

A batch study of adsorption equilibrium and kinetic for methylene blue onto synthesized zeolite

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Abstract

Synthesized zeolite (SZ) was characterized by nitrogen adsorption–desorption experiments (specific surface area measurements by the BET method), by XRD, and used for the methylene blue (MB) adsorption in synthesized water. The BET surface area (S_{BET}) was 509.9637 m²/g. The XRD indicated the formation of zeolite Y. Kinetic adsorption of methylene blue (MB) onto synthesized zeolite (SZ) was studied in a batch system. The effects of pH and contact time were examined. The maximum adsorption occurred at pH 7. The plateau of the equilibrium state was obtained after 60 min. In order to determine the best-fit-kinetic adsorption, the experimental data were analyzed using pseudo-first-order, pseudo-second-order, pseudo-third-order, esquivel, and elovich models. Linear regressive and non-linear regressive methods were used to obtain the relative parameters. The error analysis was calculated to find which method was better to fit the experimental data. The non-linear pseudo-second order model was best to fit the equilibrium data. The value of free energy (ΔG) was also determined. The present work showed that SZ can be used as a low cost adsorbent for the MB removal from water.

1. Introduction

The textile industry is one of industrial waste water source. This contaminated water is very toxic for the human and animals [1]. Methylene blue (MB) is used in coloring paper, dyeing cottons, wools, silk, leather and coating for paper stock. Although methylene blue is not strongly hazardous, it can cause some harmful effects, such as heartbeat increase, vomiting, shock, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans [2]. The test, application and development of many treatment methods were the essential subjects of many articles such as: physical, chemical, biological [3]. Chemical coagulation–flocculation [4] different type of oxidation processes [5] biological process [6], membrane-based separation processes [7] and adsorption [8] were the treatments used in the purification of waters.

The best efficient method used for the quickly removal of dyes from the aqueous solution is the physical adsorption [9]. In this case, activated carbon has been proven to be widely used adsorbent for lowering the concentration of dyes in waste water, but it presents some disadvantages such as: flammability [10], less regenerability at low temperature [11-12], weak hydrophobicity [13] ...

Actually, the best alternative to carbon adsorbent is zeolite [10]. Recently, commercial zeolites have been used to remove the dissolved pollutants in water and/or wastewater [14]. However, there are relatively limited studies done on the cationic dyes adsorption by synthesized zeolites [15]. In this work, we are interesting to the potential of SZ for the MB dye removal from simulated waste water using batch method. To optimize experimental variables (such as: pH and contact time), the adsorption kinetic efficiency of MB was studied. Linear and non-

linear methods were used to obtain the relative parameters. The error analysis was calculated to find which method was better to fit the experimental data.

2. Experimental

2.1. Adsorbent

Sodium silicate $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ (PANREAC QUIMICA), sodium aluminate NaAlO_2 (PANREAC QUIMICA) and sodium hydroxide NaOH (98% purity; PANREAC QUIMICA) were used to make the SZ.

SZ was synthesized from seed gel (1.02g NaOH , 0.552g NaAlO_2 , 4.98g H_2O , 5.68g $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$) and feed stock gel (0.035g NaOH , 3.28g NaAlO_2 , 32.7g H_2O , 35.6g $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$).

The seed gel was prepared as follows: 1.02 g of sodium hydroxide (NaOH) and 0.522 g of sodium aluminate (NaAlO_2) were dissolved in 4.98 g of distilled water. After dissolution, 5.68 g of sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$) are added to the mixture. The gel was aged during 24 hours at room temperature, under agitation, in closed polyethylene bottle.

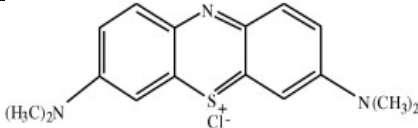
The feed stock gel was prepared in the following way: 0.035 g of sodium hydroxide NaOH and 3.28g of sodium aluminate (NaAlO_2) were dissolved in 32.7g of distilled water. After dissolution, 35.6g of sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$) were very gradually added under strong agitation. The gel was put maturing during two hours after the end of the addition.

After maturation of the feed stock gel, the seed gel is added under strong agitation at room temperature. The resulting mixture is immediately added in a reactor and kept in oven at 100°C for 24 hours. After completion of the synthesis time, the materials was filtered, washed and dried overnight at 100°C .

2.2. Adsorbate

MB (3,7-bis (Dimethylamino)-phenazathionium chloride tetramethylthionine chloride) in the present study was selected from the list of dyes used in Algeria (such as: in the textile industry, coloring paper,...) (Table. 1), was purchased from Merck (Germany).

Table 1: Selected Properties of MB [16]

Dye	MB
Structure	
Chemical formula	$\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}^+\text{Cl}^- \cdot 3\text{H}_2\text{O}$
Mass weight	373.9 g/mol

2.3. Characterization of synthesized zeolite

SZ was characterized by nitrogen adsorption at 77K, XDR and MB adsorption kinetic.

2.4. N_2 adsorption–desorption at 77 K

Nitrogen physisorption data were obtained by N_2 adsorption at 77 K, in a Micromeritics ASAP 2000 instrument. Prior to measurement, the samples were degassed at 393 K for 2 h. The specific surface area was calculated by the BET equation; the total pore volume was determined from N_2 adsorption at a relative pressure of 0.98. The micropore volumes and micropore specific surface of samples were evaluated by the t-plot method. The external Surface Area was the deduction of BET Surface Area and Micropore Area.

2.5. X-ray diffraction (XRD) characterization

Powder X-ray diffraction patterns were collected on a Bruker D8 Advance diffractometer with $\text{Cu K}\alpha$ radiation.

2.6. Adsorption of MB

Adsorption kinetic of MB onto SZ was studied in a batch system. The effects of pH and equilibrium time were examined. The adsorption parameters were optimized. In each experiment preweighed amount of adsorbent (50

mg) was added to 50 mL of dye solution (5 mg/L) taken in a 250 mL of conical flask and 0.1 M NaOH or 0.1 M HCl were added to adjust the pH. This solution was agitated at 300 rpm and centrifuged. The BM concentration in solution was determined at $\lambda_{\max} = 665$ nm by spectrophotometer UV-1700 PHARMA SPEC SHIMADZU. The MB adsorbed amount per mass unit of adsorbent (SZ) at time t, q_t (mg/g), was calculated as:

$$q_t = (C_0 - C_t) * (V/M) \quad (1)$$

where C_0 is the initial MB concentration (mg/L), C is the MB dye concentration at time t (mg/L), V is the solution volume (in L) and M is the adsorbent mass (in g) [17].

3. Results and discussion

3.1. Synthesized zeolite characterization

3.1.1 Physical characterization

The data in Table. 2 indicated the surface areas, pore volumes, and pore sizes of the SZ.

Table 2: Main physical properties of the Synthesized zeolite SZ

	SZ
Surface Area (m²/g)	
Single point surface area at $P/P_0 = 0.249501731$	525.1748
BET Surface Area S_{BET} (m ² /g)	509.9637
t-Plot Micropore Area	472.7452
t-Plot External Surface Area	37.2185
BJH Adsorption cumulative surface area of pores between 17.00 Å and 300.00 Å diameter	30.523
BJH Desorption cumulative surface area of pores between 17.00 Å and 300.00 Å diameter	39.1562
Pore Volume (cm³/g)	
Single point desorption total pore volume of pores less than 1280.510 Å diameter at $P/P_0 = 0.984788073$	0.357885
t-Plot Micropore Volume	0.231750
BJH Adsorption cumulative volume of pores between 17.00 Å and 300.00 Å diameter	0.042621
BJH Desorption cumulative volume of pores between 17.00 Å and 300.00 Å diameter	0.054722
Pore Size (Å)	
Desorption average pore width (4V/A by BET)	28.0714
BJH Adsorption average pore diameter (4V/A)	55.855
BJH Desorption average pore diameter (4V/A)	55.901

3.1.2. XRD characterization

From Figure 1, the XRD of the synthesized zeolite exhibited some significant peaks of reflections at 2θ of about 6.31, 10.31, 12.10, 15.92, 19.01, 21.67, 28.26, 30.16, 33.66, 35.29, and 38.57, which were indicative of the formation of zeolite-Y [18].

3.2. Adsorption studies

To study the effect of every parameter, it is necessary to fix the values of others.

3.2.1. pH effect

The elimination of pollutants from wastewater by adsorption is extremely influenced by the solution pH which affects the nature of the adsorbent surface charge, the ionization extent, the aqueous adsorbate species speciation and the adsorption rate. The adsorptive process through functional groups dissociation on the adsorbate and adsorbent were affected by a pH change [19].

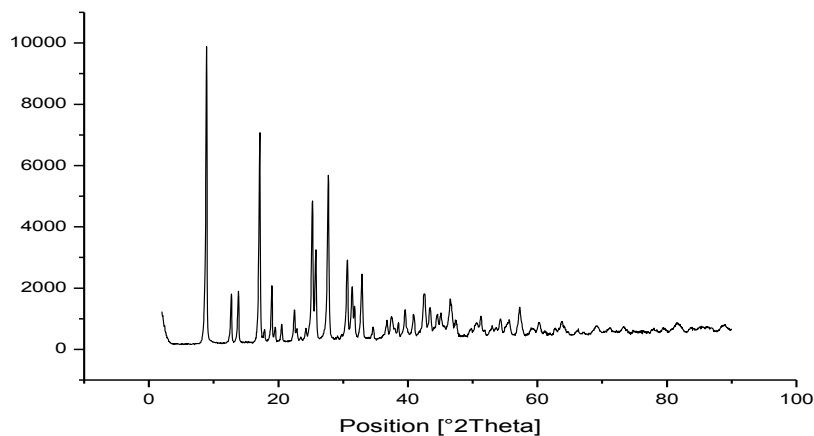


Figure 1: Synthesized zeolite XRD pattern

The effect of pH was conducted by mixing 5 mg of adsorbent with 50 mL of MB synthetic solution 5 mg/L. The solution pH was varied from 2 to 12, by adding 0.1M NaOH or 0.1M HCl solutions. The suspension was shaken for 24 h at 25 °C.

The adsorption capacity of MB increases with the increase of pH of the solution. Figure 2 shows the initial pH effect on the SZ equilibrium adsorption capacity. The solution pH affected the values of q. When the value of pH was from 5 to 11, the adsorption quantity was approximately constant.

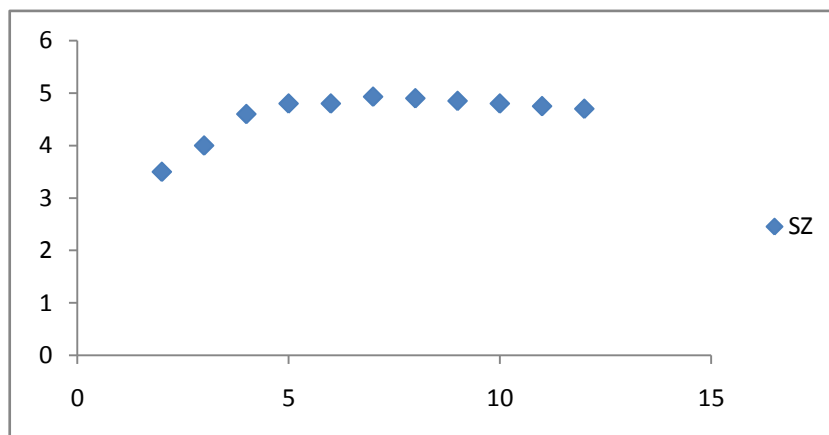


Figure 2: The initial pH effect on the SZ equilibrium adsorption capacity.

From the Figure 2, the MB maximum adsorption occurred at pH 7 and the lowest adsorption occurred at pH 2. From this study, it is clear that in the basic medium the negatively charged species tends dominating and the surface starts to acquire a negative charge. In this case the adsorbent surface is negatively charged, the MB adsorption increased, due to the increasing of electrostatic attraction between the negatively charged zeolite particles and the positively charged MB species.

3.2.3. Contact time effect

Kinetic experiments were performed by mixing 50 mL of dye solution (5 mg/L) with 50 mg of adsorbent. The initial pH for each dye solution was set at 7. The suspensions were put under agitation during 24 hours for certain time intervals, and MB concentrations in the supernatants were analyzed to calculate the adsorbed dyes on the zeolite. These experiments were realized against time (5, 10, 20, 30, 40, 50, 60, 120, 180, 240, 300, and, 360 min) (Figure 3).

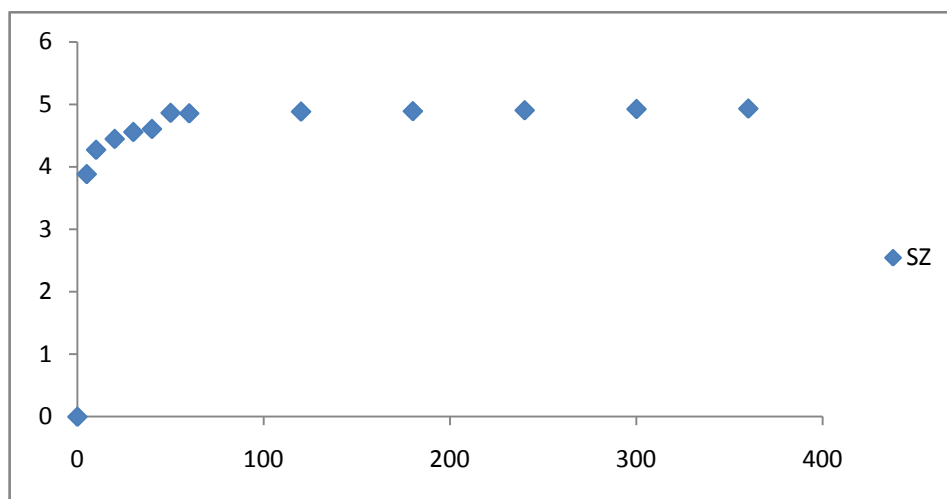


Figure 3: MB adsorption kinetic on SZ.

The plot of synthetic sample could be divided in three zones: (i) 0-30 min, which indicated the fast adsorption of MB, suggesting rapid external diffusion and surface adsorption; (ii) 30-60 min, showed a gradual equilibrium, and (iii) 60-390 min, indicated the plateau of the equilibrium state. The adsorption was rapid at the initial stage of the contact, but it gradually slowed down until the equilibrium. The fast adsorption at the initial stage can be attributed to the fact that a large number of surface sites are available for adsorption.

After a lapse of time, the remaining surface sites are difficult to be occupied. This is because of the repulsion between the solute molecules of the solid and bulk phases which make it taking long time to reach equilibrium [20].

3.2.4. Adsorption kinetics modeling and mechanism

Adsorption is a complex process which is influenced by several parameters related to adsorbent and to the physicochemical conditions under which the process is carried out [21]. In order to understand the mechanism of the adsorption process, the following equations: pseudo-first order (Lagergren Model) [2], pseudo-second order (Ho model) [22], esquivel [23], pseudo-third order [24], and elovich [25] were selected to fit the experimental kinetic data. Equations of these models were illustrated in Table. 3.

Table 3: Adsorption kinetic models and their linear and non linear forms.

Isotherm	Non Linear form	Linear form	Reference
Pseudo-first order			
Pseudo-first order (type1)	$q = q_e(1 - e^{-k_1 t})$	$\log(q_e - q) - \log(q_e) = -\frac{k_1 t}{2.303}$	[26]
Pseudo-first order (type2)		$\ln(q_e - q) - \ln(q_e) = -k_1 t$	[27]
Pseudo-first order (type3)	$C = C_0 e^{-k_1 t}$	$\ln\left(\frac{C}{C_0}\right) = -k_1 t$	[28]
Pseudo-first order (type4) Helfrich		$\ln\left[1 - \frac{C_0 - C}{C_0 - C_e}\right] = -k_1 t$	[29]
Pseudo-second order			
Pseudo-second order type 1		$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	[30]

Pseudo-second order type 2	$q = q_e \left[1 - \frac{1}{1 + k_2 t} \right]$	$\frac{1}{q} = \frac{1}{k_2 q_e^2} \frac{1}{t} + \frac{1}{q_e}$	[1]
Pseudo-second order type 3		$\left(\frac{1}{q} - \frac{1}{q_e} \right) q_e^2 = \frac{1}{k_2 t}$	[31]
Pseudo-second order type 4		$q = q_e - \left(\frac{1}{k_2 q_e} \right) \frac{q}{t}$	[32]
Pseudo-second order type 5		$(q - q_e) q_e = - \left(\frac{1}{k_2} \right) \frac{q}{t}$	[33]
Pseudo-second order type 6		$\frac{q}{t} = k_2 q_e^2 - k_2 q q_e$	[34]
Pseudo-second order type 7		$\frac{1}{q_e - q} - \frac{1}{q_e} = k_2 t$	[35]
Pseudo-second order type 8		$\frac{1}{t} = k_2 q_e^2 \left(\frac{1}{q} \right) - k_2 q_e$	[36]
Pseudo-second order type 9		$\frac{q_e}{q_e - q} - 1 = k_2 t$	[37]
Pseudo-second order type 10			$\frac{\theta}{1 - \theta} = k_2 t$
Pseudo-second order type 11		$C - \frac{1}{C_0} = k_2 t$	[39]
Pseudo-second order type 12		$\frac{1}{C} - \frac{1}{C_0} = k_2 t$	[33]
Pseudo-second order type 13		$\frac{1}{C_0 - C} = k_2 t + b$	[40]
Esquivel model (type 1)	$q = q_e \left(\frac{t}{t + K_E} \right)$	$\frac{1}{q} = \left(\frac{K_E}{q_e} \right) \frac{1}{t} + \frac{1}{q_e}$	[23]
Esquivel model (type 2)	$q = q_e \left(\frac{t}{t + K_E} \right)$	$\left(\frac{1}{q} - \frac{1}{q_e} \right) q_e = K_E \frac{1}{t}$	[23]
Pseudo-third order	$q = q_e \left[1 - \frac{1}{(1 + 2k_3 t)^{1/2}} \right]$	$\frac{1}{q^2} = \frac{1}{q_e^2} + k_3 t$	[24]
Elovich (type 1)	$\frac{dq}{dt} = k_4 \exp(-k_5 q)$	$q = k_5 \ln(k_5 k_4) + k_5 \ln(t)$	[25]
Elovich (Roginsky-Zeldovich) (type 2)	$\frac{dq}{dt} = k_7 \exp(k_6 q)$	$q = (1/k_6) \ln(k_6 k_7) + (1/k_6) \ln(t)$	[41]

where k_1 is pseudo-first order rate constant (min^{-1}), k_2 is pseudo-second order rate constant ($\text{g}/(\text{mg min})$), k_3 is pseudo-third order rate constant ($\text{g}^2/(\text{mg}^2 \text{ min})$), K_E is esquivel rate constant (min), k_4 is elovich rate constant ($\text{mg}/(\text{g min})$), k_5 is extent of surface coverage and activation energy of the process ($\text{mg}/\text{g min}$), k_6 extent of surface coverage and activation energy of the process (g/mg), k_7 elovich rate constant ($\text{mg}/(\text{g min})$), q_e is amount of adsorption at equilibrium (mg/g), and θ dimensionless parameter ($=q/q_e$).

A non-linear and linear fitting procedure using Excel and Origin software were used respectively. The constants of all models were given in Table. 4.

Table 4: Linear and non-linear pseudo-first order, pseudo-second order, esquivel, and elovich kinetic isotherms constants related to the adsorption of MB onto SZ.

Model	Linear Method	Non-linear Method
Pseudo-first order (type 1)		
q_e (mg/g)	4.930	4.769
k_1 (min^{-1})	0.030	0.308
R^2	0.663	0.982
Equation	$\log(q_e - q) - \log(q_e) = -0.013t$	$q = 4.769(1 - e^{-0.308t})$
Pseudo-first order (type 2)		
q_e (mg/g)	4.930	
k_1 (min^{-1})	0.031	
R^2	0.663	
Equation	$\ln(q_e - q) - \ln(q_e) = -0.031t$	
Pseudo-first order (type 3)		
C_0 (mg/L)	5	5
k_1 (min^{-1})	0.016	0.260
R^2	<0	0.957
Equation	$\ln\left(\frac{C}{C_0}\right) = -0.016t$	$C = 5e^{-0.260t}$
Pseudo-second order (type 1)		
q_e (mg/g)	4.975	4.907
k_2 (g/(mg min))	0.105	0.686
R^2	1	0.996
Equation	$\frac{t}{q} = 0.201t + 0.385$	$q = 4.907\left(1 - \frac{1}{1 + 0.685t}\right)$
Pseudo-second order (type 2)		
q_e (mg/g)	4.902	
k_2 (g/(mg min))	0.147	
R^2	0.946	
Equation	$\frac{1}{q} = 0.282\frac{1}{t} + 0.204$	
Pseudo-second order (type 3)		
q_e (mg/g)	4.898	
k_2 (g/(mg min))	0.147	
R^2	0.946	
Equation	$\left(\frac{1}{q} - \frac{1}{q_e}\right)q_e^2 = 6.810\frac{1}{t}$	
Pseudo-second order (type 4)		
q_e (mg/g)	4.900	
k_2 (g/(mg min))	0.145	
R^2	0.930	
Equation	$q = 1.410\frac{q}{t} + 4.900$	
Pseudo-second order (type 5)		
q_e (mg/g)	4.907	
k_2 (g/(mg min))	0.143	
R^2	0.930	
Equation	$(q - q_e)q_e = -6.992\frac{q}{t}$	

Pseudo-second order (type 6)		
q_e (mg/g)	4.921	
k_2 (g/(mg min))	0.134	
R^2	0.930	
Equation	$\frac{q}{t} = -0.659q + 3.243$	
Pseudo-second order (type 7)		
q_e (mg/g)	4.958	
k_2 (g/(mg min))	0.093	
R^2	0.948	
Equation	$\left(\frac{1}{q_e - q}\right) - \left(\frac{1}{q_e}\right) = 0.097t$	
Pseudo-second order (type 8)		
q_e (mg/g)	4.909	
k_2 (g/(mg min))	0.139	
R^2	0.946	
Equation	$\left(\frac{1}{t}\right) = 3.348\left(\frac{1}{q}\right) - 0.682$	
Pseudo-second order (type 9)		
q_e (mg/g)	4.958	
k_2 (g/(mg min))	0.467	
R^2	0.948	
Equation	$\left(\frac{q_e}{q_e - q}\right) - 1 = 0.467t$	
Pseudo-second order (type 10)		
q_e (mg/g)	4.958	
k_2 (g/(mg min))	0.465	
R^2	0.948	
Equation	$\left(\frac{\theta}{1 - \theta}\right) = 0.465t$	
Pseudo-second order (type 12)		
C_0 (mg/L)	5	
k_2 (g/(mg min))	0.044	
R^2	0.808	
Equation	$\left(\frac{1}{C} - \frac{1}{C_0}\right) = 0.044t$	
Esquivel Model (type 1)		
q_e (mg/g)	4.902	4.907
k_2 (g/(mg min))	1.382	1.458
R^2	0.946	0.996
Equation	$\left(\frac{1}{q}\right) = 0.282\frac{1}{t} + 0.204$	$q = 4.907\left(\frac{1}{t + 1.458}\right)$
Esquivel Model (type 2)		
q_e (mg/g)	4.899	
k_2 (g/(mg min))	1.392	
R^2	0.946	
Equation	$\left(\frac{1}{q} - \frac{1}{q_e}\right)q_e = 1.392\frac{1}{t}$	

Elovich (type 1)		
k_5 (mg/(g min))	0.221	
k_4 (g/mg)	111294692	
R^2	0.845	
Equation	$q = 0.221 * \ln(t) + 3.761$	
Elovich (type 2)		
k_6 (mg/(g min))	4.525	
k_7 (g/mg)	5437921.25	
R^2	0.845	
Equation	$q = 0.221 * \ln(t) + 3.761$	

3.2.5. Error estimation using the well-known special functions

In this part, the best-fitting equation is determined using the well-known special functions to calculate the error deviation between experimental and predicted data. The mathematical equations of these error functions were illustrated in Table. 5.

Table 5: Mathematical equations of error functions.

Error functions	Equations	References
ARED	$ARED = \frac{100}{n} \sum_{i=1}^n \left \frac{q_{exp} - q_{calc}}{q_{exp}} \right _i$	[42]
ARE	$ARE = \frac{\sum q_{calc} - q_{exp} / q_{exp}}{n}$	[43]
SAE = EABS	$SAE = EABS = \sum_{i=1}^n q_{exp} - q_{calc} $	[44]
ARS	$ARS = \sqrt{\frac{\sum [(q_{exp} - q_{calc}) / q_{exp}]^2}{(n - 1)}}$	[45]
MPSD	$MPSD = 100 \sqrt{\frac{\sum [(q_{exp} - q_{calc})]^2}{n - p}}$	[46]
$\Delta q(\%) = 100 * ARS$	$\Delta q(\%) = 100 \sqrt{\frac{\sum [(q_{exp} - q_{calc}) / q_{exp}]^2}{(n - 1)}}$	[47]
SSE	$SSE = \sum (q_{calc} - q_{exp})^2$	[48]
MPSED	$MPSED = \sqrt{\frac{\sum [(q_{exp} - q_{calc}) / q_{exp}]^2}{(n - p)}}$	[49]
HYBRID	$HYBRID = \frac{1}{(n - p)} \sum_{i=1}^n \left \frac{q_{exp} - q_{calc}}{q_{exp}} \right _i$	[50]

Where n is the number of experimental data points, q_{calc} is the predicted (calculated) quantity of MB adsorbed onto zeolite, q_{exp} is the experimental data, p is the number of parameters in each kinetic model, ARED is average relative error deviation (dimensionless parameter), ARE is average relative error (dimensionless parameter), ARS is average relative standard error (dimensionless parameter), HYBRID is hybrid fractional error function (dimensionless parameter), MPSD Marquardt's is percent standard deviation (dimensionless parameter), MPSED Marquardt's is percent standard deviation (dimensionless parameter), SAE=EABS is sum of absolute error (mg/g), SSE is sum of the squares of the errors (mg/g)², and $\Delta q(\%)$ is normalized standard deviation (mg/g). The constants of all error analysis were represented in Table. 6.

Table 6: Error deviation data related to the MB adsorption onto SZ using most commonly used functions.

Error functions	ARED	SAE=EABS	MPSD	SSE	HYBRID	ARE	ARS	$\Delta q(\%)=100*ARS$	MPSD
Non linear pseudo-first order type 1	3.570	1.963	0.043	0.378	0.043	0.036	0.041	4.110	9.146
Non linear pseudo-first order type 3	81.960	2.725	0.021	0.906	0.968	0.819	1.015	101.547	7.072
Linear Pseudo-2nd order type 1	15.909	8.314	0.248	10.688	0.191	0.159	0.237	23.690	50.615
Linear pseudo-2nd order type 2	12.778	6.685	0.199	6.785	0.153	0.128	0.189	18.961	40.417
Linear pseudo-2nd order type 3	12.911	6.758	0.200	6.882	0.155	0.129	0.191	19.086	40.694
Linear pseudo-2nd order type 4	13.052	6.832	0.202	7.035	0.156	0.130	0.193	19.294	41.141
Linear pseudo-2nd order type 5	13.069	6.837	0.203	7.106	0.157	0.131	0.194	19.398	41.356
Linear pseudo-2nd order type 6	13.625	7.124	0.216	7.772	0.163	0.136	0.203	20.274	43.238
Linear pseudo-2nd order type 7	17.322	9.081	0.264	12.183	0.208	0.173	0.252	25.199	53.935
Linear pseudo-2nd order type 8	13.387	7.004	0.208	7.437	0.160	0.134	0.198	19.832	42.294
Linear pseudo-2nd order type 9	1.914	0.982	0.036	0.207	0.023	0.019	0.034	3.401	7.158
Linear pseudo-2nd order type 10	1.914	0.982	0.036	0.207	0.023	0.019	0.034	3.401	7.158
Non linear pseudo-2nd order type 1	1.450	0.797	0.019	0.074	0.017	0.014	0.018	1.812	4.042
Linear esquivel model type 1	96.080	57.551	1.054	258.944	1.153	0.961	1.005	100.516	228.536
Linear esquivel model type 2	96.086	57.527	1.054	258.776	1.153	0.961	1.005	100.522	228.547

Where from, according to the Table 6, is seemed that the non-linear pseudo-second order model is the model the most suited to describe in a satisfactory way the phenomenon adsorption studied. Indeed, the highest R^2 value and the lowest ARED, ARE, SAE, ARS, MPSD, Δq , SSE, MSPED, and HYBRID values were found when modeling the data of equilibrium using the non-linear pseudo-second order model and linear pseudo-second order model (type 9 and type 10) (cf. Table. 6). By the way, a brief comparison between non-linear and linear analysis was carried out to investigate, among these error functions, the most acceptable one(s) for each regression approach, taking the adequate fitting model (i.e. pseudo-second order) as a study case. The results showed that, for the linear analysis, the regression coefficient (R^2) is the highest (i.e. pseudo-second order type 1), which makes it more adequate as error estimation tool to find the perfect isotherm fit for linear expression. For non-linear analysis, the rest of the error functions (i.e. ARED, ARE, SAE, ARS, MPSD, Δq , SSE, MSPED, and HYBRID) seem to be the best and the most appropriate.

Really, the non-linear transformation to linear regression methods distorts the experimental error, creating therefore an inherent error estimation problem which limits the studied tools validity. Moreover, the linear analysis method assumes the points scatter around the line follows a Gaussian dispersion and error estimation is the same at the equilibrium liquid-phase residual concentration value (i.e. X-axis). Nevertheless, such behaviour is impossible with equilibrium isotherm models (since isotherm models had non-linear shape) as the error distribution gets changed after transforming the data to linear [49]. Improbably, non-linear regression method would avoid such errors, making this analyzing technique the most suitable to obtain more realistic isotherm parameters [49].

3.2.6. Activation parameters assessment

To calculate the activation parameters such as entropy (ΔS), free energy (ΔG) and enthalpy (ΔH), the Eyring expression was applied [51],

$$\ln\left(\frac{k_2}{T}\right) = \ln\left(\frac{k_B}{h_p}\right) + \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (2)$$

$$\Delta H - T\Delta S = (b - a)RT \quad (3)$$

$$\ln\left(\frac{k_2}{T}\right) = a \quad \text{and} \quad \ln\left(\frac{k_B}{h_p}\right) = b$$

where k_B is the constant of Boltzmann ($1.3807 \cdot 10^{-23} \text{ J.K}^{-1}$), h_p is the constant of Plank $6.6261 \cdot 10^{-34} \text{ (J.s)}$ and, k_2 is the pseudo-second order constant. The Gibbs energy of activation may be written in terms of entropy and enthalpy of activation [52]:

$$\Delta G = \Delta H - T\Delta S = (b - a) \cdot R \cdot T \quad (4)$$

$$\Delta G = 73.916 \text{ (kJ.mol}^{-1}\text{)} \text{ at } T = 298 \text{ K}$$

The positive ΔG value proposes that adsorption reactions need energy to transform solution species to adsorbed species [53].

Conclusions

Synthesized zeolite (SZ) was characterized and used for the methylene blue adsorption in synthesized water. The adsorption–desorption isotherms of N_2 indicate that the BET surface area is equal to $509.9637 \text{ m}^2 \text{ g}^{-1}$. The XRD spectrum indicates that is zeolite Y type.

In batch studies, the adsorption was highly dependent on various operating parameters, such as: contact time, and pH. The results suggest that the MB adsorption onto this SZ increased progressively over the first 38 min and then stayed unchanged with further increasing equilibrium time. The apparent equilibrium was reached after 60 min for SZ. Surface adsorption mechanism was predominant in the initial stage of contact time, there after diffusion became rate-limiting process.

The adsorption kinetic of MB onto SZ can be better fitted by the non-linear pseudo-second-order model than by the linear pseudo-second-order model (type 9 and 10) as compared to the pseudo first order, pseudo third order, esquivel, and elovich models.

The value of free energy (ΔG) indicated that the adsorption reaction was not a spontaneous process and that the system requires energy gain from an external source.

On the whole, the experimental results showed that SZ is suitable adsorbent for removal of MB dyes.

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