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Study of the Synthesis of Activated Carbon from Brewery Grains: Application to the Removal of the Cationic Dye Methylene Blue

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Abstract: The aim of this work is the synthesis of actived carbon optimized from the brewery's residue by a simple pyrolysis process preceded by a chemical impregnation with phosphoric acid. The activated carbon obtained coded CA-D has been applied for the removal of to the cationic dye (methylen blue). With a good mass yield of 77.7%, the iodine and methylene blue index tests on CA-D are 987.9 mg/g and 658.4 mg/g, respectively. The CA-D surface functions have more acidic chemical functions (6.4 meq/g) than basic functions (1.6 meq/g) with a pH at zero charge point to 4.3. The methylene blue adsorption tests on CA-D showed that equilibrium was established after 90 minutes. The influence of parameters such as adsorbent mass, pH and the initial pollutant solution concentration were studied to determine the best adsorption conditions of methylene blue dye on CA-D. The maximum removal rate (99%) of methylene blue is obtained at a basic pH of 8 with a mass of 0.3g of CA-D. The kinetic model of pseudo-second gives a better description of the kinetics of the BM adsorption reaction on CA-D with a correlation coefficient close to 1 ($R^2 = 0.99$) and a large approximation of the theoretical (50.35 mg/g) and experimental (49.63 mg/g) adsorption capacity. The studies on adsorption isotherms show that the H-type isotherm (Freundlich isotherm) is better adapted but is also similar to the L-type (Langmuir isotherm). CA-D could then be an alternative adsorbent for the removal dyes from water.

Keywords: Brewery Brewers' Grains, Activated Carbon, Adsorption, Adsorption Capacity

1. Introduction

Rapid population growth and socio-economic development lead to a considerable production of solid waste, and the main course of action for the preservation of the environment lies essentially in its disposal or reduction. Thus, the global interest in preserving the environment in the face of agri-food waste has attracted the attention of some researchers to find technical ways to recover and limit the production of this waste [1]. As a result, a technical waste management policy has developed in recent years; Examples include energy production, composting and the synthesis of activated carbon. Our work focuses on the latter, the development of activated carbon from agri-food waste. In addition, several studies have been devoted to the synthesis of active coals from materials from various vegetable sources such as coconut shell [2], shea and cotton cakes [3], cocoa shell [4], date kernels [5]. Indeed, brewery waste is a by-product of the process of making beer from cereals. Today, the main way of valorization of this by-product in our country is only through soil modification and livestock feeding. It is in this perspective that this work is part of which the objective is to recycle brewery waste into chemically active charcoal by using phosphoric acid as a chemical activator. It is in this perspective that this work is to valorize the brewery waste

into chemically actived carbon by using phosphoric acid as chemical activator. From this objective, it will be specifically necessary to first synthesize activated carbon from brewery waste, then to characterize it and finally apply it for elimination of methylene blue cationic dye.

2. Materials and Methods

2.1. Preparation of Activated Carbon

2.1.1. The Raw Material

The precursor used in our study is a vegetable material: brewery grain. It is an agri-food by-product of the grain-based beer manufacturing process. After being collected at the Lomé brewery, they were washed with distilled water and then ground and dried at room temperature for seven days. Then, it was sieved using AFNOR SIEVE to recover particles less than 2mm, which were finally impregnated with 40% phosphoric acid. The impregnated mixture was dried at room temperature for 72 hours and then dried in the oven (Interlab Instruments Type (DP1-I)) for four hours.

2.1.2. Carbonization

The impregnated mixture is charred in an oven (W. C HERAEUS HANAU type RSK 10) previously heated for 2 hours before the start of the experiment to reach an equilibrium temperature. The carbonization is done at 400°C for a duration of 2 hours. The activated carbon obtained is cooled to room temperature in a desiccator and then washed with a 0.1M hydrochloric acid (HCl) solution [6] and then rinsed again with distilled water to a constant pH (pH equal to 6.4). The actived carbon washed is dried in the oven at 105°C for at least 8 hours. The dried activated carbon is kept in a hermetically sealed bottle until the characterization tests.

2.2. Characterization of Activated Carbon

2.2.1. Mass Yield

The mass yield represents the ratio of the mass of the activated coal to the mass of the dried grain used. Mass measurements were made using a high-precision scale (Interlabs Instruments type Sartorius analytic).

$$Mass\ yield\ (\%) = \frac{mass\ of\ carbon}{mass\ of\ brewer's\ grains} \cdot 100$$

2.2.2. Methylene Blue Index

The procedure used is that of the CEFIC method [7]. It consists of introducing 0.1g of activated carbon into 100 mL of the standard methylene blue analytical solution. The mixture is stirred for 20 min and then filtered using Wattman filter paper. The residual concentration of methylene blue is determined after a spectrophotometer (6705 UV/Vis Spectrophotometer JENWAY) reading at a wave length of 620 nm. The value of the methylene blue index is estimated by the following equation:

$$Q_{BM} = \frac{(Ci - Cr).V.M}{mCA} X100$$

QBM (the adsorption capacity of the AC expressed in mg.g^{-1}); Ci (the initial concentration of the BM solution in mol.L^{-1}); Cr (the residual concentration of the BM solution in mol.L^{-1}); V (the volume of the BM solution in mL); M (the molar mass of BM in g mol^{-1}); mCA (the mass of AC used in g).

2.2.3. Iodine Index

It was determined using the experimental protocol proposed by the American Society for Testing and Materials (ASTM), which is based on the AWWA standard [3]. This method involves putting 1 g of dry activated carbon in contact with 10.0 ml of a 5% hydrochloric acid (Sigma-Aldrich) solution and then bringing the mixture to a boil for about 30 s. Then 100.0 ml of a standard iodine solution (Fulka) of N_1 concentration equal to 0.10N in the mixture and then stirred for a short time for 30 s. The new mixture is filtered and then a volume of 50ml of the filtrate is taken for titration by a solution of sodium thiosulphate (Fulka) of N_2 concentration equal to 0, 10 N using starch as the end-of-assay indicator. The volume V (mL) of the sodium thiosulphate solution used is noted. The amount (X') of iodine adsorbed by the relationship is determined:

$$X'(meq) = 100 \cdot N_1 - \frac{(110 \cdot N_2 \cdot V)}{50}$$

With N_1 the normality of the iodine solution, N_2 the normality of the sodium thiosulfate solution, V the volume (mL) of the sodium thiosulfate solution used for assay.

The iodine value of the activated carbon is then calculated using the following equation:

$$X'(meq) = 100 \cdot N_1 - \frac{(110 \cdot N_2 \cdot V)}{50}$$

With N_1 the normality of the iodine solution, N_2 the normality of the sodium thiosulfate solution, V the volume (mL) of the sodium thiosulfate solution used for the determination.

The iodine value of the activated carbon is then calculated using the following equation:

$$Indice\ d'iode = \frac{X}{m} \cdot A$$

With *A* the correction factor obtained after the calculation of the normality of the residual filtrate, m the mass (g) of activated carbon, *X* the quantity in mg of iodine adsorbed. *X* is given by:

$$X(mg) = 126,93 \cdot X'(meq)$$

2.2.4. PH at Zero Charge Point (pHPZC)

The pH at zero charge point (pH$_{PZC}$) of activated carbon is determined using the method of Lopez-Ramon et al [8]. This method involves putting 0.1 g of dry activated carbon in contact with 20 mL of 0.1 mol. L-1 NaCl solutions of pH between 2 and 10 for 3 days of agitation. Each solution is then filtered through a filter paper (Double Rings Filter Paper) and a new pH measurement is performed with the WTW 330i/SET pH meter. The C curve is plotted as a function of initial pH to find the pH$_{PZC}$. The pH$_{PZC}$ is then the pH of the

solution for which the curve C passes through the first bisector (final pH = initial pH).

2.2.5. Surface Chemical Functions

The measurements are carried out according to the Boehm method and taken from Michel's research [9]. From this method, 0.1 M solutions of NaOH, Na_2CO_3, $NaHCO_3$, CH_3CH_2ONa and HCl (Fulka) are prepared using distilled water. 1g dry activated carbon is brought into contact with 100 mL of each of these solutions. Each solution is agitated for 24 hours to ensure that as many surface groups of activated carbon as possible have reacted.. At the end of this period, the solutions are filtered using double ring filter paper. Each of the five solutions is measured by pH-metry (pH-meter WTW 330i/SET). The basic solutions are determined by 0.1 M hydrochloric acid, the acid solution by sodium hydroxide 0.1 M.

To the equivalence we have:

$$C_eV_e = CV. \text{ were } C = \frac{C_eV_e}{V}$$

$$n = (C_i - C) \cdot V_i$$

n (quantity of groups per gram of activated carbon); V_e (volume of hydrochloric acid or sodium hydroxide at the equivalence); C_e (concentration of the hydrochloric acid or soda solution); V (volume of the solution to be determined); C (concentration of the solution to be determined); V_i (volume of the starting solution); C_i (concentration of the starting solution).

2.3. Adsorption Methods

2.3.1. Influence of Contact Time and Initial Concentration

The experimental procedure followed is the Batch method. It consists in bringing together the same mass of 0.2 g of CA-D activated charcoal in a series of identical flasks each containing 100 mL of the methylene blue solution at different concentrations (100 mg/L, 200 mg/L, 300 mg/L of the methylene blue solution). The whole is constantly agitated to ambient temperature. Samples were taken at various intervals to determine the steady state from which the residual concentration of methylene blue in solution Becomes almost constant.

2.3.2. Influence of the PH of the Solution

We put in contact a mass of 0.3g of activated carbon with different solutions of methylene blue at pH equal to 2, 4, 6, 8 and 10. These solutions of the same concentration of 100 mg/L and volume equal to 100 mL each were subjected to constant agitation at room temperature to determine the residual concentration of methylene blue after 2 hours of testing.

2.3.3. Influence of Activated Carbon Mass

Masses of 0.1g to 0.6g of activated charcoal were each brought into contact with 100 mL of methylene blue solution at 100 mg/L. The contact surface variation (AC mass variation) was performed for a contact time of 2 hours.

2.3.4. Study of the Chemical Kinetics of Methylene Blue Adsorption on CA-D

This study consists of contacting 0.2 g of activated carbon in 100 mg/L of 100 mL methylene blue solution. Then determine the parameters of the first-order and second-order chemical kinetics from the Cartesian equation data and the correlation coefficient obtained from the linear plot of: $ln(q_e-q)$ based on time t for first-order pseudo kinetics and t/q depending on time time for pseudo-second-order kinetics.

2.3.5. Study of Adsorption Isotherms

This is an important factor in the study of the adsorption process since it allows us to evaluate the ability of the adsorbents to adsorb the pollutant (here methylene blue) and also to know the amount of pollutant adsorbed to equilibrium (adsorbate-adsorbent equilibrium property). To determine the kind of adsorption, it is therefore necessary to calculate the amount of pollutant (methylene blue) absorbed by activated carbon. Then the graph $Q_e = (\ )$ must be plotted. Due to their simplicity, kinetic models such as Langmuir and Freundlich will be used.

3. Experimental Results and Discussion

3.1. Characterization of Activated Carbon

3.1.1. Mass Yield

The mass yield of carbonization of spent grain at 400°C is 77.7%. This result is similar to that obtained by GUEYE et al. in 2011 [10]. Thus, from this mass yield we can deduce that the degree of activation or burn off is 22.3%; a value lower than 50%, which would mean that our coal would have a good microporosity as pointed out by some authors like Elena Fernandez [11].

3.1.2. Iodine Value and Methylene Blue Value

The iodine value and the methylene blue value are parameters that provide an assessment of the specific surface of the activated carbon. These indices usually serve to know the nature of the pores (microporous, mesoporous). As for our activated carbon, the value of these indices are recorded in the table below.

Table 1. Iodine and methylene blue values of CA-D activated carbon.

	Iodine value (mg/g)	Methylene Blue Index (mg/g)
Activated carbon CA-D	987,9	658,4

The iodine value of our activated carbon is 987.9 mg/g. According to the study of Tchakala et al. (2012) [12], the high value of the iodine index would reflect an interesting adsorbent power of microporous molecules. Furthermore, the literature shows that actived carbons with an iodine index higher than 950 mg/g would have a good power of adsorption of small molecules, those which are responsible for the tastes and odors in water [13].

The methylene blue index is the endpoint for evaluating the adsorption capacity of medium-sized molecules on coal

by mesopores. In the case of our study the index value is 658.4 mg/g CA-D; a result similar to that obtained by Ousmaila et al in 2016 [13] and by Maazou et al on activated carbons elaborated from balanite nut shells [14]. Such a value of methylene blue index suggests that in addition to micropores due to the high value of iodine index, CA-D coal could also have meso and macropores.

3.1.3. PH at the Point of Zero Charge and Surface Chemical Functions

The pH at the point of zero charge is 4.4 as shown in Figure 1. This pH is acidic, which can be explained by the nature of the activator, phosphoric acid, and reflects the relatively large number of acidic sites introduced during the chemical activation.

This result of pHpzc equal to 4.4 is in agreement with that obtained for surface chemical functions which are mostly
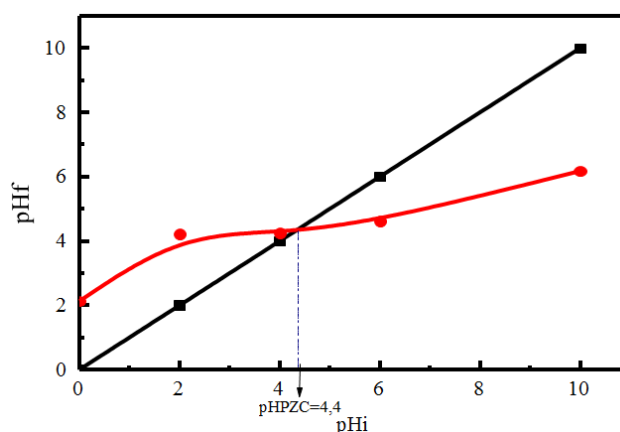
acidic.

Figure 1. Determination of pH at zero charge point (pHPZC).

Table 2. Surface functions of CA-D activated carbon (meq/g CA).

	Acides					Basics
	Carboxylique	Lactone	Phénol	Carbonyl	Total Acid	Basic total
CA-D	0,14	2,12	2,74	1.42	6.42	1,65

The analysis of these results shows the predominance of acidic functions over basic functions. In agreement with the pH_{pzc} can be explained the strength of the activator 40%. Indeed, phosphoric acid is a strong oxidant, it can oxidize surface carbon atoms and make them lose electrons to be positively charged [3]. Furthermore:

If the pH of the solution is lower than pH_{pzc}, the surface functional groups of the adsorbents will be protonated by an excess of H^+ protons from the solution, the support is a negatively charged adsorbate attractor.

On the contrary, if the pH of the solution is higher than pH_{pzc} the surface functional surface groups will be deprotonated by the presence of OH^- ions in the solution, the support is attractor of positively charged adsorbate, (which would promote the adsorption of cationic dyes, increase of electrostatic forces between the negative charge of the adsorbent and the positive charge of dye) [15].

3.2. Adsorption Experiments of Methylene Blue on CA-D Activated Carbon

3.2.1. Influence of Contact Time and Initial Concentration

Figure 2 shows the evolution of the adsorption capacity of BM over time at room temperature of approximately 30°C. The results obtained showed that the equilibrium time obtained for the adsorption of methylene blue is independent of the initial concentration of that pollutant in solution. The results also show us the existence of three trends of abatement over time. A first trend that is fast, a second that shows a reduction in slowdown and a last that shows a equilibrium from the 90th minute adsorption time. This may be explained firstly by the decrease in the concentration gradients of the pollutant in solution during adsorption. Moreover, the extension of the contact time beyond 90 minutes does not lead to any improvement in the adsorption

percentages of methylene blue in solution. It can then be deduced that the equilibrium time for the adsorption of methylene blue on CA-D activated carbon is 90 minutes. Mbaye GUEYE obtained an equilibrium time of 120 min for the elimination of BM with CA-CJ-H$_3$PO$_4$ [16], Tchakala obtained equilibrium times of 40 and 70 minutes respectively by adsorption of methylene blue on activated carbons prepared from shea cake (CA-K) and cotton seed (CA-C) [3], compared with 5 hours based on Houas et al. [17] for methylene blue adsorption on commercial activated carbon and 48 hours based on KHELIFI et al [18] for BM adsorption on oxidized activated carbon. This difference in the behaviour of BM with regard to these different activated carbons is obviously due to their origins, their manufacturing method and their porous texture.
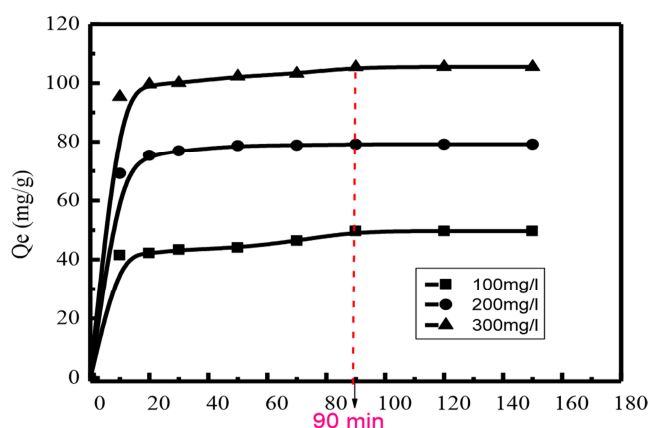

Figure 2. Influence of contact time and initial concentration of methylene blue adsorption on the adsorption capacity of CA-D activated carbon (mCA = 0.2g, V= 100ml).
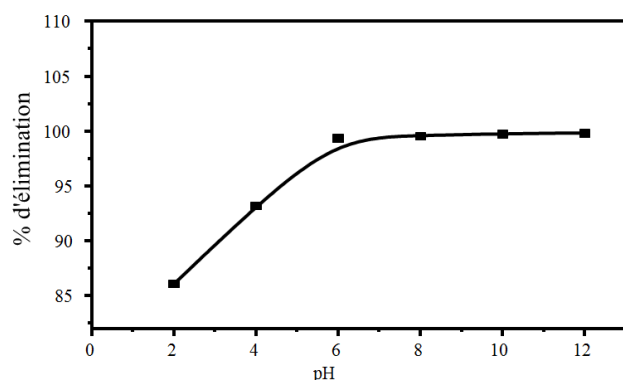
Figure 3. Curve showing the influence of pH on the adsorption of methylene blue by CA-D (mCA=0.3g, V= 100ml, Concentration = 100mg/l).

3.2.2. Influence of pH on the Adsorption of Methylene Blue on CA-D

The result of this study shows the evolution of the percentage of adsorption of the cationic dye methylene blue in solution at a concentration of 100mg/L in contact with

masses of activated carbon ranging from 0.1g to 0.6g at free pH and at room temperature. Logically and as already reported by many authors, including Tchakala [3], it can be seen that the percentages of adsorption increase with the mass of activated carbon used, reaching here more than 99.8% elimination of the methylene blue for a mass of 300 mg of activated carbon. This can be explained by the fact that the increase in the mass of the adsorbent increases the specific surface and therefore the number of available adsorption sites. Therefore the probability of encounter (molecule-site) increases, hence the increase in the amount of dye adsorbed. Similar results are obtained by many Mbaye Gueye [16].

3.2.3. Chemical Kinetics of Methylene Blue Adsorption on CA-D Activated Carbon

The results of the evaluation of the chemical kinetics of adsorption of methylene blue on CA-D activated carbon are reported in Table 3 below:

Table 3. Summary table of parameters from the Chemical Kinetics of Methylene Blue Adsorption on CA-D Activated Carbon Linear Transforms.

Pseudo first order						
	$q_{e, \, exp}$ (mg/g)	$q_{e, \, exp}$ (mg/g)	$q_{e, \, cal}$ (mg/g)	k_1 (min^{-1})	r_1^2	$\Delta q/q$ (%)
CA-D	49.63	49.63	9.952	0.014	0.90	80.0
Pseudo second order						
	$q_{e, \, exp}$ (mg/g)	$q_{e, \, exp}$ (mg/g)	$q_{e, \, cal}$ (mg/g)	K_2 (g/mg/min)	r_2^2	$\Delta q/q$ (%)
CA-D	49,63	49,63	50,35	0,004	0,99	1,4

From these results, we note that the correlation coefficient R_2^2 is higher than R_1^2, moreover the value of the experimental adsorption capacity (qe_{exp}) is much closer to the calculated adsorption capacity (qe_{cal}) from the linear form in the case of the pseudo-second order kinetics, as also justified by the higher error rate ($\Delta q/q$) in the case of the pseudo-first order kinetics 80% versus 1.4% in the pseudo-second order. In summary, it can be said that the pseudo-second order kinetic model gives a better description of the kinetics of the adsorption reaction of methylene blue on CA-D activated carbon, than the pseudo-first order kinetic model. Similar results were found by Tchakala [3] who showed that the adsorption of methylene blue on CA-K and CA-C activated carbons is well described by the pseudo second order kinetics.

3.2.4. Adsorption Isotherms

Adsorption isotherms play an important role in determining the maximum capacities and in identifying the type of adsorption. These adsorption isotherms are obtained by plotting the amount of Methylene Blue adsorbed per g of activated carbon (Q_e) against the equilibrium concentration of Methylene Blue (C_e). The experimental results obtained (figure 4) indicate that the adsorption isotherm of Methylene Blue is of the type H (Freundlich isotherm) but is also close to the type L (Langmuir isotherm) according to the classification of Giles et al [19] and taken up by Tchakala in his thesis work [3].
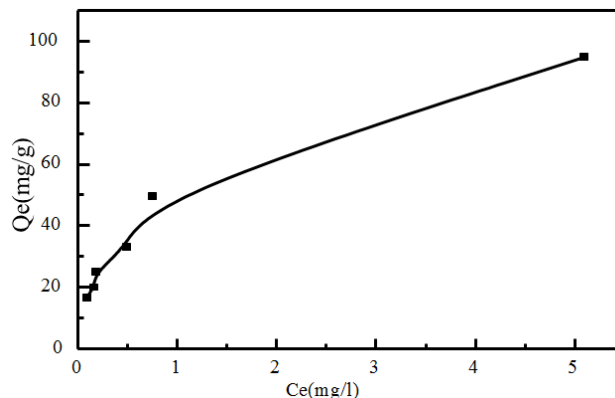

Figure 4. Adsorption isotherms of Methylene Blue on activated carbon (C = 100 mg/L, V = 100 mL, m=0.2g, free pH).

We also applied the Langmuir and Freundlich models to these isotherms. Table 4 below shows the results from the linear transforms of the Langmuir isotherm and the Freundlich isotherm respectively.

Table 4. Summary table of the parameters of the linear transforms of the Langmuir isotherm and the Freundlich isotherm.

LANGMUIR				
	Qo(mg/g)	KL	RL	R_1^2
CA-D	63,29	3,59	0,0027	0,90
FREUNDLICH				
	n	1/n	KF (mg/g)	R_2^2
CA-D	2,28	0,438	48,74	0,97

The results reported in Table 4 show correlation coefficient values close to 1 for both types of isotherms (R_1^2 = 0.90) for Langmuir and R_2^2 = 0.97 for Freundlich). This allows us to hypothesize that the two types of isotherms can better describe the adsorption process of methylene blue on CA-D activated carbon. Moreover, since the Freundlich correlation coefficient (R_2^2 = 0.97) is higher than the Langmuir correlation coefficient (R_1^2 = 0.90), it can be concluded that the adsorption process of methylene blue on CA-D activated carbon is better adapted to the Freundlich adsorption isotherm, but tends to the Langmuir isotherm On the other hand, the value of the Langmuir isotherm separation factor RL = 0.0027 (0 < RL< 1) suggests that the methylene blue adsorption process is favorable on CA-D activated carbon [20]. Considering also the adsorption intensity value n = 2.28 (1< n <10), we can then confirm that the pore heterogeneity condition [21] is verified on our CA-D carbon.

4. Conclusion

Activated carbon synthesized from brewery grains (CA-D) was characterized and then used for the removal of the cationic dye methylene blue. The overall results obtained from these experiments show that good activated carbon can be produced by simple pyrolysis. From this study, the CA-D activated carbon obtained (with a mass yield of 77.7%) has the following characteristics:

1) An iodine value of 987.9 mg/g, which implies that this carbon is suitable for the adsorption of small molecules (size < 2nm);

2) A methylene blue value of 658.4 mg/g is acceptable to indicate the presence of meso- and macropores; An acidic pH at the point of zero charge (pH$_{PZC}$ = 4.3), which is consistent with the surface functions being more acidic in nature (6.4 meq/L) than basic (1.6 meq/L).

The adsorption of BM on CA-D was found to be maximal at basic pH after T$_e$ = 90 min with a mass of 0.3g of CA-D activated carbon.

References

[1] K. M. KIFUANI, «Adsorption of a basic dye, Methylene Blue solution», Int. J. Biol. Chem. Sci., vol. 12, no 1, p. 558-575, 2018.

[2] C. Balogoun, M. Bawa, S. Osseni, et M. Aina, «Preparation of activated carbons by chemical means with phosphoric acid based on coconut shell», Int. J. Bio. Chem. Sci, vol. 9, no 1, p. 563, jull. 2015, doi: 10.4314/ijbcs.v9i1.48.

[3] TCHAKALA Ibrahim, "Contribution to the study of the preparation of activated carbons from carbonaceous residues of food processing industries (case of shea cake and cotton cake): characterization and applications in water treatment", Thesis, UNIVERSITE DE LOME, TOGO, 2013.

[4] L. D. Kouadio et al., «preparation and characterization of activated carbon from the cocoa shell.», p. 11.

[5] S. Hazourli, M. Ziati, A. Hazourli, et C. Mouna, «Valorization of a natural ligno-cellulosic residue in activated carbon - example of date pits», Rev. Ener. Renouv., ICRESD 07 Tlemcen, p. 187-192, janv. 2007.

[6] C. R. Weber TW, «Pore and Solid diffusion model for fixed bed adsorbent», J. Am. Inst. Chem. Engg, p. 228-238, 1974.

[7] Belhireche Nabil et Beledjale Ismahane, "Contribution to the preparation of adsorbent materials from date palm by-products", Master's thesis, Echahid Hamma Lakhdar University. El Oued, ALGERIA, 2016. http://193.194.92.111/bitstream/123456789/3345/1/660-045-01.pdf

[8] N'guessan Joachim KROU, "Experimental study and modeling of an AD-OX sequential process for the elimination of organic pollutants", UNIVERSITY OF TOULOUSE, TOULOUSE, 2010.

[9] Ourania A. I et al., «Preparation of activated carbons from agricultural residues for pesticide adsorption.», Chemosphere, n° 80, p. 1328-1336, 2010.

[10] M. Gueye, J. Blin, et C. Brunschwig, «Study of the synthesis of activated carbons from local biomasses by chemical activation with H$_3$PO$_4$», 2iE Scientific Day, Campus 2iE Ouagadougou, p. 6, Apr 2011.

[11] Elena Fernandez Ibañez, "Study of the carbonization and activation of hard and soft plant precursors", Doctoral Thesis, University of Neuchatel, 2002.

[12] I. Tchakala, L. Bawa, G. Djaneye-Boundjou, K. Doni, et P. Nambo, «Optimization of the process for preparing Activated Carbons by chemical means (H$_3$PO$_4$) from Shea cakes and cotton cakes», Int. J. Bio. Chem. Sci, vol. 6, no 1, p. 461-478, août 2012, doi: 10.4314/ijbcs.v6i1.42.

[13] O. S. Mamane, A. Zanguina, I. Daou, et I. Natatou, «Preparation and characterization of activated carbons based on kernel shells of Balanites Eagyptiaca and Ziziphus Mauritiana», p. 59-67, juin 2016.

[14] S. D. Maazou, H. I. Hima, M. M. M. Alma, Z. Adamou, and I. Natatou, «Elimination of chromium by activated carbon produced and characterized from the shell of the kernel of Balanites aegyptiaca», International Journal of Biological and Chemical Sciences, vol. 11, no 6, p. 3050-3065, 2017.

[15] F. Benamroui, «Removal of cationic dyes by activated carbons synthesized from agricultural residues», PhD Thesis, 2015.

[16] M. Gueye, «Development of activated carbon from lignocellulosic biomass for water treatment applications», thesis, Fondation 2iE, 2015. https://agritrop.cirad.fr/579887/

[17] A. Houas, M. K. Bakir, et E. Elaloui, «Study of the elimination of methylene blue», J. Chim. Phys, vol. 96, p. 486, 1999.

[18] A. Khelifi, L. Temdrara, et A. Addoun, «Effect of porous texture and chemical structure on the adsorption of methylene blue by oxided activated carbons.», Journal of the Algerian Chemical Society/Journal de Société Algérienne de Chimie, vol. 19, no 1, 2009.

[19] C. H. Giles, D. Smith, et A. Huitson, «A general treatment and classification of the solute adsorption isotherm. I. Theoretical», Journal of colloid and interface science, vol. 47, no 3, p. 755-765, 1974.

[20] B. H. Hameed, A. L. Ahmad, et K. N. A. Latiff, «Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust», Dyes and pigments, vol. 75, no 1, p. 143-149, 2007.

[21] N. Khalid, S. Ahmad, A. Toheed, et J. Ahmed, «Potential of rice husks for antimony removal», Applied radiation and Isotopes, vol. 52, no 1, p. 31-38, 2000.