
12. Avlonitis S.A., Poulios I., Sotiriou D., Pappas M., Moutesidis K. Simulated Cotton Dye Effluents Treatment and Reuse by Nanofiltration. Desalination. 2008; 221 (1-3): 259-267. https://doi.org/10.1016/j.desal.2007.01.082.
13. Gupta V. K., Jain R., Nayak A., Agarwal S., Shrivastava M. Removal of the Hazardous Dye-Tartrazine by Photodegradation on Titanium Dioxide Surface. Materials Science and Engineering. 2011; 31 (5): 1062–1067. https://doi.org/10.1016/j.msec.2011.03.006.
14. Aljeboree A. M., Alshirifi A. N., Alkaim A. F. Kinetics and Equilibrium Study for the Adsorption of Textile Dyes on Coconut Shell Activated Carbon. Arabian Journal of Chemistry. 2017; 10: S3381–S3393. https://doi.org/10.1016/j.arabjc.2014.01.020.
15. Gupta V.K., Kumar R., Nayak A, Saleh T.A., Barakat M.A. Adsorptive Removal of Dyes from Aqueous Solution onto Carbon Nanotubes: A Review. Advances in Colloid and Interface Science. 2013; 193–194: 24–34. https://doi.org/10.1016/j.cis.2013.03.003.
16. Shah I., Adnan R., Wan S.W.N., Mohamed N., Iron Impregnated Activated Carbon as an Efficient Adsorbent for the Removal of Methylene Blue: Regeneration and Kinetics Studies. PLOS ONE. 2015; *10* (4): e0122603.
17. Bhatnagar A., Hogland W., Marques M., Sillanpää M. An Overview of the Modification Methods of Activated Carbon for Its Water Treatment Applications. Chemical Engineering Journal. 2013; 219: 499-511. https://doi.org/10.1016/j.cej.2012.12.038.
18. Girish C. R. Various Impregnation Methods Used for the Surface Modification of the

Adsorbent: A Review. International Journal of Engineering and Technology. 2018; 7 (4.7): 330–334. https://doi.org/10.14419/ijet.v7i4.7.20571.
19. Stêpniewska Z., Sochaczewska A., Woliñska A., Szafranek-Nakonieczna A., Paszczyk M. Manganese Release from Peat Soils. International Agrophysics. 2010; *24* (4): 369-374.
20. Naeem S., Baheti V., Militky J., Wiener J., Behera P., Ashraf A. Sorption Properties of Iron Impregnated Activated Carbon Web for Removal of Methylene Blue from Aqueous Media. Polymer fibers. 2016; 17: 1245–1255. https://doi.org/10.1007/s12221-016-6423x.
21. Boehm H.P. Some Aspects of the Surface Chemistry of Carbon Blacks and Other Carbons. Carbon. 1994 ; 32 : 759–769. https://doi.org/10.1016/0008-6223(94)90031-0.
22. Mamane O. S., Zanguina A., Daou I., Natadou I. Préparation et Caractérisation de Charbon Actif à Base de Coques de Noyaux de Balanites Egyptiaca et de Zizyphus Mauritiana. Journal de la Société Ouest-Africaine de Chimie. 2016; 41: 59-67.
23. Maazou D. B., Hilma H. I., Malam M. M., Adamou Z., Natateri I. Elimination du Chrome par du charbon actif élaboré et caractérisé à partir de la coque de noyau de Balanite Aegyptiaca. International Journal of Biological and Chemical Sciences. 2017; 11 (6): 3050–3065. https://doi.org/: https://dx.doi.org/10.4314/ijbcs.v11i6.39.
24. Fayoud N., Alami Y.S., Tahiri S., Albizane A. Kinetic and Thermodynamic Study of the Adsorption of Methylene Blue on Wood Ashes. Journal of Materials and Environmental Science. 2015; 6 (11): 3295–3306.
25. De Luna M. D.G., Flores E. D., Genuino D. A.D., Futalan C.M., Wan M.W. Adsorption of Eriochrome Black T (EBT) Dye Using Activated Carbon Prepared from Waste Rice Hulls-Optimization, Isotherm and Kinetic Studies. *Journal* of the *Taiwan Institute* of *Chemical* Engineers. 2013; 44 (4): 646–653. https://doi.org/10.1016/j.jtice.2013.01.010.
26. Kan, C.C., Ibe, A.H., Rivera, K.K.P., Arazo, R.O., de Luna, M.D.G. Hexavalent Chromium Removal from Aqueous Solution by Adsorbents Synthesized from Groundwater Treatment Residuals. Sustainable Environment Research. 2017; 27: 163e171. https:// doi.org/10.1016/j.serj.2017.04.001.
27. Lagergren, S. About the Theory of So-Called Adsorption of Soluble Substances. Kongliga. Svenska vetenskaps-akademiens handlingar. 1898; 24: 1-39.
28. Ho, Y.S., McKay, G. A Comparison of Chemisorption Kinetic Models Applied to Pollutant Removal on Various Sorbents. Process Safety and Environmental Protection. 1998; 76: 332e340. https://doi.org/10.1205/095758298529696.
29. Lima E.C., Adebayo M.A., Machado F. M. Chapter 3- Kinetic and Equilibrium Models of Adsorption in Carbon Nanomaterials as Adsorbents for Environmental and Biological Applications. C.P. Bergmann, F.M. Machado Editors, ISBN 978-3-319-18874-4, Springer. 2015. p.33-69. DOI 10.1007/978-3-319-18875-1_3.
30. Langmuir I. The Adsorption of Gases on Plan Surfaces of Glass, Mica and Platinum. Journal of the American Chemical Society. 1918; 40: 1361–1403. https://doi.org/10.1021/ja02242a004.
31. Freundlich H. Over the Adsorption in Solution. Journal of Physical Chemistry. 1906; 57: 384-470.
32. Cazetta A.L., Vargas A.M.M., Nogami E.M., Kunita M.H., Guilherme M.R., Martins, A.C., Silva T.L., Moraes J.C.G., Almeida V.C. NaOH-Activated Carbon of High Surface Area Produced from Coconut Shell: Kinetics and Equilibrium Studies from the Methylene Blue Adsorption. Chemical Engineering Journal**.** 2011; 174: 117–125.

How to cite this article: Akissi Lydie Chantal Koffi, Djamatché Paul Valéry Akesse, Amadou Kouyate et.al. Adsorption of methylene blue on MnO_2-modified activated carbon prepared from cocoa pod shells. *International Journal of Research and Review*. 2022; 9(10): 34-42. DOI: *https://doi.org/10.52403/ijrr.20221006*

******