



Bio-sorption of Methylene Blue by Defatted Seed of *Adansonia digitata*

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Abstract

The study was carried to evaluate the ability of defatted seed of *Adansonia digitata* (DFSE) to remove methylene blue dye from contaminated water. The optimum parameters such as contact time, particle size, absorbent dose, initial dye concentration, and pH were investigated by performing batch experiments models. The kinetics and the isotherms adsorption were evaluated by varying the initial concentration and using the optimum parameters. The optimum of contact time is 90 min and the removal capacity is 99.34 %. A mass of 700 mg is sufficient to reach the maximum removal of methylene blue (99.44 %). The maximum adsorption is obtained with an initial methylene blue concentration of 75 ppm (98.53 %). The optimum particle size is 100 μm . The kinetics of the adsorption process are in accordance with the pseudo-second order model. Experimental values of the adsorption capacity are close proximity to the optimum values predicted by the pseudo-second order model. The Langmuir, Freundlich, Dubinin-Radushkevich and Tempkin isotherms are not suitable to explain the experimental isotherm.

Introduction

The textile industry is a large consumer of water and rejects a large quantity of liquid containing polluted by dyes or heavy metals. The annual production of 40 million tons of textile fibers generates wastewater volumes estimated at several billion cubic meters per year [1]. Wastewater from the textile industry is typically made up of many contaminants including acids, bases, dissolved solids, toxic compounds, and dyes. These are the most visible, even at low concentrations, because of the appearance they give to the water.

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They must be removed to discolor the waters before the wastewater is discharged [2]. The dangerousness of these pollutants is aggravated by their indefinite persistence in the environment due to their nature. The very high cost for the elimination of these heavy metals in soils and waters by classic physico-chemical methods such as chemical precipitation [3], recovery by electrolysis [4], the use of ion exchange resins [5], solvent extraction [6] or membrane filtration [7], push industrialists who are the main polluters to ignore the problem. Indeed, these methods are excessively expensive and only give low yields for metal concentrations below 100 mg/L [8]. In addition, these methods generate significant quantities of sludge after treatment. For dyes, their disposal from wastewater is essential for both health and the environment. Traditional wastewater treatment technologies have proven ineffective in purifying wastewater polluted with certain types of dyes [9]. Several methods have been used to remove dyes from wastewater. The implementation of physico-chemical and biological processes such as separation [10], oxidation [11], osmosis, photodegradation [12], microbial biodegradation [13]–[15] are difficult and expensive. Some of these processes have a main disadvantage due to the formation of unknown compounds different from the original dye molecule [16], [17]. These intermediates may have different toxicity [18] and remain in solution after treatment of polluted waters. The adsorption method is the easiest to implement with low cost compared to other processes used in industry. A large number of adsorbents such as nanoparticles, clays, zeolites, cellulose by-products, activated carbon, agro-industrial waste, etc. are applied to remove dyes from wastewater [19], [20]. The adsorption process is also the most effective technology for removing dye from wastewater. No intermediates from the degradation of the dye molecules appeared because the dye molecules were directly transferred from the solution to the solid phase of the adsorbent. In addition, the quantities of adsorbent used are quite small. At the end of the process, the adsorbent-laden dye can be stored in the dry phase without harming the environment. The solid phase can be regenerated later for reuse in the process.

In this context, we have proposed the use of the residue of the seeds of *Adansonia digitata*. defatted, which is a very low-cost absorbent for removing methylene blue from industrial effluents. Indeed, methylene blue is a recalcitrant cationic dye widely used in industry which is toxic, and which causes several risks for the environment and health. Hemolytic anemia, hyperbilirubinemia and acute renal failure have been reported as a consequence of neonate exposure to methylene blue [21]. The mechanisms of biosorption of these dyes on the defatted seed have been studied by determining the influence of parameters such as pH, concentration.

Material and Methods

Preparation of the adsorbent

Fruits of *Adansonia digitata* called monkey bread were harvested at the 17°3'41" west latitude and 14°46'13" north latitude. The seeds were collected, and the flesh have been removed. The resulting seeds were rinsed twice with tap water first and distilled water to remove all the fibers. They were shadow dried for a week. After this first process, the seed were dried in an oven at 50°C for 48 hours. The seeds were ground with a grinder before being defatted with hexane using the Soxhlet technique. The resulting powder named was air dried before being stored in a plastic container. The dried defatted seed powder (DFSE) adsorbent was again crushed and sieved to get different sized fractions, namely, 100, 250, 315, 400, 1500 μm . These different fractions were stored in airtight containers for further use.

Point zero charge pH_{PZC}

The pH of the point of zero charge (pH_{PZC}) for DFSE was determined by a titration procedure. To a series of eleven 150 mL conical flasks 45 mL of a solution of KNO_3 0.01 M were added and the pH was accurately adjusted using HCl or NaOH 0.01 N solutions from pH = 2 to pH = 12 and completed with a solution KNO_3 0.01 M to 50 mL. The initial pH (pH_i) was accurately measured again. To each flask, 0.1 g of DFSE was added and the flask was capped and shaken manually each 4 hours. After 48 hours, the final pH (pH_f) was measured. The pH is plotted against pH_i . The point of intersection of the curve and the abscissa axe at $\Delta\text{pH} = 0$ gave the pH_{PZC} .

Batch adsorption tests

All the experiments were conducted in discontinuous batch. A weighed sample of DFSE was mixed with 50 mL of the methylene blue solution in 150 mL conical flasks. The mixture was stirred for a fixed time at 25°C. After this process, the liquid was separated from the adsorbent by filtration through a Whatman Filter N°1. The residual methylene blue concentration was determined using a Lambda 365 Perkin Photometer. The experimental data were used to determine the removal capacity and the quantity of methylene blue adsorbed on the DFSE:

$$\text{Removal capacity (\%)} = \frac{(C_0 - C_e) \times V}{C_0} \times 100$$
$$q_e = \frac{(C_0 - C_e) \times V}{m}$$

where C_0 and C_e are respectively the initial and the final metal concentrations (mg/L) in the liquid phase, V (L) is the volume of the liquid phase and m (g) is the adsorbent mass used.

Effect of time contact on the removal capacity

The equilibrium time was determined using a Methylene Blue solution at a concentration of 50 ppm. Each 50 mL Methylene Blue solution was treated with 0.25 g of DFSE at time ranging from 10 to 120 minutes. The experiments were conducted at the same pH and the flasks contents were stirred at 500 rpm at a temperature of 25°C.

Adsorbent dose effect on the removal capacity

50 mL of a 50 ppm methylene blue solution was treated with a mass of DFSE adsorbent ranging from 0.1 to 1.0 g. The experiments were conducted at the same pH and the flasks contents were shaken at 500 rpm at temperature of 25°C for the optimal time determined previously.

Effect of solution pH on the removal capacity

The effect of solution pH on the dye removal capacities of the DFSE adsorbent was investigated between pH = 2 and pH = 11. The experiments were performed by adding a 0.3 g of DFSE powder into six 150 mL conical flasks containing 50 mL of 50 ppm dye solutions and the pH of the solution was adjusted using 0.1 N HCl or 0.1 N NaOH. The flasks were shaken at 500 rpm and at temperature of 25°C for 120 minutes.

Effect of adsorbent particle size on the removal capacity

The ideal particle size for the adsorbent was determined by treating each category (100, 250, 315, 400 and 1500 μm) with 50 ml of a 50 ppm Methylene Blue solution at the optimum pH. The flasks were shaken at 500 rpm and at a temperature of 25°C for 120 minutes.

Effect of methylene blue solution concentration on the removal capacity

The effect of dye solution on the removal capacity were determined by setting the optimum temperature, granulometry of the adsorbent, the pH of the solution and adsorbent dose and varying the methylene blue concentration between 12.5 to 100 ppm. The flasks contents were stirred at 500 rpm at a temperature of 25°C.

Results and Discussion

Fourier Transforms Infrared Spectroscopy (FTIR) analysis

Figure 1 presents the FTIR of the DFSE seed and the residue after adsorption of methylene blue on DFSE. The FTIR of DFSE shows broad bands centered at 3673 cm^{-1} and 3281 cm^{-1} which are respectively, characteristic of the presence of free hydroxyl groups and associated hydroxyl groups. Bands which appear in the range $2988\text{-}2900\text{ cm}^{-1}$ are due to the stretching vibration of C—H groups. The peaks pointed at 1744 cm^{-1} and 1635 cm^{-1} are due to the stretching vibration of C=O and C=N functions [22]. The bands at 1242 cm^{-1} and 1031 cm^{-1} attributable respectively to C—O—C and C—O vibrations suggest the presence of lignin structure in DFSE. Upon adsorption of methylene blue on DFSE the aspect of the FTIR spectrum has slightly changed. The bands due to the associated hydroxyl groups, to C=O and to C=N groups disappear suggesting a change in the structure of DFSE. Bands due to the stretching vibration of C—H groups remained unchanged in the range $2988\text{-}2900\text{ cm}^{-1}$. The changes are indicative of a strong interactions between DFSE and methylene blue.

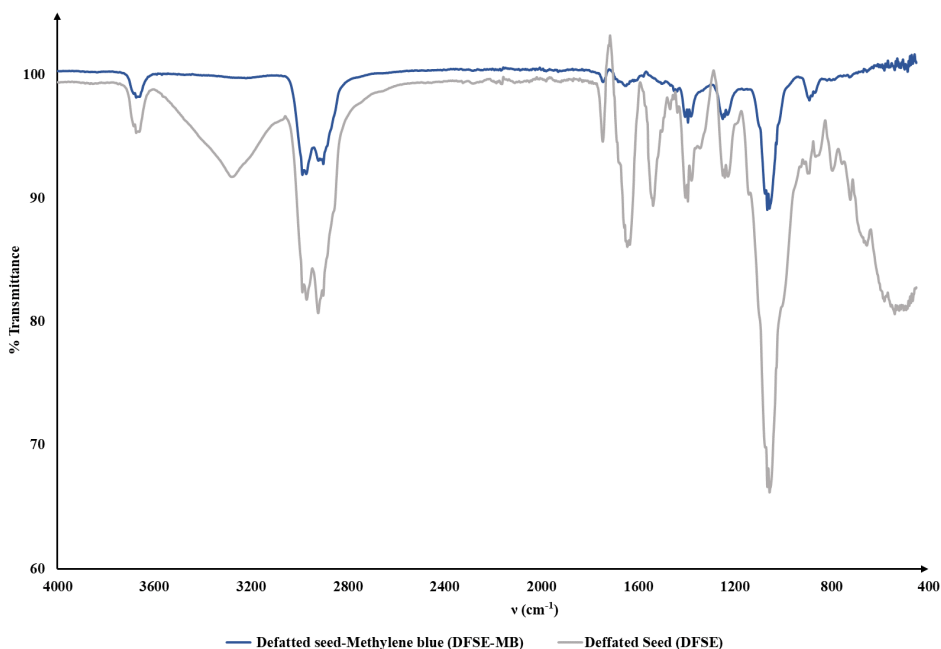


Figure 1. FTIR of DFSE and DFSE-MB.

Influence of contact time

Figure 2 shows the effect of contact time on the adsorption efficiency of methylene blue on the defatted *Adansonia digitata* seed. The concentration of methylene blue is 50 ppm and the adsorbent mass used is 0.25 g. The maximum removal capacity is reached at 90 minutes with 99.34 %. After 10 minutes of contact, 97.35 % of the methylene blue were removed by DFSE. Beyond 10 minutes, the adsorption capacity continues slowly to reach its maximum at 90 min. After 90 min, a release phenomenon is observed which continues up to 180 min to give a rate of 98.75%. After 90 min the removal capacity increases very slowly to reach 98.86 % at 240 min. In order to investigate the impact of the other physicochemical parameters on the methylene blue adsorption on DFSE, all the experiments were conducted with a fixed contact time of 90 minutes.

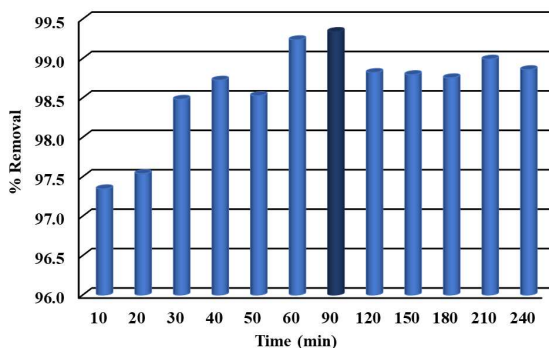


Figure 2. Influence of contact time on methylene blue removal capacity by DFSE.

Influence of the adsorbent mass

The influence of the mass of adsorbent on removal capacity of methylene blue by DFSE was studied. DFSE mass used ranges from 0.1 g to 1 g with a contact time of 90 min using methylene blue solution concentration of 50 ppm. Figure 3 shows that the best removal capacity value (99.44 %) is obtained with a mass of DFSE of 0.7 g. From 0.1 g to 0.6 g the removal capacity grows slowly from 96.79 % to 99.39 %. Beyond DFSE mass of 0.7 g, the removal capacity decreases at 98.71 % for 0.8 g before increasing again to 99.19 % for 0.9 g. A new decreasing is observed at 98.97 % for 1 g. The zig-zag behavior of the removal capacity after 0.7 g suggest a phenomena of adsorption-release of methylene blue by DFSE in the range 0.7 g and 1 g (Figure 3).

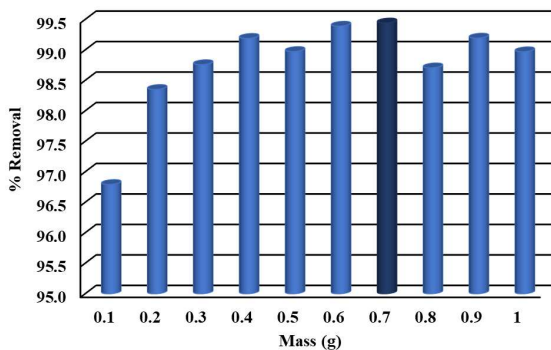


Figure 3. Influence of adsorbent mass on methylene blue removal capacity by DFSE.

Influence of solution pH on the removal capacity

The influence of the pH on the removal capacity of methylene blue by DFSE was studied. As shown in Figure 4 the removal capacity of methylene blue by DFSE is pH dependent. In fact, the varying pH of solutions changes the concentration of the functional groups of the adsorbent. When the pH values increases from 2 to 3 the removal capacity increases from 99.59 % to 99.70 %. When the pH values increases from 3 to 11, a zig-zag behavior of the methylene blue uptake is observed (Figure 4) and the maximum capacity removal (99.60 %) is reached at pH = 7. In fact, methylene blue is a cationic species, thus at pH = 7, the negatively charged surface of the adsorbent can interact easily with the cation yielding a better removal capacity. For lower pH values competition between hydrogen ions and the cationic methylene blue species is won by hydrogen ions. The point zero charge (pH_{PZC}) of the adsorbent value observed of 6.7 indicates, at this pH value, the net surface charge of the adsorbent is zero. For pH values smaller than the pH_{PZC} , the functional groups are protonated, and the adsorbent present a positive surface charge and can easily interact with negatively charged species. For pH values higher than the pH_{PZC} , the functional groups are deprotonated, and the adsorbent present a negative surface charge and can adsorb easily positively charged species. This observation is in accordance with the maximum removal capacity observed at pH = 7.

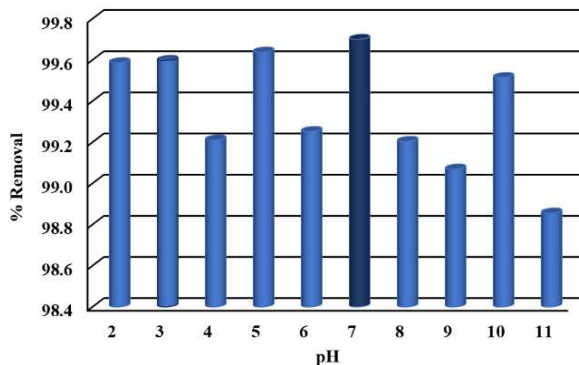


Figure 4. Influence of pH on methylene blue removal capacity by DFSE.

Influence of the particle size of DFSE on the removal capacity

The specific surface area of the adsorbent influences drastically the removal capacity [25]. As shown by authors, the finer the particles, the higher the specific surface area. Consequently, the finer the particles the higher the removal capacity. Indeed, the larger surface/volume ratio of small particles increases their adsorption capacity. As observed in Figure 5, the percent removal of methylene blue decreases when the particle size of DFSE increases. The maximum of the removal capacity value of 99.33 % is observed for the finest particles sizes of 100 μm . For 250 μm the methylene blue uptake is 98.73 %. When the particle size increases the removal rate decreases slightly to reach 97.0.2 % at 1500 μm . In the rest of the work, particle size of 100 μm of DFSE were used.

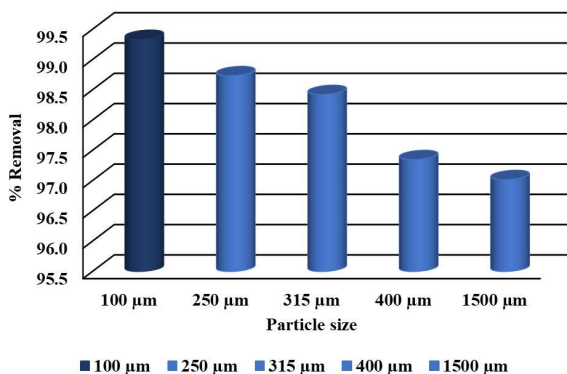


Figure 5. Influence of particle size on methylene blue removal capacity by DFSE.

Influence of initial methylene blue concentration

The effect of the initial concentration of methylene blue on DFSE was studied by varying the concentration from 12.5 to 100 ppm as shown in Figure 6. The removal capacity of methylene blue at 12.5 ppm by DFSE is 93.49 % and reached a value of 98.53 % for a methylene blue concentration of 75 ppm. Above 75 ppm, the adsorption rate remains almost constant. Between 12.5 and 75 ppm, there is a high driving force between the DFSE adsorbent and the methylene blue solution. This has the consequence of increasing the efficiency of the adsorption of methylene blue by DFSE. The quasi-constant removal value observed when the initial concentration increases from 75 ppm to 100 ppm can be explained by the saturation of the DFSE adsorption sites reached more quickly. These observations are reported by several authors for various dyes and adsorbents.

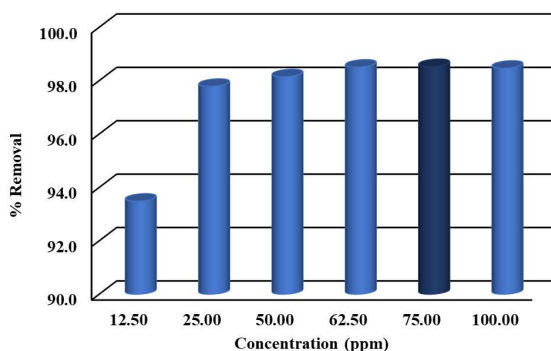


Figure 6. Influence of methylene blue concentration on removal capacity by DFSE.

Adsorption isotherms

The adsorption isotherm expresses the relationship between the equilibrium concentration of the adsorbate in solution and the amount of equilibrium adsorption on the adsorbent at a given temperature. The variables of each type of adsorption isotherm give information about the surface properties, the affinity between the adsorbate and the adsorbent and the mechanism of adsorption. Some isotherm models provided for gas phase adsorption are used for liquid medium adsorption. In this work the isotherms of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich, were evaluated [23].

Langmuir's model assumes that the adsorption phenomenon takes place in a monolayer and under a homogeneous surface. The linear form of the Langmuir equation is reported as :

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_0} + \frac{1}{Q_0} C_e$$

where q_e is the adsorbed amount at equilibrium in mg/g, C_e is the equilibrium concentration in solution in mg/L, K_L is the Langmuir equilibrium constant (L/mg), and Q_0 is the maximum adsorption capacity in mg/g.

The Freundlich model assumes that the multilayer adsorption takes place on the heterogeneous surface. The linear form of the Freundlich equation is reported as :

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

where q_e is the adsorbed amount at equilibrium in mg/g, C_e is the equilibrium concentration in solution in mg/L, K_F (L/mg) is the Freundlich constant, and n is the heterogeneity factor. K_F is referred to the adsorption capacity, whereas the $1/n$ value measures if the adsorption process is irreversible ($1/n = 0$), favorable ($0 < 1/n < 1$), or unfavorable ($1/n > 1$).

The Dubinin-Radushkevich model makes it possible to estimate the characteristic porosity of adsorbents and the apparent energy of adsorption. The linear form of the Dubinin-Radushkevich equation is reported as :

$$\ln q_e = \ln Q_{max} - B_D \varepsilon^2 ; \quad \varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right)$$

where q_e is the adsorbed amount at equilibrium in mg/g, C_e is the equilibrium concentration in solution in mg/L, Q_{max} (mg/g) is the theoretical capacity of isotherm saturation and B_D (mol^2/J^2) is the constant of the Dubinin-Radushkevich isotherm. ε is the potential of Polanyi.

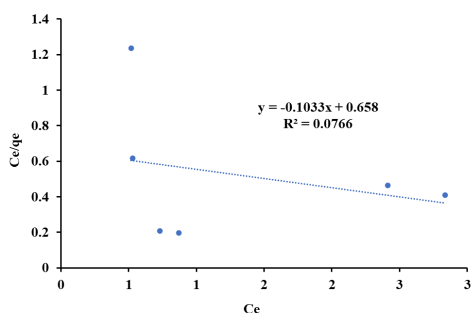
Temkin's isothermal model assumes that due to adsorbate-adsorbate interactions, the heat of adsorption of all adsorbate particles in the layer decreases linearly with surface coverage. The linear form of the Temkin equation is reported as :

$$q_e = \frac{RT}{b_t} \ln K_T + \frac{RT}{b_t} \ln C_e$$

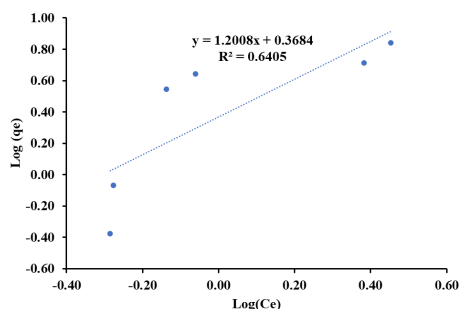
where q_e is the adsorbed amount at equilibrium in mg/g, C_e is the equilibrium concentration in solution in mg/L, b_t and K_T are parameters determined from the slope and the intercept by applying respectively. K_T corresponds to the equilibrium binding constant in L/mol and represents the maximum binding energy; b_t refers to the heat of adsorption.

Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm constants were determined from the plots of relative equations.

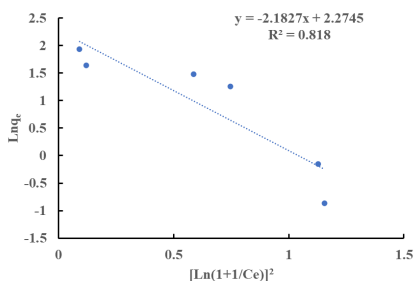
Figure 7 shows the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich curves for MB adsorption. The isotherm parameters as presented in Table 1 show the comparison of correlation coefficients for Langmuir, Freundlich, Dubinin-Radushkevich and Temkin models. Examination of the data showed that the Temkin isotherm provided the best fit with the highest correlation coefficient R^2 with value of 0.830. Moreover, the Dubinin-Radushkevich and the Freundlich models present good R^2 values of 0.710 and 0.640 respectively. The Langmuir model give the worst R^2 value of 0.077. The Temkin, the Dubinin-Radushkevich and the Freundlich models were more obeyed than the Langmuir model. These observations suggested that the adsorption system was heterogeneous.



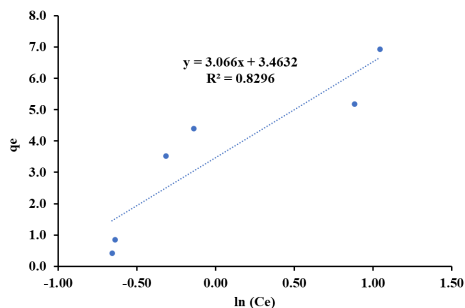
Langmuir isotherm



Freundlich isotherm



Dubinin-Radushkevich isotherm

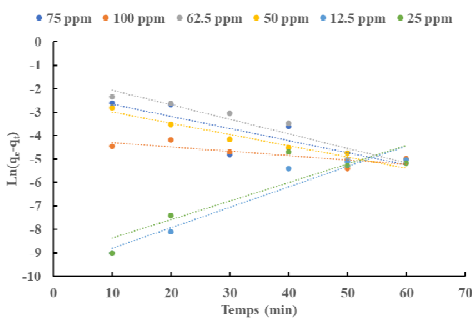


Temkin isotherm

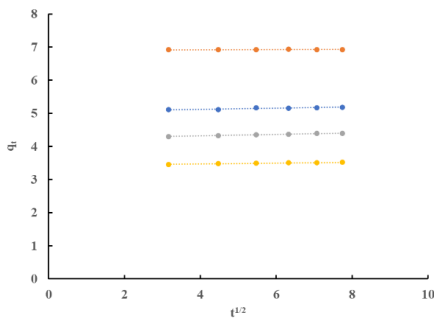
Figure 7. DFSE adsorption isotherms.

Table 1. Adsorption isotherms parameters DFSE.

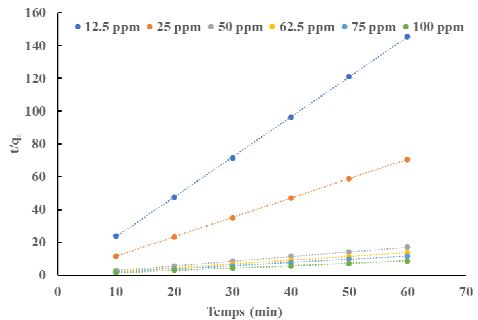
Langmuir isotherm			Freundlich isotherm		
$\frac{C_e}{q_e} = \frac{1}{K_L Q_0} + \frac{1}{Q_0} C_e$			$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$		
Q_0 (mg/g)	K_L (L/mg)	R^2	$\frac{1}{n}$	K_F	R^2
-9.681	-0.157	0.077	1.201	1.445	0.641
Dubinin-Raduskevich			Temkin isotherm		
$\ln q_e = \ln Q_{max} - B_D \varepsilon^2$			$q_e = \frac{RT}{b_t} \ln K_T + \frac{RT}{b_t} \ln C_e$		
Q_{max}	ε	R^2	b_t (J/mol)	K_T (L/mole)	R^2
19.015	1.674	0.717	808.486	3.094	0.830



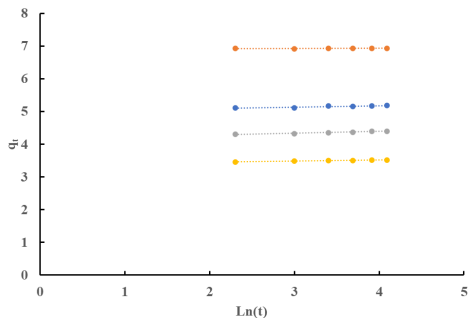
Pseudo-first ordre



Diffusion intra particulaire



Pseudo-second ordre



Elovich

Figure 8. Kinetics models for adsorption of on MB on DFSE.

Table 2. Kinetic parameters of the adsorption of methylene blue on DFSE.

C_0 (ppm)	$q_{e,exp}$ (mg/g)	Pseudo-first order			Pseudo-second order		
		$\ln(q_e - q_t) = \ln q_e - k_1 t$			$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$		
		k_1 (min ⁻¹)	$q_{e,cal}$ (mg/g)	R^2	k_2 (g/mg min)	$q_{e,cal}$ (mg/g)	R^2
12.5	0.419	0.087	6.26×10^{-5}	0.923	-0.897	0.411	0.999
25	0.856	0.079	1.04×10^{-4}	0.800	-0.161	0.849	1.000
50	3.518	-0.048	2.37×10^{-1}	0.953	0.063	3.529	1.000
62.5	4.399	-0.062	6.26×10^{-5}	0.874	0.092	4.423	1.000
75	5.182	-0.052	1.18×10^{-1}	0.593	0.046	5.198	0.999
100	6.934	-0.019	1.65×10^{-2}	0.672	0.0027	6.930	1.000
C_0 (ppm)	$q_{e,exp}$ (mg/g)	Intraparticle diffusion			Elovich		
		$q_t = k_i t + I$			$q_t = \frac{1}{\beta} \ln \alpha \beta + \frac{1}{\beta} \ln t$		
		k_i (mg/g min)	I	R^2	β (g/mg)	α (mg/min)	R^2
12.5	0.419	-0.002	0.426	0.796	-250.000	-8.44×10^{-50}	0.709
25	0.856	-0.002	0.862	0.524	-250.000	-3.17×10^{-97}	0.505
50	3.518	0.012	3.429	0.909	31.645	1.22×10^{45}	0.965
62.5	4.399	0.022	4.231	0.992	17.921	1.51×10^{31}	0.968
75	5.182	0.017	5.054	0.797	22.989	3.87×10^{48}	0.802
100	6.934	0.002	6.914	0.457	181.818	n/a	0452

Kinetic modeling of adsorption

In order to evaluate the adsorption processes of methylene blue on defatted seed of *Adansonia digitata* four kinetic models such as pseudo-first-order, pseudo-second-order, Elovich and Intra-particle diffusion models were applied (Figure 8).

Pseudo-first order

Assuming that a surface active site is occupied by an adsorbate unit, Lagergren [24]

proposed a pseudo-first-order kinetic equation. This equation is widely used in scientific work to study the adsorption kinetics of chemical species in solution by a solid adsorbent. The linear form of this model expressed by the following formula:

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

where q_e is the equilibrium adsorption capacity (mg/g), q_t is the adsorption capacity at time t (mg/g), k_1 (min^{-1}) is the rate constant for the of pseudo-first order kinetic. The plot of $\ln(q_e - q_t)$ vs t shows the validity or not of the pseudo-first order kinetics model for different initial concentrations of methylene blue. Figure 8 shows that for all the initial concentrations of methylene blue, the plots do not give a straight line as observed with the values of R^2 which diverge strongly from the ideal value of 1 (Table 2). The pseudo-first-order kinetic model is not suitable for describing the adsorption process.

Pseudo-second order

The equation established by Ho and McKay's [25] allows to describe the pseudo-second order model assuming an interaction of two active sites with one unit of adsorbate. The linear form of this equation is given below:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

where q_e is the equilibrium adsorption capacity (mg/g), q_t is the adsorption capacity at time t (mg/g), k_2 (g/mg min) is the rate constant for the pseudo-first order kinetic. Figure 8 shows the plots of t/q_t vs t for different concentrations. We observe that for all the initial concentrations of methylene blue, we have a straight line with an excellent correlation coefficient R^2 [0.9999 and 1] (Table 2). From these diagrams, the values of the quantity adsorbed at equilibrium, for each initial concentration and the rate constants k_2 were calculated and recorded in Table 2. The values of q_e calculated and the values of q_e are close proximity. The pseudo-second-order kinetic model is the more suitable model for describing the adsorption process.

Intra-particle diffusion model

The equation established by Morris and Weber [26] describes the intra-particle diffusion model whose linear model:

$$q_t = k_p t^{1/2} + C$$

where q_t is the amount of dye adsorbed (mg/g) at time t ; C (mg/g) is the boundary layer

thickness and k_p is the rate constant of intra-particle diffusion model ($\text{mg/g}\cdot\text{s}^{1/2}$). The plot of the equation should be linear if intra-particle diffusion is involved in the adsorption mechanism. Also, intra-particle diffusion is the velocity control step if the straight line passes through the origin. If the straight line does not intersect the origin, this indicates that the intra-particle is not the only velocity control step. None of the equation plots for MB adsorption at different initial concentrations are linear and all R^2 correlation coefficients are less than 0.9 (Table 2). These observations indicate that intra-particle diffusion is not the rate-controlling step.

Elovich model

The kinetic model named Elovich [27], illustrated by the linear form of the equation describes chemisorption on heterogeneous surfaces:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t$$

where q_t is the amount of dye adsorbed (mg/g) at time (t), α represents the initial sorption rate ($\text{mg g}^{-1} \text{min}^{-1}$) and β is related to the extent of surface coverage and activation energy for chemisorption (g mg^{-1}). On the plots of the equation (Figure 2), no straight line is observed for the differences in the initial concentrations of methylene blue. The parameters α , β and the correlation coefficients R^2 are calculated from the linear plots and recorded in Table 2. All of the correlation coefficients values were far from unity. This model is not suitable for studying the sorption of MB on DFSE.

Conclusion

In the present article, delipidated *Adansonia digitata* seeds were used in the cleaning of wastewater containing methylene blue dye. FTIR analysis and point zero charge were performed to determine the properties of the adsorbent. The adsorption kinetics were well described by the pseudo second order model, proving that a chemisorption would be the rate controlling step. The adsorption isotherms for methylene blue were not well adapted to the different models studied (Langmuir, Freundlich, Temkin, Dubinin-Raduskevich, Harkin Jura and Halsey). None of these isotherms provided a good fit to the adsorption data, indicating that the interaction was primarily chemical in nature. The short contact time, the low ratio adsorbent/volume and the pH value of 7 obtained to reach the maximum adsorption capacity, demonstrate that the prepared adsorbent is an inexpensive durable adsorbent, very effective which can be applied in the removal of industrial dyes

from wastewater. We plan to continue research on the recycling of the adsorbent and its affinity for other industrial dyes, as well as its performance in highly contaminated wastewater.

References

- [1] Wang, L.K., Hung, Y.-T., Lo, H.H., & Yapijakis, C. (2005). *Waste treatment in the process industries*. CRC Press.
- [2] Jassim, S.A-R., Al-Robai, H.A., & Al-Tae, M.M. (2013). Removing reactive orange dye by using ceramic purifier type (AKPL1). *Iraqi National Journal of Chemistry*, 50, 121-127. <https://www.iasj.net/iasj/download/a92ccbe46ea07d2f>
- [3] Husein, M.M., Vera, J.H., & Weber, M.E. (2008). Removal of lead from aqueous solutions with sodium caprate. *Separation Science and Technology*, 33, 1889-1904. <https://doi.org/10.1080/01496399808545911>
- [4] Choumane, R., & Peulon, S. (2019). Electrodeposited birnessite thin film: An efficient eco-friendly sorbent for removing heavy metals from water. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 577, 594-603. <https://doi.org/10.1016/j.colsurfa.2019.06.013>
- [5] Ducoroy, L., Bacquet, M., Martel, B., & Morcellet, M. (2008). Removal of heavy metals from aqueous media by cation exchange nonwoven PET coated with β -cyclodextrin-polycarboxylic moieties. *Reactive and Functional Polymers*, 68, 594-600. <https://doi.org/10.1016/j.reactfunctpolym.2007.10.033>
- [6] Bassaid, S., Chaib, M., Bouguelia, A., & Trari, M. (2008). Elaboration and characterization of poly (acrylic acid-co-crotonic acid) copolymers: Application to extraction of metal cations Pb(II), Cd(II) and Hg(II) by complexation in aqueous media. *Reactive and Functional Polymers*, 68, 483-491. <https://doi.org/10.1016/j.reactfunctpolym.2007.10.030>
- [7] Li, L., Wei, D., Wei, G., & Du, Y. (2013). Transformation of cefazolin during chlorination process: Products, mechanism and genotoxicity assessment. *Journal of Hazardous Materials*, 262, 48-54. <https://doi.org/10.1016/j.jhazmat.2013.08.029>
- [8] Volesky, B., & Holan, Z.R. (1995). Biosorption of heavy metals. *Biotechnology Progress*, 11, 235-250. <http://dx.doi.org/10.1021/bp00033a001>
- [9] Shaul, G.M., Holdsworth, T.J., Dempsey, C.R., & Dostal, K.A. (1991). Fate of water soluble azo dyes in the activated sludge process. *Chemosphere*, 22, 107-119. [http://dx.doi.org/10.1016/0045-6535\(91\)90269-J](http://dx.doi.org/10.1016/0045-6535(91)90269-J)

- [10] He, J., Cui, A., Deng, S., & Chen, J.P. (2018). Treatment of methylene blue containing wastewater by a cost-effective micro-scale biochar/polysulfone mixed matrix hollow fiber membrane: Performance and mechanism studies. *Journal of Colloid and Interface Science*, 512, 190-197. <http://dx.doi.org/10.1016/j.jcis.2017.09.106>
- [11] Akrou, H., Jellali, S., & Bousselmi, L. (2015). Enhancement of methylene blue removal by anodic oxidation using BDD electrode combined with adsorption onto sawdust. *Comptes Rendus Chimie*, 18, 110-120. <http://dx.doi.org/10.1016/j.crci.2014.09.006>
- [12] Naushad, M., Sharma, G., & Alothman, Z.A. (2019). Photodegradation of toxic dye using Gum Arabic-crosslinked-poly(acrylamide)/Ni(OH)₂/FeOOH nanocomposites hydrogel. *Journal of Cleaner Production*, 241, 118263. <http://dx.doi.org/10.1016/j.jclepro.2019.118263>
- [13] Bharti, V., Vikrant, K., Goswami, M., Tiwari, H., Sonwani, R.K., Lee, J., Tsang, D.C.W., Kim, K-H., Saeed, M., Kumar, S., Rai, B.N., Giri, B.S., & Singha, R.S. (2019). Biodegradation of methylene blue dye in a batch and continuous mode using biochar as packing media. *Environmental Research*, 171, 356-364. <http://dx.doi.org/10.1016/j.envres.2019.01.051>
- [14] Vijayaraghavan, K., & Yun, Y.-S. (2008). Bacterial biosorbents and biosorption. *Biotechnology Advances*, 26, 266-291. <http://dx.doi.org/10.1016/j.biotechadv.2008.02.002>
- [15] Aksu, Z., & Karabayır, G. (2008). Comparison of biosorption properties of different kinds of fungi for the removal of Gryfalan Black RL metal-complex dye. *Bioresource Technology*, 99, 7730-7741. <http://dx.doi.org/10.1016/j.biortech.2008.01.056>
- [16] Mengting, Z., Kurniawan, T.A., Fei, S., Ouyang, T., Othman, M.H.D., Rezakazemi, M., & Shirazian, S. (2019). Applicability of BaTiO₃/graphene oxide (GO) composite for enhanced photodegradation of methylene blue (MB) in synthetic wastewater under UV-vis irradiation. *Environmental Pollution*, 255, 113182. <http://dx.doi.org/10.1016/j.envpol.2019.113182>
- [17] Su, S., Liu, Y., Liu, X., Jin, W., & Zhao, Y. (2019). Transformation pathway and degradation mechanism of methylene blue through β -FeOOH@GO catalyzed photo-Fenton-like system. *Chemosphere*, 218, 83-92. <http://dx.doi.org/10.1016/j.chemosphere.2018.11.098>
- [18] Malato, S., Fernández-Ibáñez, P., Maldonado, M.I., Blanco, J., & Gernjak, W. (2009). Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends. *Catalysis Today*, 147, 1-59. <http://dx.doi.org/10.1016/j.cattod.2009.06.018>

- [19] Royer, B., Cardoso, N.F., Lima, E.C., Vaghetti, J.C.P., Simon, N.M., Calvete, T., & Veses, R.C. (2009). Applications of Brazilian pine-fruit shell in natural and carbonized forms as adsorbents to removal of methylene blue from aqueous solutions—Kinetic and equilibrium study. *Journal of Hazardous Materials*, 164, 1213-1222. <http://dx.doi.org/10.1016/j.jhazmat.2008.09.028>
- [20] Bhatnagar, A., & Sillanpää, M. (2010). Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment—A review, *Chemical Engineering Journal*, 157, 277-296. <http://dx.doi.org/10.1016/j.cej.2010.01.007>
- [21] Albert, M., Lessin, M.S., & Gilchrist, B.F. (2003). Methylene blue: dangerous dye for neonates, *Journal of Pediatric Surgery*, 38, 1244-1245. [http://dx.doi.org/10.1016/S0022-3468\(03\)00278-1](http://dx.doi.org/10.1016/S0022-3468(03)00278-1)
- [22] Tarley, C.R.T., & Arruda, M.A.Z. (2004). Biosorption of heavy metals using rice milling by-products. Characterisation and application for removal of metals from aqueous effluents. *Chemosphere*, 54, 987-995. <http://dx.doi.org/10.1016/j.chemosphere.2003.09.001>
- [23] Rizzi, V., Gubitosa, J., Signorile, R., Fini, P., Cecone, C., Matencio, A., Trotta, F., & Cosma, P. (2021). Cyclodextrin nanosponges as adsorbent material to remove hazardous pollutants from water: The case of ciprofloxacin, *Chemical Engineering Journal*, 411, 128514. <http://dx.doi.org/10.1016/j.cej.2021.128514>
- [24] Shahwan, T. (2015). Lagergren equation: Can maximum loading of sorption replace equilibrium loading?. *Chemical Engineering Research and Design*, 96, 172-176. <http://dx.doi.org/10.1016/j.cherd.2015.03.001>
- [25] Aichour, A., & Zaghouane-Boudiaf, H. (2019). Highly brilliant green removal from wastewater by mesoporous adsorbents: Kinetics, thermodynamics and equilibrium isotherm studies. *Microchemical Journal*, 146, 1255-1262. <http://dx.doi.org/10.1016/j.microc.2019.02.040>
- [26] Weber, Walter J., & Morris, J. Carrell (1963). Kinetics of adsorption on carbon from solution. *Journal of the Sanitary Engineering Division*, 89, 31-59. <http://dx.doi.org/10.1061/JSEDAI.0000430>
- [27] Cope, F.W. (1972). Generalizations of the Roginsky-Zeldovich (or Elovich) equation for charge transport across biological surfaces. *Bulletin of Mathematical Biophysics*, 34, 419-427. <https://doi.org/10.1007/BF02476452>