

## Removal of a cationic dye from aqueous solution by adsorption on to bassorin hydrogel

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<https://doi.org/10.48317/IMIST.PRSM/morjchem-v11i1.32109>

Received 24 Aug 2022,

Revised 28 Dec 2022,

Accepted 07 Jan 2023.

**Citation:** Ratiki EL., Abida F., Ouass A., Khadouddi I., Hatim Z., Rifi E.H., Kheribech A. (2023). Removal of a cationic dye from aqueous solution by adsorption on to bassorin hydrogel, *Mor. J. Chem.*, 14(2), 318-332 Doi: <https://doi.org/10.48317/IMIST.PRSM/morjchem-v11i1.32109>

**Abstract:** Polysaccharide-based hydrogels represent a class of materials with potential properties useful in biomedical, agricultural and environmental fields. In this work, bassorin hydrogel extracted from the Gum Tragacanth (GT) was used for the removal of a cationic dye, methylene blue (MB), from aqueous solutions. The extracted COOH-rich polysaccharide, as a plant-derived substances, was the basis for obtaining cross-linked and water-insoluble ionic hydrogel. The adsorbent possesses an important swelling property, a large surface porosity and high adsorption capacity. A series of experiments was carried out in order to study the influence of parameters such as contact time, initial MB concentration (10-100 mg. L<sup>-1</sup>), adsorbent dose (1-13 g.L<sup>-1</sup>) and initial pH solution (2-10) in batch procedures at room temperature (25±2°C). The results showed that 100 min of contact time was sufficient for attaining equilibrium. The adsorption percentage increases from 55% to 84.3% when the mass of the hydrogel increases from 1g to 3g. The optimum pH for MB removal by the hydrogel was around 9. The adsorption is best described by the Langmuir model; which assumes a monolayer adsorption. Second-order model better describes the adsorption of MB on the hydrogel. We can conclude that the bassorin hydrogel has a potential, to be used as an adsorbent for wastewater treatment and purification processes to eliminate emergent contaminants.

**Keywords:** Adsorption, Bassorin hydrogel, Methylene blue, Kinetic studies, Adsorption isotherms.

### 1. Introduction

The production of industrial dyes poses major problems in terms of effluent treatments since their properties often make them difficult to degrade. Appropriate methods are used to treat and remove organic pollutants (Levallois, 2006) like physico-chemical and biological methods such as coagulation-flocculation, oxidation, adsorption, precipitation and membrane filtration (Panswed *et al.*, 1986; Muqeet *et al.*, 2020; Hameed *et al.*, 2007; Arroub *et al.*, 2015; Sun *et al.*, 2012; Ouedrhiri *et al.*, 2021; Thinakaran *et al.*, 2008; Jodeh *et al.*, 2014; Wu *et al.*, 2008). These methods have been extensively studied and have revealed a high efficiency of water discoloration. Most of these

techniques are expensive and very often generate derivatives and by-products that are more toxic than the initial molecule. The adsorption technique is widely used for the specific recovery for the treatment of industrial effluents. However, there are a significant number of adsorbents using different materials, each with advantages and disadvantages. At present, activated carbon is the most widely used because of its high adsorption capacity (Kouar *et al.*, 2021). However, this adsorbent has a high cost. Hydrogels (insoluble but swellable polymeric networks in water) with high sorption capacity, high functionality and hydrophilicity pave a probable way for decolorization of water, as being cost effective (Ensm, 2015). Several routes have been utilized for preparation of hydrogel based on polysaccharides such as cellulose, starch and natural gums. This class of polysaccharide have attracted great attention, mainly due to their appropriate water absorbency, biocompatibility and biodegradability, abundance in nature and economic as compared to bio-resourceable synthetic polymers (Guo *et al.*, 1998, Pourjavadi *et al.*, 2008, Kiani *et al.*, 2012, Errich *et al.*, 2021; Mohammadifar *et al.*, 2006). The properties of hydrogels depend on various important parameters such as hydrophilicity and the degree of cross-linking of polymer chains (Brannon-Peppas, 1990). Hydrogels are three-dimensional hydrophilic polymer structures that can absorb, inflate and retain huge amounts of water or aqueous fluids (Jones *et al.*, 2005). The water retention capacity of hydrogels is due to the presence of functional groups such as hydroxylic (-OH), carboxylic (-COOH), amide (-CONH-), primary amide (-CONH<sub>2</sub>) and sulfonic (-SO<sub>3</sub>H) groups in the polymer network (Ganji *et al.*, 2010). Tragacanth gum, an anionic polysaccharide, represent a class of materials with potential properties useful in biomedical, agricultural and environmental fields. This biopolymer is biocompatible, biodegradable and non-toxic nature. It's formed by a chain of  $\alpha$ -D-galacturonic acid, some units being substituted in (O-3) by ( $\beta$ -D-xylopyranosyl) sometimes terminated by galactose or fucose. This is a natural polymer which is derived from renewable sources and consists of two fractions named water-soluble fractions namely tragacanthin and water-swellable part namely bassorin. In this work, bassorin hydrogel was extracted from the Gum Tragacanth (GT) and used for the removal of a cationic dye, methylene blue (MB), from aqueous solutions. A series of experiments was carried out and the optimum condition for adsorption was studied by altering pH (2-10), temperature (25-60°C), adsorbent dose (1-13 g) and contact time (0.5-3hr).

## 2. Materials and methods

### 2.1 Materials

Gum Tragacanth (GT) used in this study was collected from plants growing in south Sahara of Morocco. Methylene blue (MB) was purchased from Sigma Chemical Co., St. Louis, MO, USA. All other chemicals are of analytical grade.

### 2.2 Preparation and analysis of bassorin hydrogel

The used hydrogel bassorin (HB) was extracted from gum Tragacanth (GT). Firstly, GT was extensively washed with distilled water to remove water soluble surface contaminants. After washing, GA was dried at room temperature for 24 h. The product was then ground and sieved to obtain a homogenous particle size. Powdered gum with a mesh size between 200 and 500 mm was used in this study.

One g of prepared powder was mixed with 300 mL of distilled water at 25 °C. The resulting mixture was kept under low stirring for 24 hours to allow total hydration. About 9g of this gelified mixture was freezing to separate the soluble and insoluble phase. The obtained bassorin hydrogel, which is the insoluble phase and the main constituent of adragante gum (78%), was dried and stored for

analysis. Swelling measurements was determined according to the method described by Liu M and coll (Liu *et al.*, 2001); 0.1 g of bassorin powder was immersed in 100 ml of distilled water at room temperature until the equilibrium swelling was reached (Przytulska *et al.*, 2022). The swollen absorbent was then weighed after the removal of the extra water using a vacuum filtration. The swelling rate of the hydrogel was then calculated according to the following relationship:

$$SR = \frac{ws - wd}{ws} \quad \text{Eqn. 1}$$

Where: where  $W_s$  is the weight of the swollen hydrogel and  $W_d$  the weight of the dried hydrogel

### 2.3. Preparation and analysis of aqueous dye solutions

Dye solution was prepared by dissolving 0.5 g of MB in 1000 mL of distilled water. The experimental solutions of different concentrations ranging from 10 to 100 mg. L<sup>-1</sup> were prepared by further dilutions of stock solution. The solution was scanned for max measurement 664 nm of dye standard curve developed through the measurement of the absorbance of dye solution by double beam spectrophotometer.

### 2.4 Batch sorption

Initially, hydrogel sorption tests were carried out with masses ranging from 1 to 13 g in an aqueous MB absorbance of solution was determined at the wavelength of 664 nm. The result was expressed in the adsorption capacity of the hydrogel according to the following formula:

$$Q_{ads} = \frac{(C_0 - C_t)}{M} \times V \quad \text{Eqn. 2}$$

Where:  $C_0$ ,  $C_t$ : is the initial and the equilibrium concentration (mg. L<sup>-1</sup>) respectively.  $m$  (g): is the weight of hydrogel.  $V$  (L): is the volume of the solution. The adsorption efficiency of MB bassorin hydrogel was calculated by the following relationship :

$$\%R = \frac{(C_0 - C_t)}{C_0} \times 100 \quad \text{Eqn. 3}$$

The effect of various operational parameters such as contact time, initial MB concentration, (10-100 mg. L<sup>-1</sup>) adsorbent dose (1-13 g) and initial pH solution (2-10) was evaluated in batch procedures at room temperature (25±2°C).

### 2.5 Modeling of adsorption kinetic

The modelling of the kinetic adsorption of MB on the hydrogel was carried out using the kinetic models of the surface reaction. We used linear equations of pseudo-order 1 and pseudo-order (Hassan *et al.*, 2020).

Model of the kinetics of the pseudo first order:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad \text{Eqn. 4}$$

Where:  $q_e$  and  $q_t$  are respectively the quantities of dye (mg<sup>-1</sup>. g) adsorbed on the hydrogel at equilibrium and at time  $t$ .  $K_1$  is the speed constant (min<sup>-1</sup>). By integrating and applying the initial conditions (at  $t = 0$ ,  $q_t = 0$  and at  $t = t_e$ ,  $q_t = q_e$ ), equation 4 takes the following form:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad \text{Eqn. 5}$$

$K_1$  and  $q_e$  are obtained by representing Log ( $q_e - q$ ) as a function of  $t$ .

Pseudo-second-order kinetics model:

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad \text{Eqn 6}$$

$K_2$  is the pseudo-second-order rate constant ( $\text{g}^{-1}.\text{mg}^{-1}.\text{min}^{-1}$ ). By integrating and applying the conditions (at  $t = 0$ ,  $q_t = 0$  and at  $t = t_e$ ,  $q_t = q_e$ ), equation 6 takes the linear form

$$\frac{t}{q_t} = \frac{1}{K_2 - q_e^2} + \frac{t}{q_e} \quad \text{Eqn 7}$$

$q_e$  and  $K_2$  are obtained by representing  $\frac{t}{q}$  as a function of  $t$ .

## 2.6 Adsorption isotherms

The modeling of isotherm adsorption was done using Langmuir and Freundlich equilibrium models.

The Langmuir model was used in its linear form given by the equation below Langmuir (Hamdaoui *et al.*, 2006 and Gnana *et al.*, 2014)

$$\frac{1}{Q_e} = \frac{1}{Q_m} = \frac{1}{K Q_m - C_e} \quad \text{Eqn8}$$

$Q_e$ : Equilibrium adsorption capacity ( $\text{mg. g}^{-1}$ ) Eqn 2.

$Q_m$ : Maximum adsorption capacity ( $\text{mg. g}^{-1}$ ). This equation makes it possible to calculate the parameters.

$Q_m$  and  $K$ : from the ordinate at the origin and the slope. The linear Freundlich equation was used.

$$\log Q_e = \log k_f + \frac{1}{n} \log C_e \quad \text{Eqn9}$$

With:

$Q_e$ : Equilibrium adsorption capacity ( $\text{mg. g}^{-1}$ ).

$C_e$ : Residual solute concentration at equilibrium ( $\text{mg. L}^{-1}$ ).

$K_f$  and  $n$ : Characteristic constants of the efficiency of an adsorbent with respect to a given solute.

This equation allows to calculate the parameters  $K_f$  and  $\frac{1}{n}$  from the ordinate at the origin and the slope respectively to confirm the nature of adsorption, the Langmuir isotherm can be expressed by the separation factor  $R_L$  defined by the following relation:

$$R_L = \frac{1}{(1 + K_L \times C_0)} \quad \text{Eqn10}$$

Where  $C_0$  is the initial concentration ( $\text{mg. L}^{-1}$ ) and  $K_L$  is Langmuir's constant ( $\text{L}^{-1}.\text{mg}$ )

( $R_L > 1$ ) indicates that the adsorption is unfavorable

( $R_L = 1$ ) indicates that the adsorption is linear.

( $R_L = 0$ ) indicates that adsorption is favorable

## 2.7. Thermodynamic study

The thermodynamic parameters were carried out from the thermal data of sorption of MB dye onto bassorin hydrogel. The parameters like entropy change ( $\Delta S$ ), enthalpy change ( $\Delta H$ ) and Gibbs free energy change ( $\Delta G$ ) were calculated, via the van't Hoff approach and the Gibb free energy equation:

$$\Delta G_{ads} = \Delta H_{ads} - T \Delta S_{ads} \quad \text{Eqn 11}$$

$$\Delta G = T \ln K_C \quad \text{Eqn12}$$

$T$ : temperature (Kelvin)

$R$ : ( $8.314 \times 10^{-3} \text{ KJ.mol}^{-1}.\text{K}^{-1}$ ) is the ideal gas constant

Distribution coefficient determined as follows:  $K_c = \frac{Q_e}{C_e}$

With:

$Q_e$ : Adsorption capacity at equilibrium ( $\text{mg. g}^{-1}$ )

$C_e$ : Concentration at equilibrium of the solute in solution (mg. L<sup>-1</sup>)

$\Delta H_0$  and  $\Delta S_0$  are determined from the slope and intercept of the plot of  $\ln k_c$  versus  $\frac{1}{T}$  using the following Van't Hoff equation:

$$\log k_c = \frac{\Delta S^0}{2.303} \times R - \frac{\Delta H^0}{2.303 \times R \times T} \quad \text{Eqn13}$$

To identify the chemical functional groups the characterization of bassorin, was studied by Fourier transform infrared spectroscopy (FT-IR) in an interval ranging from 400 to 4000 cm<sup>-1</sup>.

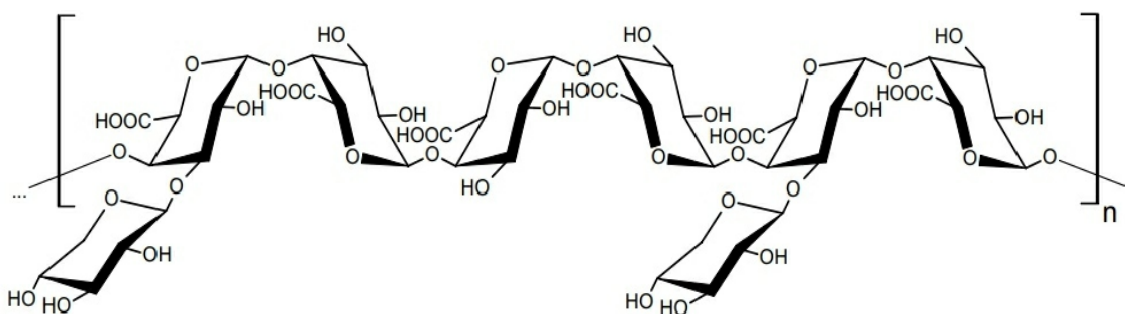
### 3. Result and discussion

#### 3.1 Characterization of bio-sorbent

The properties of the prepared hydrogel depend on its chemical structure and its microstructure. Some properties of used sorbent have been determined and presented which show the variables characteristics [Table 1](#). The chemical formula, FTIR spectra, cristalline structure and microstructure of the extracted bassorin are presented. [Figure 1](#), shows the presence of functional groups such as hydroxylic (-OH) and carboxylic (-COOH). The RXD shown in [Figure 2a](#) indicate that the sample can be classified as semicrystalline structure that it will help to absorb more waters. The FTIR spectra presented in [Figure 2b](#) shows the band observed at 3289.47 cm<sup>-1</sup> assigned to stretching vibrations of (OH) groups. The bands at 1600cm<sup>-1</sup> correspond to carbonyl groups. The band found at 1236 cm<sup>-1</sup> could be assigned to characteristic of (C-H) banding group. Bands at 1052.63 cm<sup>-1</sup> attributed to carboxylate group. Prepared hydrogel [Figure 3a](#), shows great viscosity and structural stability. Indeed, the functional groups of bassorin such as: hydrogen bonds, hydrophobic bonds, and Van der Waals bonds which is considered to form a cross-linking [Figure 3b](#) through intermolecular bonds leading to the formation of crystallites and junction zones. This intermolecular rearrangement is due to the freezing used to extract bassorin.

**Table1:** Summary description of variables Characteristics Of bassorin hydrogel.

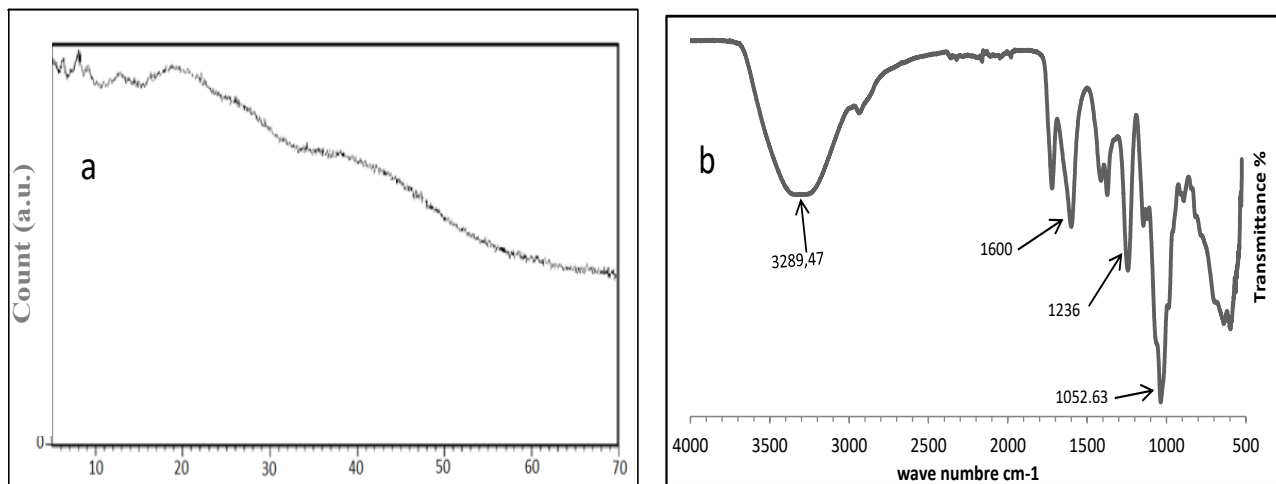
Source	Structure	Crosslinking	Physical apparence	Electrical charge
Natural origine	Semi-cristalline	Physical crosslinked	translucent	Ionic



**Figure1:** Chemical structure of bassorin polysaccharide formed by a chain (1-4) α-D-Acide galacturonic (Liu et al.,2001)

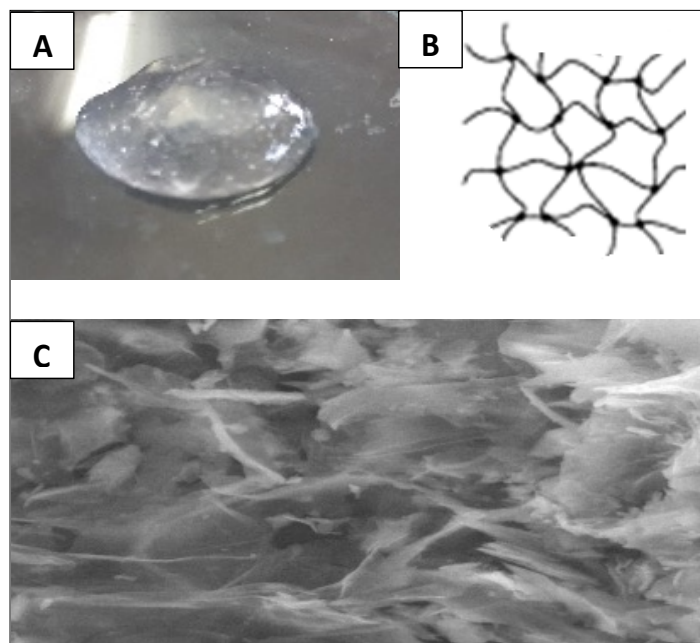
During this process, the free water in the polymer solution freezes by cooling and polymer chains are excluded. The local concentration of the polymer increases and hydrogen bonds between the chains are formed

leading to the formation of the cross-link junctions. The polymer gels into microcrystals and solid three-dimensional network were formed [Figure 3a](#). The [Figure 3c](#) illustrates the SEM image of hydrogel, the network reveals the presence of agglomerates thin sheets with formation of micro-porous microstructure.



**Figure 2:** a) XRD and b) Infrared spectrum of extracted Bassorin

Gels usually have a cloudy appearance due to microscopic heterogeneity. However, the gel prepared in this work using water as solvent was translucent in appearance, giving an aqueous solution of high-viscosity. The favorable property of the prepared hydrogel was ability to swell in contact with an aqueous solution.

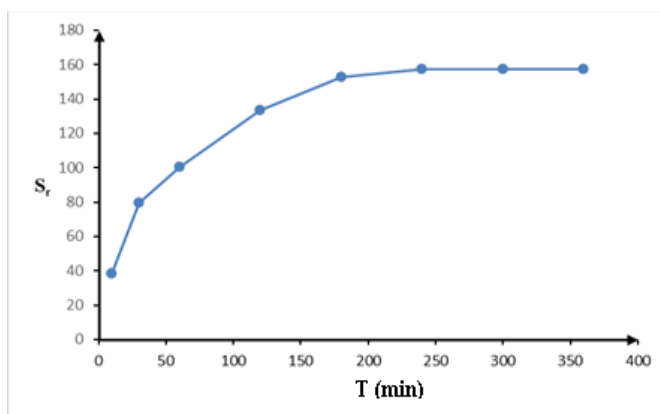


**Figure 3:** Microstructure of bassorin hydrogel (a) swollen hydrogel (b) crosslinking formed by intermolecular linkage and (c) SEM image (1cm = 2 μm).

The evolution of the swelling rate ( $S_r$ ) of the hydrogel versus time is shown on the [Figure 4](#). The result shows that the rate of swelling initially increased rapidly over time and then reached a constant value and became independent of time. A contact time of 180 min recorded a maximum swelling rate of about  $157.20\text{g.g}^{-1}$ . The swelling of the hydrogel can be explained by porous microstructure and by the existence of the driving forces mainly to a difference in osmotic pressure inside and outside the



hydrogel. This difference is attributed to the fact that the inside of the Bassorin hydrogel is an ionic medium and the external medium (water) is neutral and in order to achieve an equilibrium the water therefore has a tendency to migrate to the hydrogel, once the latter is negatively charged the chains repel each other. Because of the anionic nature the swelling behavior of the hydrogel is highly dependent on the pH.



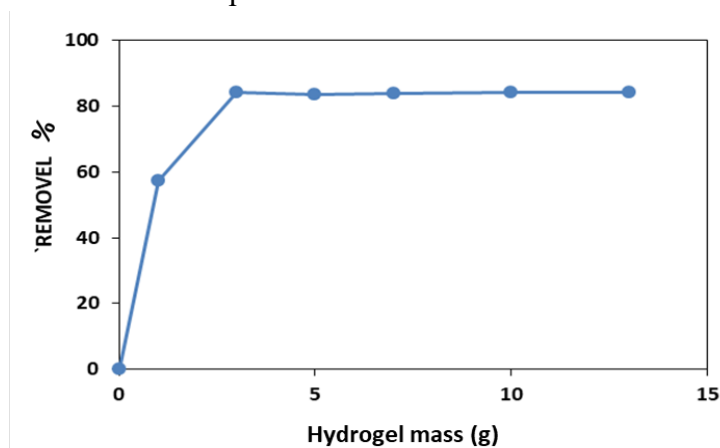
**Figure 4:** Evolution of the swelling rate of the Bassorin hydrogel in distilled water as a function of the contact time.

### 3.2 Adsorption study

The adsorption of MB on the hydrogel was studied according to different parameters: the mass of bio-adsorbent, the pH, the concentration of the adsorbate solution, the contact time between the bio-adsorbent/adsorbate and the temperature of the MB solution. For each parameter the sorption capacity was calculated.

#### 3.2.1 Effect of bassorin amount

To select an appropriate amount of sorbent affecting the removal of MB a series of tests were realized with different gel dose from 1 to 13 g.L<sup>-1</sup> in 100 mL of volume solution with 10 mg. L<sup>-1</sup> dye concentration. The experimental results are shown in **Figure 5**. The sorption removal of hydrogel bassorin decreased from 57% to 84.3 % as hydrogel amount increased from 1 to 3g. The increase in adsorption capacity for low adsorbent masses could be explained by the availability of free adsorption hydrogel sites. The increase in the mass of the Bassorin hydrogel leads to the formation of agglomerations of hydrogel particles which limit its adsorption capacity. So, the mass of 3 g is the optimum sorbent dose for the MB adsorption reaction.



**Figure 5:** Evolution of adsorption percentage as a function of the Bassorin Mass

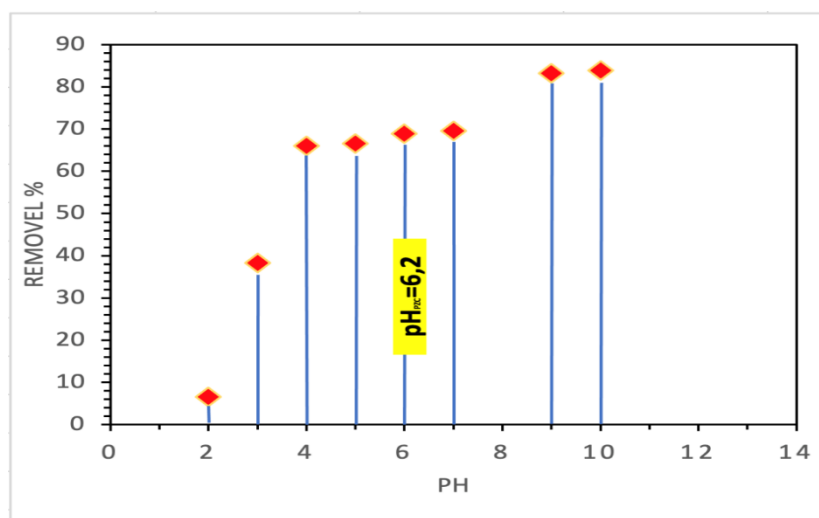
### 3.2.2 effect of PH

The initial pH of the solution plays an important role in the adsorption process, it influences the surface charge of adsorbent and adsorbate samples. Gum tragacanth solutions are usually acidic in the pH range of (5-6). The maximum initial viscosity is at PH=9, but usually exhibited maximum stability near pH= 5. determined an optimum pH of 9 for the adsorption of MB on the bio-adsorbent (Bulut *et al*, 2006; Pavan *et al*, 2008; Ncibi *et al*, 2007; Mourid *et al*, 2018).

In our study, the effect of pH on the adsorption capacity of BM has been studied over a wide pH range (2 to 10) with an initial concentration of 10 mg. L<sup>-1</sup>, an adsorbent mass of 5 g and at room temperature. The results summarized in the Table 2 and the Figure 6 show an increase of adsorption capacity of MB on the bassorin hydrogel with the increasing pH of the MB solution to stabilize at pH = 9. This result is in agreement with the value of the pH<sub>pzc</sub> = 6.2 and the pH = 9 is the optimum for the adsorption of methylene blue on Bassorin hydrogel. This is explained by the fact that in a basic medium, the surface of the Bassorin hydrogel is negatively charged, hence there is an attractive interaction with the organic sites of the MB adsorbate.

**Table 2:** Effect of the initial PH of MB solution percentage adsorption and capacity adsorption on hydrogel bassorin

PH (initial)	Abs	[BM]	%R	Q (mg.g <sup>-1</sup> )
2	1.484	9.344	6.550	0.021
3	1.01	6.176	38.21	0.127
4	0.593	3.389	66.11	0.220
5	0.586	3.342	66.58	0.221
6	0.551	3.108	68.92	0.229
7	0.541	3.041	69.59	0.231
9	0.322	1.577	84.23	0.280
10	0.321	1.570	84.30	0.281

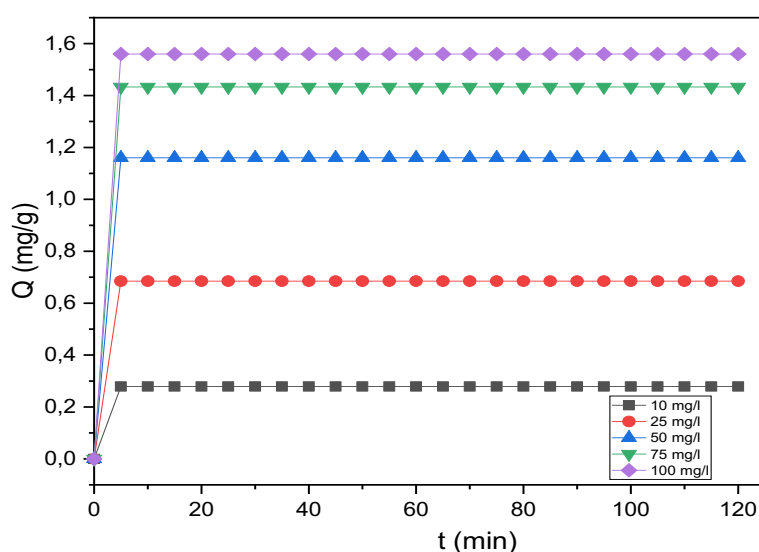


**Figure 6:** Evolution of adsorption percentage as a function of pH



### 3.2.3 effect of initial dye concentration

The effect of the concentration of MB on the adsorption capacity of the hydrogel was determined using concentrations of MB from 10 to 100 mg. L<sup>-1</sup>, an optimal hydrogel mass of 3g and a stirring time was set at 180 minutes. The result reported in **Figure 7** shows a gradual increase in adsorption capacity from 0.279 mg. g<sup>-1</sup> in the presence of 10 mg. L<sup>-1</sup> of adsorbate to 1.433 mg. g<sup>-1</sup> when the concentration of adsorbate becomes 75 mg. L<sup>-1</sup>. The adsorption capacity was stabilizing at 1.57 mg. L<sup>-1</sup>. The increase in the concentration of adsorbate MB is accompanied by the increase in adsorption capacity and the capacity was higher with concentrations above 100mg.L<sup>-1</sup> of hydrogel. This result can be explained by the diffusion of the aromatic cations of the BM dye on the surface of the hydrogel. This diffusion is accelerated by the increase in the concentration of adsorbate. The observed palliation represents the saturation step of the available adsorption sites at the surface by the fixation of MB cations (Bulut *et al.*, 2006).



**Figure 7:** Evolution of the adsorption capacity as a function of the MB concentration

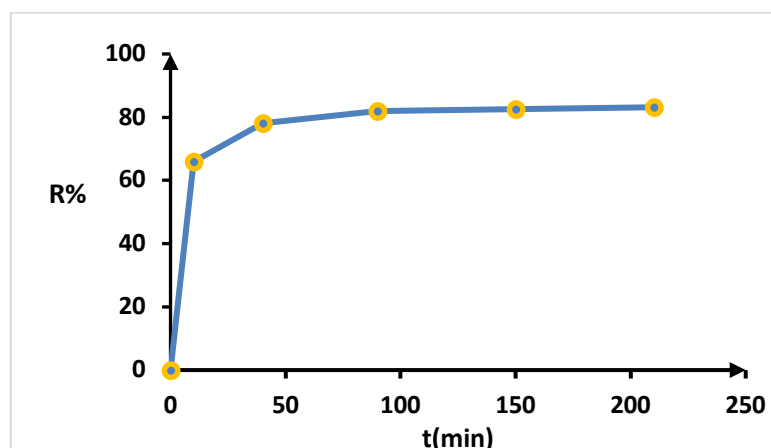
### 3.2.4. Effect of contact time

The effect of contact time on the sorption of MB was investigate at intervals times from 10 to 200 minutes. The result **Figure 8** indicates that the sorption of dye increases during the first 4 minutes reaching a value of 68% and sorption remains constant with a value of 84.3 %. The rapid increase in adsorption capacity from the first hydrogel-MB contact was explained by the availability of adsorption sites on the surface of the hydrogel. The observed palliation was due to the saturation of the adsorption sites.

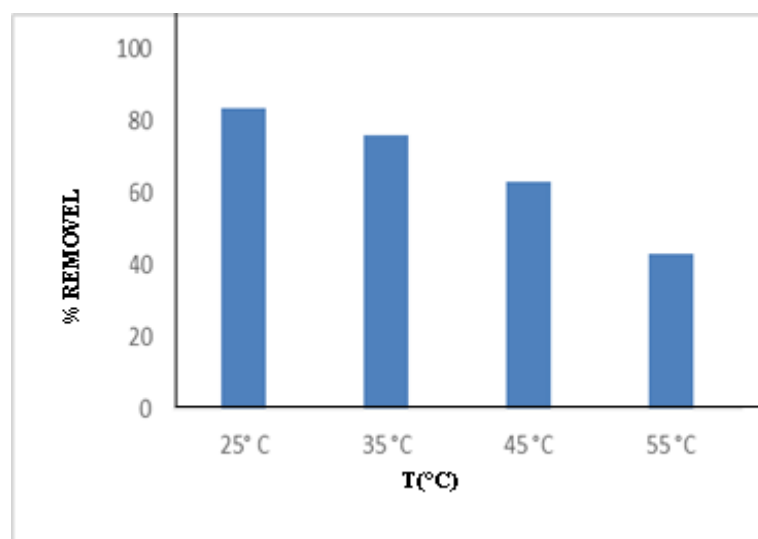
### 3.2.5. Effect of temperature

The effect of temperature on the sorption was evaluated at 25, 35, 45 and 55 °C, applying the same protocol performed to analyze the effect of mass. The tests are carried out with 100 ml of an aqueous solution of MB **Figure 9** shown that the highest percentage of adsorption (84.3%) is at an ambient temperature of 25°C. Beyond this temperature the percentage of adsorption decreases gradually revealing that the adsorption of MB on bassorin hydrogel is exothermic in nature, and that low temperature promotes favorable adsorption. We can conclude that the adsorption study showed that

pH of the medium, initial dye concentration and volume positively affected the removal efficiency of MB dye as compared to time of contact and temperature of the solution



**Figure 8:** Evolution of adsorption percentage as a function of time



**Figure 9:** Evolution of adsorption percentage as a function of temperature

### 3.3 Kinetic study

The study of the kinetic parameters of the surface reaction of pseudo-order 1 and pseudo-order 2 has been carried out. The results show that the adsorption capacity calculated with the first-order kinetic model is much lower than that obtained experimentally with a correlation coefficient of 0.935. The correlation coefficient obtained from the second-order kinetic model is equal to 0.999, with values comparable to the experimental values. This result indicates that the second-order kinetic model is more appropriate for describing MB adsorption on Bassorin hydrogel and the adsorption is governed by the surface reaction characterized by the fixation of MB aromatic sites on the hydrogel surface.

**Table 1:** Pseudo-order 1 and pseudo-order 2 parameters for MB adsorption on bassorin hydrogel.

Pseudo-first-order model			Pseudo-second-order model			
R2	K1 (min <sup>-1</sup> )	Qe.cal (mg.g <sup>-1</sup> )	R2	K2(g.mg <sup>-1</sup> .min <sup>-1</sup> )	Qe.cal (mg.g <sup>-1</sup> )	Qe.exp (mg.g <sup>-1</sup> )
0.935	0.112	1.006	0.99	0.121	0.27	0.279

### 3.4. Adsorption isotherm

The two parameter sorption isotherms Langmuir and Freundlich have been used to compare the experimental equilibrium adsorption data by linear and non-linearized form of these isotherm models. The calculated Langmuir and Freundlich parameters recorded in the [Table 4](#) and [Figure 10](#) show the linearization curves. Correlation coefficients indicate that hydrogel-MB adsorption can be described by Langmuir and Freundlich models. From results it can be seen that linearized form of Freundlich isotherm have lower ( $R^2 = 0.885$ ) value. The correlation coefficient ( $R^2 = 0.99$ ) and the max capacity ( $Q_{\max}$ ) from the Langmuir isotherm and its value is compatible with that determined experimentally. This model is best suited to describe the adsorption of MB on the surface of the hydrogel. [Figure 10](#), shows the variation of  $\log q_e$  as a function of  $\log C_e$ .

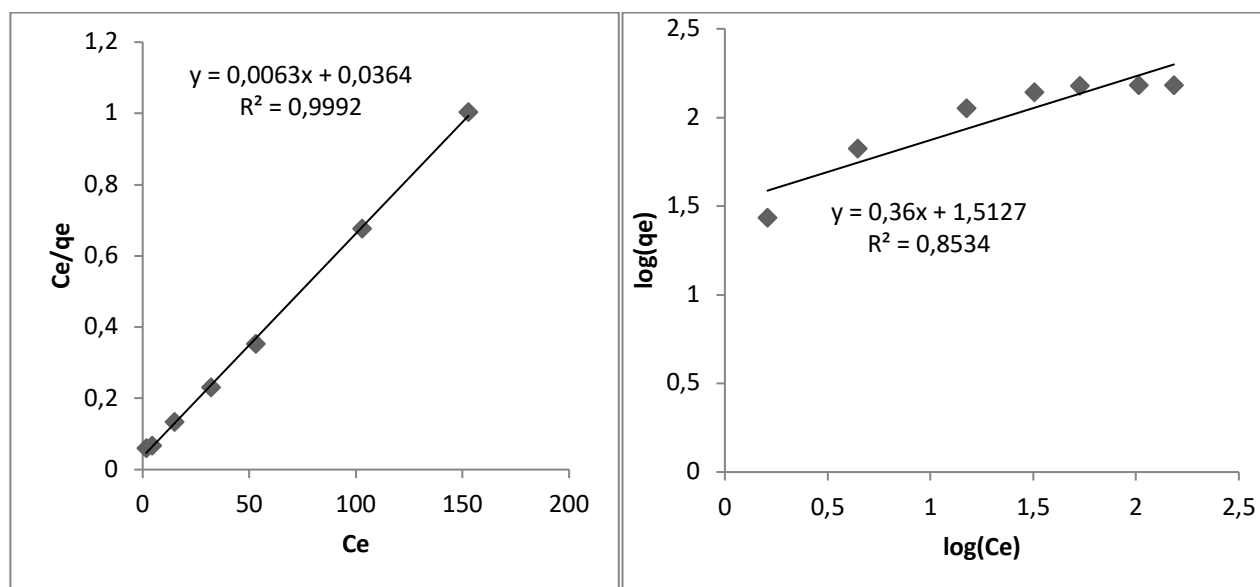
The coefficient  $\frac{1}{n}$  shall indicate the validity of the adsorption A value of  $\frac{1}{n}$  between 0 and 1 indicates favorable adsorption ([Tcheka et al., 2021](#)). of the adsorbent-adsorbate system

When the value of  $\frac{1}{n}$  is equal to 1, the adsorption is linear

if it is greater than 1, the adsorption is of physical nature;

if it is less than 1, the chemical adsorption is favorable.

The value of  $\frac{1}{n}$  equal to 0.59 [Table 4](#) indicate a favorable adsorption of MB on bassorin hydrogel.



**Figure 10:** Langmuir and Freundlich isotherms for MB adsorption on bassorin hydrogel

**Table 4:** Langmuir and Freundlich parameters for MB adsorption on Bassorin hydrogel

Langmuir Model			Freundlich Model		
R <sup>2</sup>	KL (L.mg <sup>-1</sup> )	Q <sub>max</sub> (mg.)	R <sup>2</sup>	K <sub>f</sub>	1/n
0.999	0.14307	1.75	0.885	.08816	.059

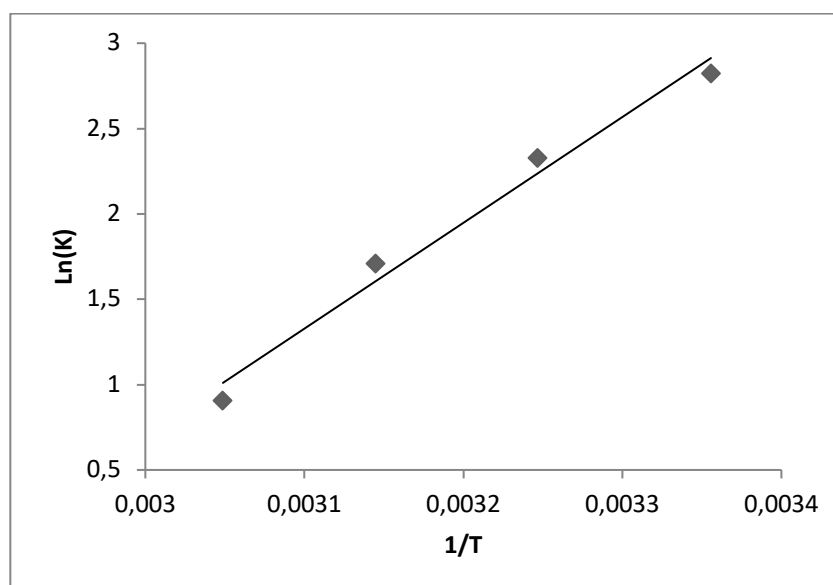
### 3.5. Thermodynamic study

The thermodynamic parameters like entropy change ( $\Delta S_0$ ), enthalpy change ( $\Delta H_0$ ) and Gibbs free energy change ( $\Delta G_0$ ) were calculated to investigate the spontaneity, feasibility of sorption process as function of temperature. The thermodynamic parameters data are shown in [Table 5](#). The negative

values of  $\Delta G^\circ$  (-5.9284 kJ.mol<sup>-1</sup>, -5.9444 kJ. mol<sup>-1</sup>, -5.9605 kJ.mol<sup>-1</sup> and -5.9766 KJ.mol<sup>-1</sup>) indicates that the sorption of MB by Bassorin hydrogel is a spontaneous and favorable process in the temperature range (298 to 328 K) which is in agreement with the literature (Pavan *et al.*, 2008). The equilibrium constant  $K_d$  decreases as the temperature incrisies. The adsorption of MB on hydrogel of exothermic nature is more favorable at room temperature (298 K). The negative value of  $\Delta H^\circ$  (-5.4487 KJ.mol<sup>-1</sup>) confirms the exothermic nature of sorption process. The negative value of  $\Delta G^\circ$  at optimized temperature confirms the spontaneous nature of sorption process. The decrease in order at the hydrogel/solution interface during the dye sorption process was suggested by the positif value of entropy change ( $\Delta S^\circ$  =1.6074 kJ. mol<sup>-1</sup>).

**Table 5:** Thermodynamic parameters of MB adsorption on Bassorin hydrogel

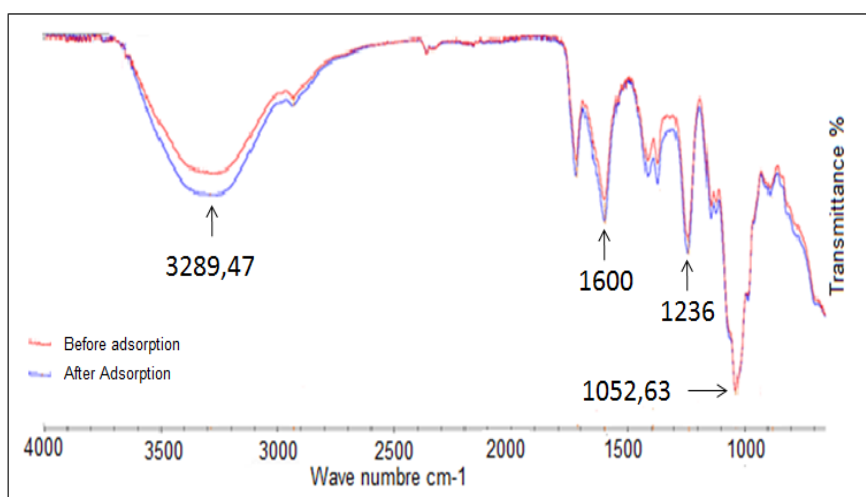
T(K)	$\Delta H^\circ$ (kJ / mol)	$\Delta S^\circ$ (J / mol/ K)	$\Delta G^\circ$ (kJ / mol)
298	-	-	-5.9284
308	-	-	-5.9444
318	-5.4487	1.6074	-5.9665
328			-5.976



**Figure 11:** Thermodynamic parameters of MB adsorption on bassorin hydrogel.

### 3.6 Infrared characterization of Bassorin after dye adsorption

The infrared spectra (400-4000 cm<sup>-1</sup>) for functional groups of the Bassorin powder before and after adsorption of the dye are presented in Figure 12. The result shows the characteristic bands of the bio-sorbent with a slight shift of the peaks corresponding to the variation in the energy of the functional groups of the Bassorin. this is due to the electrostatic interactions between the functional groups of the MB and the Bassorin. The nature of the physical interaction remains in agreement with the results of the thermodynamic study.



**Figure 12:** Infrared spectrum of bassorin in the presence and absence of methylene blue

We can conclude that today, there is a need to adopt eco-friendly highly effective and low-cost adsorbent for the remediation of pollutant of water. Materials with natural origins are commonly used for the removal of heavy metal ions and dyes from different wastewaters. The extracted (COOH-) rich polysaccharide are a plant-derived substances that constitute a group of hydrogel products as the basis for obtaining physical cross-linked and water-insoluble ionic network capable of holding large amounts of water in their three-dimensional networks. The bassorin hydrogel has a potential, to be used as an adsorbent for wastewater treatment and purification processes to eliminate the emergent contaminants.

### 3. Conclusion

This work focused on the removal of a cationic methylene blue dye from aqueous solution by adsorption on to Bassorin hydrogel. The bio-sorbent was extracted by simple and low-cost method from tragacanth gum and used without a crosslinking chemical agent. The experimental results show that the adsorbent possesses an important swelling property and high adsorption capacity. The pH of the medium, initial dye concentration and volume positively affected the removal efficiency of MB dye as compared to time of contact and temperature of the solution. The maximum sorption capacity was 84.3% obtained at higher pH and the sorption is better described by the Langmuir model which assumes monolayer adsorption. Second-order model 2 better describes the adsorption of MB on the hydrogel. The sorption mechanism is therefore directed by the surface reaction. Bassorin hydrogel extracted from natural plants by simple méthode can represent a class of materials with potential properties in environmental field.

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(2023) ; <https://revues.imist.ma/index.php/morjchem/index>