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Modification of lignocellulosic biomass as agricultural waste for the biosorption of basic dye from aqueous solution

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Abstract
In this work the efficiency of applying raw or modified date stones by sodium hydroxide as biosorbents for the removal of methylene blue (MB) from water solutions was examined. The date stones (DS) and NaOH-modified date stones were characterized with FTIR analysis. Effects of various parameters like biosorbent dose, initial pH, contact time, temperature, initial dye concentration and particle size on rate of biosorption have been studied. Also optimum values of these parameters have been reported. The isotherms studies carried out are reported and it was observed that MB biosorption follows the Langmuir isotherm. Kinetics data were evaluated by pseudo-first-order, pseudo-second-order and intraparticle diffusion models. The results showed that the biosorption processes of methylene blue on DS and NMDS followed well pseudo-second-order kinetics. The calculated thermodynamics parameters, namely, ΔG, ΔH and ΔS showed that the biosorption of methylene blue on raw biomass and modified was spontaneous, endothermic and increased randomness in the solid/solution interface. The monolayer biosorption capacities of methylene blue were found to be 76.54 mg/g for DS and 130.54 mg/g for NMDS, respectively at 323 K. The set of the results obtained indicated that DS and NMDS could be an alternative for more costly adsorbents used for dye removal.

Keywords: Date stones, biosorption, FTIR, methylene blue, modification.

1. Introduction
The dyes currently occupy an important place in the industrial sector. They are widely used in the paper industry, cosmetics, tanning effluents, food and especially in the textile industry. These releases, surfactants compounds, biotical compounds, solid suspensions, dispersing and wetting agents, dyes and trace metals are toxic to most living organisms. The heterogeneity of their composition makes difficult or visually impossible to obtain lower pollution limits equal to or those imposed by environmental standard, after treatment techniques traditional. World production is estimated at 700000 tons / year, of which 140000 tons are released in effluents at different stages of implementation and making [1]. Most of these dyes are toxic, mutagenic and carcinogenic. Moreover, they are very stable to light, temperature and microbial attack, making the recalcitrant compounds. For these reasons, the removal of dyes from waste effluents becomes environmentally important. Therefore, several methods have been developed to remove the dyes from wastewater. Among these methods, adsorption currently appears to offer the best potential for the entire treatment [2]. The adsorption onto activated carbon is widely used. But it is very expensive and has high operating costs [3,4]. Hence many researchers have studied cheaper substitutes, which are relatively inexpensive and have a reasonable adsorption capacity.
Many agriculture wastes biosorbents have been used to remove of methylene blue from aqueous solutions such a wood cores of jujube [5], date stones [6,7],argan shells [8] hazelnut shells [9], wheat shells [10], mansonia wood sawdust [11], oil palm trunk fibre [12], rice husk [13], olive pomace [14],yellow passion-fruit waste [15], pistachio hull waste [16] and banana peel [17].
The objective of this work is, the one hand, improve the biosorption capacity of the powder of date stones, obtained in a previous work [6], using the powder of date stones, with a very small particle size, raw or chemically modified, of the another varieties of palm-trees and on the other hand develop cheaper , environmentally friendly and efficient biosorbents.
The raw date stones and NaOH-modified date stones were characterized by attenuated total reflectance-Fourier transform infra-red (ATR-FTIR) analysis.

Factors affecting biosorption, such as, biosorbent dose, contact time, pH, temperature, biosorbent particle size and initial dye concentration have been evaluated. The biosorption kinetics of MB onto the biosorbent was tested by pseudo-first-order, pseudo-second-order and intraparticle diffusion models. The equilibrium data have been analyzed using Langmuir and Freundlich isotherms models. The thermodynamics parameters were also evaluated from the biosorption measurements.

2. Materials and methods

2.1. Adsorbate

Methylene blue (chemical formula: 319.86 g/mol, molecular weight: $C_{16}H_{18}N_3SCl$, CI: 52015), the basic dye used as the model adsorbate in the present study is a monovalent cationic dye, supplied by Merck and was not purified prior to use. A stock solution of 1g/L was prepared by dissolving 1g of MB powder in 1 liter of distilled water. The working solutions were prepared by diluting the stock with distilled water to give the appreciate concentration of the working solutions. The Chemical structure MB is shown in Fig.1.The pH of dye solution was adjusted using HCl (0.01M) or NaOH (0.01M).

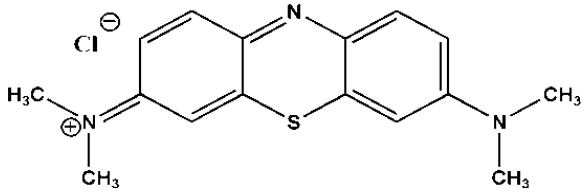

Figure 1: Chemical structure of methylene blue.

2.2. Biosorbents

The raw date stones of Abakiss variety is cheaper economically variety were collected in South Morocco (Tinghir). They are washed and placed in an oven at 105 °C for 24 hours, then ground in a grinder RETSCH SM10 and sieved. 1g of dates stones powder prepared is mixed with 100 mL of NaOH (0.1 M), stirred for 24 h at room temperature. After decantation and filtration, the biomass washed with distilled water several times then dried in an oven at 80 °C for 24 h. The NaOH-modified date stones were ground and sieved again to different particle sizes. The functional groups of DS and NMDS were identified by ATR-FTIR spectroscopy with resolution 4 cm^{-1} in a JASCO4100 spectrometer.

2.3. Batch experimental procedure

Biosorption measurement was determined by batch experiments, 0.25 g of DS or 0.15 g of NMDS biosorbent at size 50-100 µm with 50 mL of aqueous solution of methylene blue of 100 mg /L in a series of 100 mL conical flasks. The mixture was shaken at 20°C using an external circulation thermostat for 60 min and pH of solution above 5.33. The impudence of biosorbent dose (1, 2, 3, 4, 5, 6,7 and 8 g/L), contact time (5, 10, 20, 30,40, 50, 60, 90, 120, 150 and 180 min), temperature (293, 303, 313 and 323 K) , biosorbent particle size (50-100 ,100-315, 315-500 and 500 -1000 µ m) ,pH (3,4,5,8,9 and 10) and initial concentration dye (100, 200, 300 ,400 ,500 ,600 ,700 ,800 mg/L) were evaluated during the present study. The equilibrium concentrations of the solution were analyzed using a spectrophotometer (UV-visible 2300- TECHCOMP). The standard calibration curve was prepared by recording the absorption of various concentrations values of MB dye at a maximum absorption wavelength of the λ_{max} = 661 nm .The percentage removal (%) and the quantity adsorbed q_e (mg/g) of dye on DS and on NMDS were calculated using the following equations (1) and (2), respectively:

$$\% \text{ Removal} = \frac{(C_0 - C_e)\times 100}{C_0} \quad (1)$$

$$q_e = \frac{(C_0 - C_e)\times V}{W} \quad (2)$$

where, q_e (mg/g) is the quantity adsorbed, C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium concentrations of MB solution, respectively ,V(L) is the volume of solution and W (g) is the mass of biosorbent used.

2.4. Modeling

2.4.1. Biosorption kinetics

The applicability of the pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetics models [18] was tested for the biosorption of methylene blue onto DS and NMDS. These models can be expressed as:

- Pseudo-first-order:

$$\log (q_e - q_t) = \log q_e - \frac{K_1}{2{,}303} t \quad (3)$$

- Pseudo-second-order:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

- Intraparticle diffusion:

$$q_t = K_i t^{1/2} + C \quad (5)$$

Where q_t (mg/g) and q_e (mg/g) are the amounts adsorbed at time and equilibrium, respectively ,k_1 (min^{-1}) is the pseudo-first-order rate constant, K_2 ($g.mg^{-1}.min^{-1}$) is the pseudo-second-order rate constant , K_i ($mg.g^{-1}.min^{-1/2}$) is the intraparticle diffusion rate constant and C (mg/L) is the intercept.

2.4.2. Biosorption isotherms

Equilibrium experiments were carried out by taking known amount of DS or NMDS in 100 mL conical flasks containing 50 mL of the dye solution of different initial dye (100-800 mg/L) at temperature (20-50°C). Then most commonly employed biosorption isotherm models were applied in present study as Langmuir and Freundlich.

The Langmuir equation can be described by the following linear form [19]:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (6)$$

Where, K_L is the Langmuir constant (L/mg) and q_m is the maximum amount of adsorbate retained on the medium used (mg/g). The evaluation of the isotherm and their feasibility of the biosorption process were checked less separation factor R_L equation. The mathematical expression of the equation is:

$$R_L = \frac{1}{1 + K_L C_0} \quad (7)$$

The R_L value indicates the mode sorption isotherm process, if the process is unfavorable (R_L>1) or linear (R_L=1) or favorable (0 < R_L <1) or irreversible (R_L = 0) [20].

The Freundlich equation for the biosorption isotherm is purely an empirical isotherm having no theoretical basis and is validity extends to non-uniformity of the biosorption surface [21].The linearized Freundlich equation is represented by the following equation [19]:

$$\text{Ln}\, q_e = \text{Ln}\, K_F + \frac{1}{n} \text{Ln}\, C_e \quad (8)$$

Where, K_F ((mg/g) (l/ mg) $^{1/n}$) is the Freundlich constant and 1/ n is the intensity of the biosorption.

2.4.2. Biosorption thermodynamics

Thermodynamic behavior of biosorption of MB on DS and NMDS was evaluated by the parameters: Gilbs free energy change (ΔG°), enthalpy (ΔH°) and entropy (ΔS°).These parameters were calculated using the following equation [22]:

$$\Delta G° = - RT \text{Ln}\, K_c \quad (9)$$

$$K_C = \frac{C_a}{C_e} \quad (10)$$

$$\Delta G° = \Delta H° - T \Delta S° \quad (11)$$

where, R is the constant of perfect gases 8.314 ($J.mol^{-1}.K^{-1}$), T is the absolute temperature (K), K_c is the equilibrium constant, C_a is the equilibrium dye concentration on the biosorbent (mg/L) and C_e is the equilibrium dye concentration in solution (mg/L).

3. Results and discussion

3.1. Spectroscopy Infrared

Fig.2 show the functional groups responsible for biosorption of methylene blue on DS and NMDS such as hydroxyl, carboxyl, carboxylate, carbonyl groups were confirmed by FTIR. The results of FTIR spectrum of DS obtained are similar to results obtained by Belala [7]. Comparing the spectrum of DS with that of NMDS we can essentially note the presence of carboxylate ($–COO^-$) groups (band at 1644 cm^{-1}) [23] and the absence of carboxylic (–COOH) groups (band at 1747 cm^{-1}) [24] on spectrum of NMDS. The carboxylate groups of NMDS due to the saponification of the carboxylic acids of raw date stones. The general reaction of modification is represented in Fig.3.

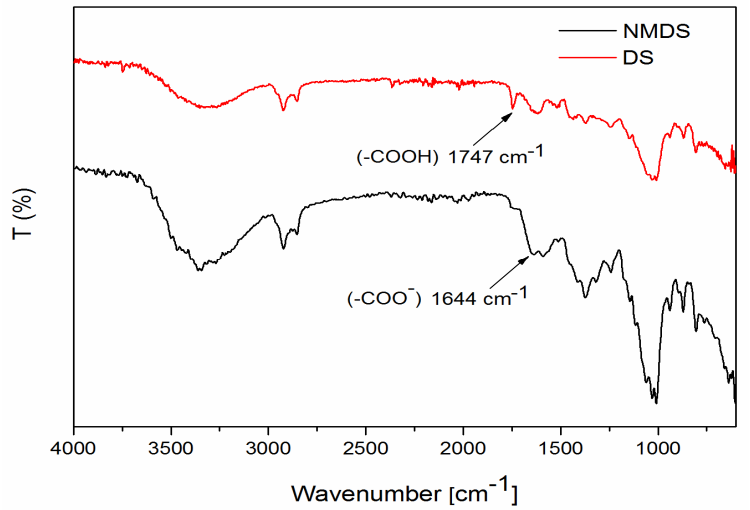

Figure 2: FTIR spectra DS and NMDS.

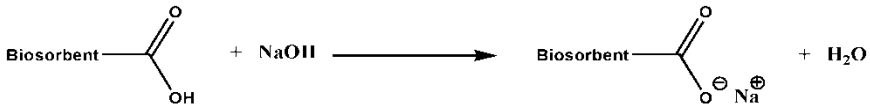

Figure 3: Reaction of modification carboxylic acids on the surface of raw DS biosorbent.

3.2. Effect of biosorbent dose

Fig.4 shows the effect of raw date stones and NaOH-modified date stones dose on removal percentage of methylene blue. We note that the biosorption performance increases with biosorbent dose. This may be to the increased number of active sites of DS and NMDS [25] .The DS and HMDS doses optimal are 5 g/L and 3g/L, with a percentages removal of 90.55 % and 91.82 %, respectively. After these doses, the removal is almost constant for DS and NMDS.

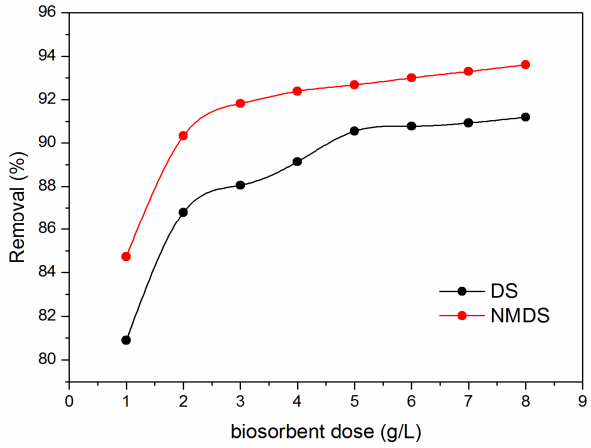

Figure 4: Effect biosorbent dose on biosorption of MB
(C_0 = 100 mg / L, T = 293 K, t = 60 min, pH = 5.77, S = 50-100 µm).

3.3. Effect of contact time

The effect of contact time for the removal of MB (pH = 5.57) at concentration of 100 mg/L with DS dose = 5g/L or NMDS dose = 3g/L at 293 K is shown in Fig.5. The removal of MB, as function of time, was noted to occur in three phases .The first phase is rapid during 20 min. The second phase, comprised between 20 and 60 minutes, is slow .The Third phase (t> 60 min) is period of equilibrium biosorption of MB onto DS and MNDS due the occupation of the majority of sites by dye ions [26]. In the following work a contact time of 60 minutes seems more than enough to reach equilibrium for DS and NMDS.

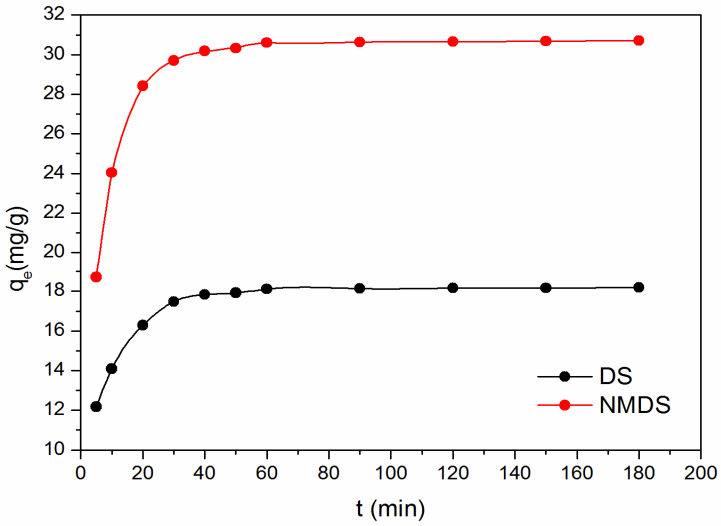

Figure 5: Effect of contact time on the biosorption of MB onto DS and NMDS
(C_0 =100 mg / L, T = 293 K, DS dose = 5g/L, NMDS dose = 3g/L, pH = 5.57, S = 50-100 µm).

3.4. Effect of biosorbent particle size

The biosorption of MB dye was studied at for different particle size (50-100,100-315,315-500 and 500-1000 µm) of the DS or NMDS biosorbents in optimal conditions. Fig .6 shows that amounts adsorbed of MB by DS and NMDS increases from 6.50 to 18.11 mg/g and from 9.23 to 30.59 mg/g, respectively, when biosorbents particles size decreases 500-1000 to 50-100 µm. The results obtained show, firstly, the effectiveness of NMDS compared to DS and, secondly, that of the latter relative to other biosorbent of the same type but of different species and of different particle size [6-7].

The fast and higher capacity with smaller biosorbent particles could be attributed to the fact that smaller particles provide a larger and easily accessible surface area [27]. The Fig.6 also indicate that NMDS affinity for MB is higher than DS. 50-100 µm was used as optimal particle size for further experiments.

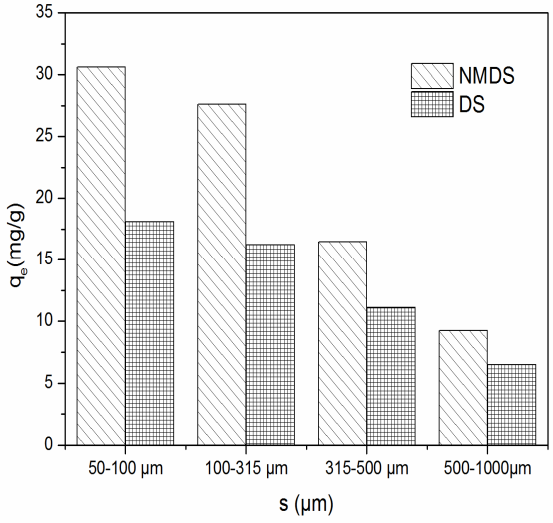

Figure 6: Effect of particles size on biosorption of MB onto DS and NMDS
(C_0 =100 mg / L, T = 293 K, DS dose = 5g/L, NMDS dose = 3g/L, t = 60 min, pH = 5.57).

3.5. Effect of temperature

In order to study the effect of temperature, several experiments were carried out in the range of temperatures of 293 to 323 K. The results obtained are shown in Fig.7. The results indicated that the biosorption of MB onto DS or NMDS was an endothermic process. Increase in temperature resulted in increased biosorption of dye. An increase in temperature also results in mobility of dye molecules and decrease in the retarding forces acting on the molecules [28].

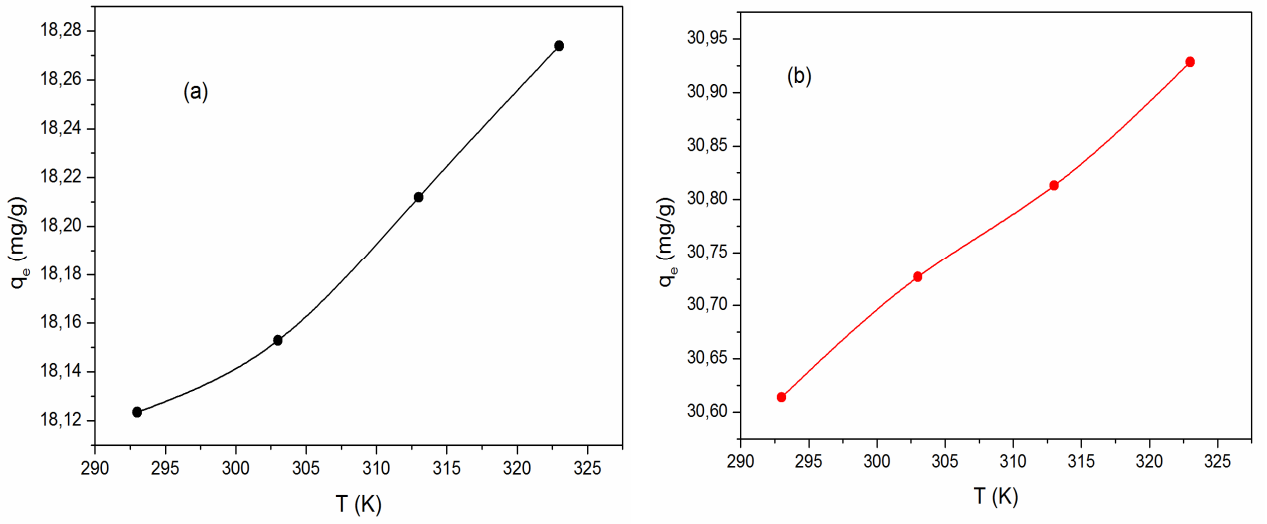

Figure 7: Effect of temperature on biosorption of MB onto DS (a) and NMDS (b) (t = 60 min, DS dose = 5g/L, NMDS dose = 3g/L, pH = 5.57, S = 50-100 µm).

3.6. Effect of pH

pH is one of the monitoring factors in the biosorption process. It affects the activity of functional groups on the biosorbent surface [29]. Fig.8 shows the effect of the solution pH (3-10) on the biosorption of MB on DS and NMDS under equilibrium conditions. At lower pH, the surface may get positively charged ,thus making (H^+) ions compete effectively with cations causing a decreases in the amount of dye adsorbed. At higher pH the fibers biopolymers, mainly lignin and chains, may get negatively charged, which enhances the positively charged dye cations through electrostatic forces of attraction [30].

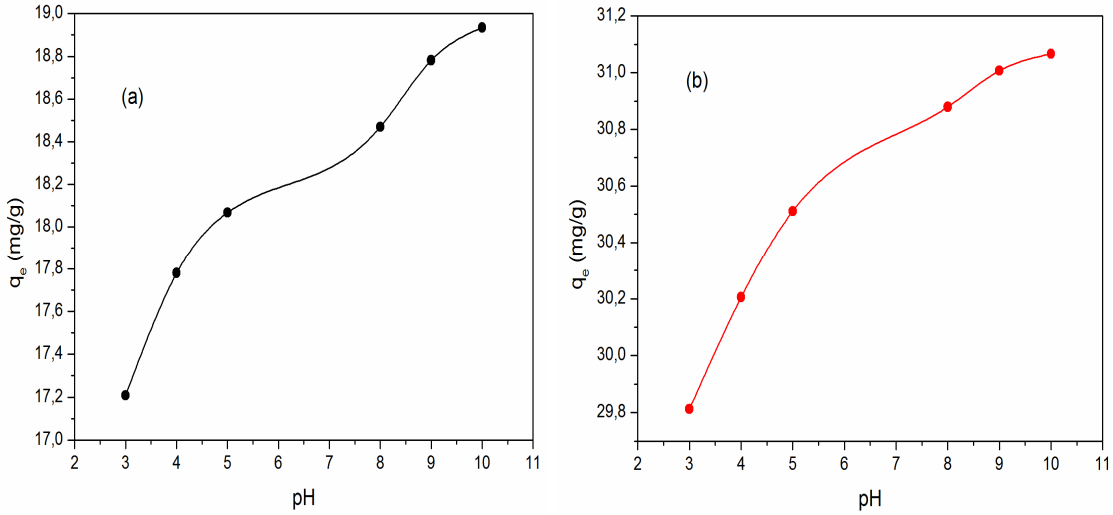

Figure 8: Effect of pH on biosorption of MB onto DS (a) and NMDS (b) (C_0 =100 mg / L, T = 293 K, DS dose = 5g/L, NMDS dose = 3g/L, t = 60 min, S = 50-100 µm)

3.7. Desorption and rebiosorption of MB

In order to repeatedly use the adsorbent and to recover the MB, the biosorption tests were conducted with HNO_3 aqueous solution. The results indicate that the adsorbed MB DS and MB NMDS can be recovered by treating it with a HNO_3 (0.1M) solution. Rebiosorption tests were also carried out to evaluate the practical

utility of DS an NMDS. After 4 replications of biosorption and desorption, only almost 10% of the biosorption capacity decreases after 4 cycles (Fig.9).

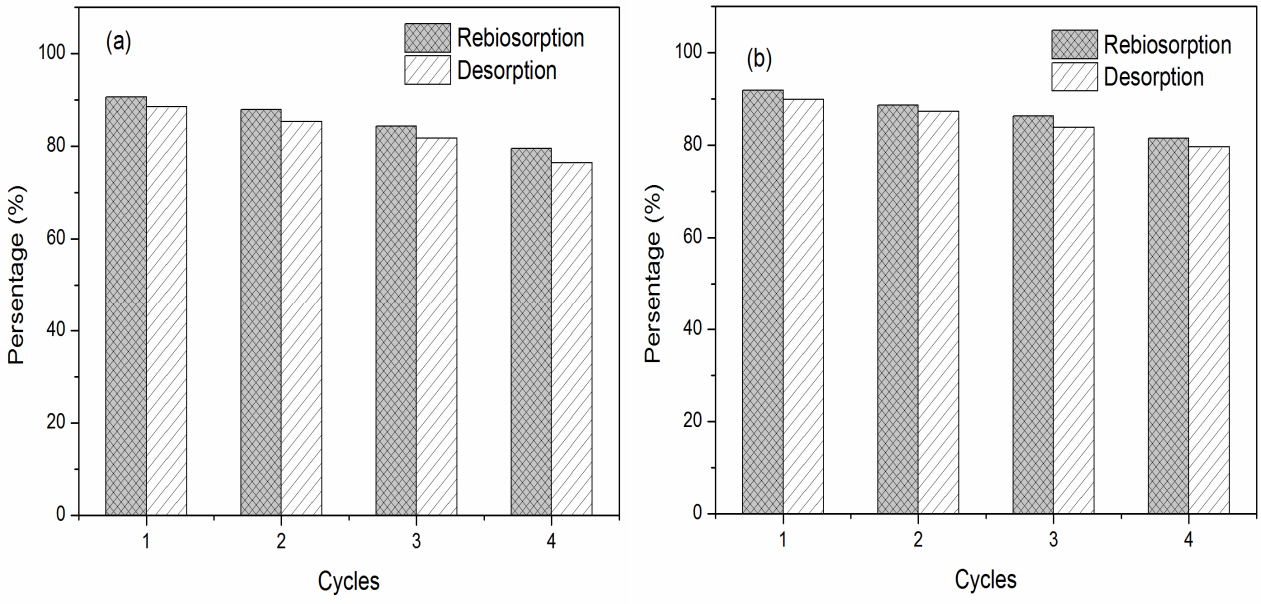

Figure 9: Desorption-rebiosorption cycles of MB onto DS (a) and NMDS (b).

3.8. Kinetics parameters

The rate constants are determined from the corresponding plots (Figs .10, 11 and 12), which summarized in Table 1. The analysis of results obtained suggests the biosorption of MB on DS and NMDS may best described by the pseudo second order with high correlation coefficients (> 0.99) .The Fig.12 shows that the intraparticle diffusion model indicates three different regions: The first linear is rapid external surface completed before 20 min, the second linear portion is gradual biosorption stage by intraparticle diffusion after 20 min to 60 min, the third linear is equilibrium biosorption started after 60 min. The MB is slowly transported via intraparticle diffusion into the particle and finally retained by microspores [31].

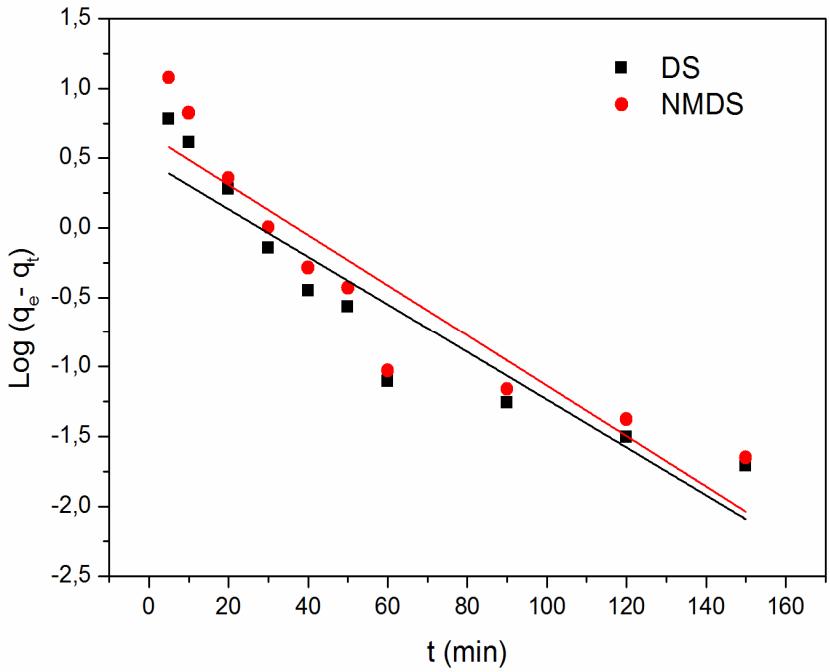

Figure 10: Pseudo-first-order Kinetics model for biosorption of MB onto DS and NMDS (C_0 =100 mg / L, T = 293 K, DS dose = 5g/L, NMDS dose = 3g/L, pH = 5.57, S = 50-100 µm).

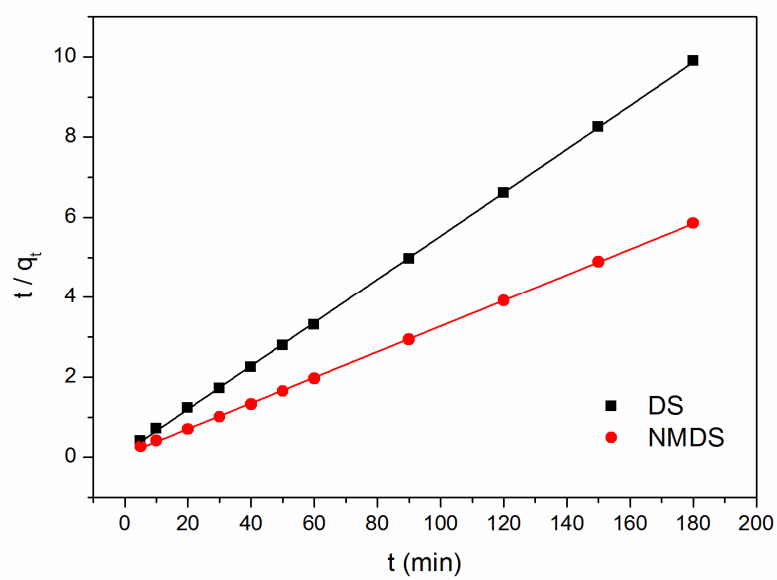

Figure 11: Pseudo-second-order Kinetics model for biosorption of MB onto DS and NMDS (C_0 =100 mg / L, T = 293 K, DS dose = 5g/L, NMDS dose = 3g/L, pH = 5.57, S = 50-100 µm).

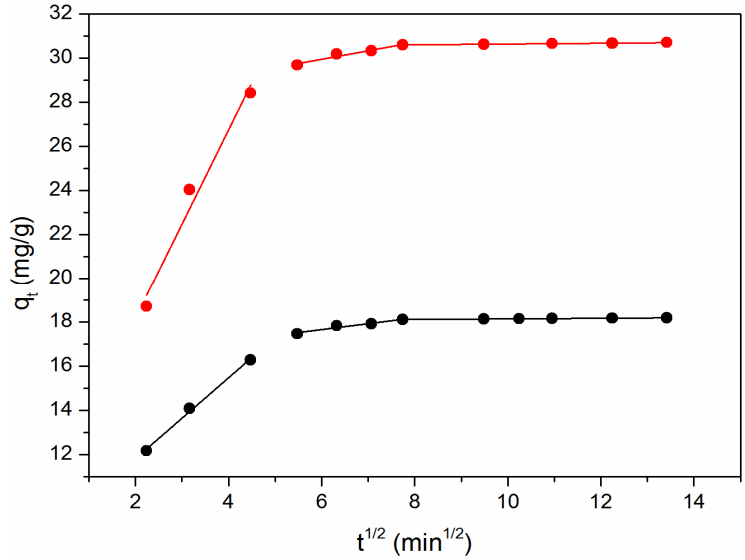

Figure 12: Intrapaticle Kinetics model for biosorption of MB onto DS and NMDS (C_0 =100 mg / L, T = 293 K, DS dose = 5g/L, NMDS dose = 3g/L, pH = 5.57, 50-100 µm).

Table1: Kinetics parameters for biosorption of MB onto DS and NMDS.

Bosorbent	q_e exp (mg/g)	**Pseudo-first-order model**			**Pseudo-second-order model**			**Intraparticle diffusion model**		
		q_e cal (mg/g)	K_1 (min^{-1})	r^2	q_e cal (mg/g)	K_2 ($g.mg^{-1}.min^{-1}$)	r^2	K_{int} ($mg.g^{-1}.min^{-1/2}$)	C (mg/L)	r^2
DS	18.19	3.00	0.039	0.861	18.45	0.026	0.999	0.267	16.05	0.923
NMDS	30.70	4.69	0.041	0.850	31.15	0.016	0.999	0.385	27.63	0.945

3.9. Isotherms parameters

The Langmuir and Freundlich parameters for biosorption of methylene blue onto DS and NMDS are determined from the corresponding plots (Figs.13 and 14) at initial concentration of MB between 100 and 800 mg/L and temperature 323 K. These parameters are summarized in table 2. The results reveal that the equilibrium data agree well with the Langmuir equation comparing to Freundlich isotherm, for DS and NMDS adsorbents. Both the monolayer biosorption and surface heterogeneity of biosorbents affected the removal of MB from solution [32].

According to the values of R_L, all the systems show favorable adsorption of MB. The low values of R_L indicate high and favorable biosorption of methylene blue onto DS and NMDS.
A comparison between the biosorption capacities of DS and NMDS presented in Table2 shows that the biosorption capacities of NMDS is very higher than that of DS. Hence, it can be concluded that modified date stones with NaOH could be employed as effective low-cost adsorbent for removal of methylene blue from aqueous solution.

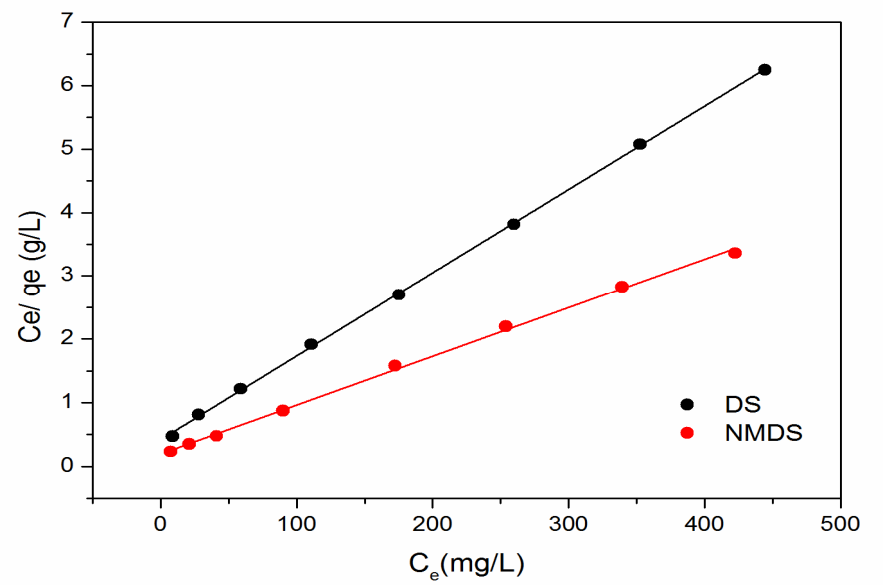

Figure 13: Langmuir isotherm for biosorption of MB onto DS and NMDS
(t = 60 min, T = 323 K, DS dose = 5g/L, NMDS dose = 3g/L, C_0 = 100- 800 mg/L, pH = 5.57, S = 50-100 µm).

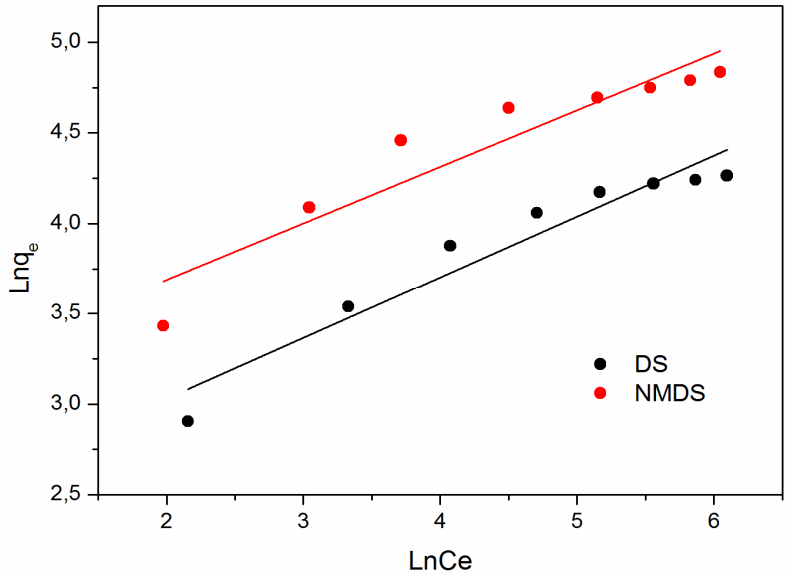

Figure 14: Freundlich isotherm for biosorption of MB onto DS and NMDS
(t = 60 min, T = 323 K, DS dose = 5g/L, NMDS dose = 3g/L, C_0 = 100- 800 mg/L, pH = 5.57, S = 50-100 µm).

Table2: Isotherms parameters for biosorption of MB onto DS and NMDS.

Biosorbent	**Langmuir**				**Freundlich**		
	K_L (L/mg)	q_m (mg/g)	R_L	r^2	K_F ((mg/g)(l/mg) $^{1/n}$)	1/ n	r^2
DS	0.031	76.10	0.038- 0.241	0.999	10.559	0.336	0.921
NMDS	0.039	130.54	0.031 - 0.203	0.998	24.416	0.312	0.872

The maximums monolayer biosorption capacities of MB on DS (76.10 mg/g) and NMDS (130.54 mg /g)

obtained in this study, comparing of these results with that obtained by Dbik (5.78 mg /g) [6] and Jeguirim (43.50 mg/g) [7], indicated that the NMDS a higher selectively for the removal MB.

3.10. Thermodynamics parameters

The values of ΔG° for biosorption of MB onto DS and NMDS at various temperature were obtained from Eq. (9).The values of ΔH° and ΔS° were determined from the slope and intercept of LnK_c versus 1/T (Fig.15). All Thermodynamic parameters are presented in Table 3.The negative values of ΔG° indicates the feasibly of process and spontaneous nature of the dye biosorption onto DS and NMDS. Decrease in value of ΔG° from -5.521 to -6.333 KJ /mol for DS and from-5.589 to -6.855 KJ /mol for NMDS with increases in temperature suggest decreases in feasibly of biosorption at higher temperatures. The positive value of ΔH° shows the endothermic nature of biosorption process. The positive ΔS° value suggests an increase in the randomness at the solid/solution interface during the biosorption process [33].

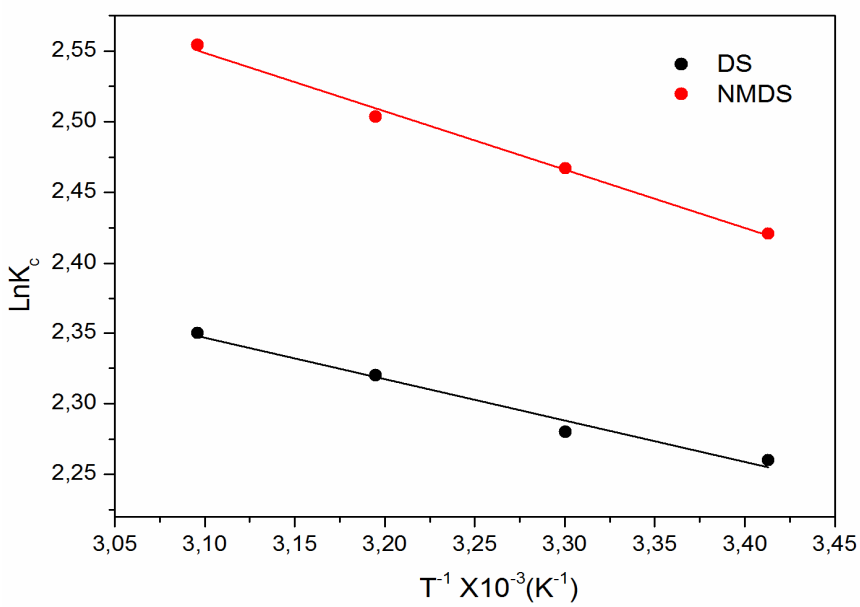

Figure 15: Plots of LnK_C versus 1/T for biosorption of MB onto DS and NMDS

Table3: Thermodynamics parameters for biosorption of MB onto DS and NMDS.

Biosorbent	ΔG°(KJ/mol)				ΔH° (KJ.mol^{-1})	ΔS° (J.mol^{-1}.K^{-1})	r²
	293 K	303K	313 K	323 K			
DS	-5.521	-5.753	-6.036	-6.333	2.431	27.037	0.970
NMDS	-5.589	-6.212	-6.511	-6.855	3.426	31.803	0.991

Conclusion

The present work focuses on the removal of methylene blue from aqueous solution using the raw date stones (DS) and modified with NaOH (NMDS) as a low-cost biosorbents.

The biosorption parameters have been examined such as biosorbent dose, initial pH, temperature, contact time, initial concentration dye and particle size.

The biosorption of MB on two biosorbents is fast and equilibrium is reached in 60 min in optimal conditions. The kinetics of MB adsorption onto the biosorbents can be described well by pseudo-second-order kinetics model. The Langmuir isotherm model provided best fit the experimental equilibrium data indicating monolayer sorption on heterogeneous surface of DS and NMDS. The values thermodynamic parameters indicate the feasibility, spontaneous, endothermic nature of biosorption.

The materials used in this work, specially modified date stones, possess an adsorption capacity significantly greater than those of other adsorbents studied.

Based on results, the date stones especially modified by NaOH are an effective and alternative biomass for removing dyes from aqueous solution in industrial processes.

References

1. Zollinger H., *New York, USA, VCH publishers* (1987) 92–102.
2. *Gupta, V., Ali I., Mohan D., J. Colloid Interface Sci.265* (2003) 257–264.
3. Chakraborty, S., De S., Das Gupta S., Basu J.K., *Chemosphere* 58 (2005) 1079–1086.
4. Hameed B.H., *J. Hazard. Mater.*162 (2009) 939–944.
5. El messaoudi N., Lacherai A., El khomri M., Ezahri M., Bentahar S., *Inter. J. Eng. Res. Technol.*3 (2014) 1671–1678.
6. Dbik A., El Messaoudi N., Lacherai A., *J. Mater. Environ. Sci.*5 (2014) 2510–2514.
7. Belala Z., Jeguirim M., Belhachemi M., Addoun F., Trouvé G., *Desalination* 271 (2011) 80–87.
8. El khomri M., Lacherai A., El messaoudi N., Bentahar S., Ezahri M., *Inter. J. Eng. Res.Technol.*3 (2014) 1657–1663.
9. Dogan M., Abak H., Alkan M., *Water Air Soil Pollut.*192 (2008) 141–153.
10. Bulut Y., Aydin H.A., *Desalination* 194 (2006) 259–267.
11. Ofomaja A.E., *Desal. Water Treat.*3 (2009) 1–10.
12. Hameed B.H., El-Khaiary M.I., *J. Hazard. Mater.*154 (2008) 237–244.
13. Vadivelan V., Kumar K., *J. Colloid Interface Sci.*286 (2005) 90–100.
14. Banat F., Al-Asheh S., Al-Ahmad R., Bni-Khalid F., *Bioresour. Technol.*98 (2007) 3017–3025.
15. Pavan F.A., Lima E.C., Dias S.L.P., Mazzocato A.C., *J. Hazard. Mater.*150 (2008) 703–712.
16. Gholamreza Moussavi, Rasoul Khosravi**,** *Chem. Eng. Res. Des.*89 (2011) 2182–2189.
17. Khalfaoui Amel, Meniai Abdeslam Hassena, Derbal Kerroum, *Energy Procedia* 19 (2012) 286–295.
18. Muthanna Ahmed J., Samar Theydan K., *Powder Technol.*229 (2012) 237–245.
19. Asuha S., Zhou X.G.S., *J. Hazard. Mater.*181 (2010) 204–210.
20. Kumar M., Tamilarasan R., *Chem. Eng. Res. Des.*1 (2013) 1108–1116.
21. Bajpai D.N., *Chand, New Delhi* (1998) 712–737.
22. Auta M., Hameed B.H., *Chem. Eng. J.* 237 (2014) 352–361.
23. Gusmão K.A.G., Gurgel L.V.A., Melo T.M.S., Gil L.F., *J. Environ. Manag.*118 (2013)135–143.
24. Farinella N.V., Matos G.D., Arruda M.A.Z., *Bioresour. Technol.*98 (2007) 1940–1946.
25. Rais Ahmad, *J. Hazard. Mater.*17 (2009) 767–773
26. El-Sayed G. O., *Desalination* 272 (2011) 225–232.
27. Barka N., Abdennouri M., EL Makhfouk M., *J.Taiwan Inst. Chem. Eng.*42 (2011) 320–326.
28. Ouasif H., Yousfi S., Bouamrani M.L., El Kouali M., Benmokhtar S., Talbi M., *J. Mater. Environ. Sci.*4 (2013) 1–10.
29. Charumathi D., Das N., *Desalination* 285 (2012) 22–30.
30. Chaker Ncibi M., Mahjoub B., Seffen M., *J. Hazard. Mater.*139 (2007) 280–285.
31. Gouamid M., ouahrani M.R., Bensaci M.B., *Energy Procedia* 36 (2013) 898–907.
32. Aksu Z., Tezer S., *Process Biochem.* 40 (2005) 1347–1361.
33. Muhammad Saif Ur R., Ilgook K., Jong-In H., *Carbohyd. Polym.* 90 (2012) 1314–1322.