# Synthesis of Sodium Alginate-Derived Carbon Aerogel for Adsorptive Removal of Methylene Blue

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**ABSTRACT** *In this study, carbon aerogel was prepared from sodium alginate via the sol-gel technique. The morphological study clearly revealed that the synthesized aerogel possessed a highly porous structure with a specific surface area of 470 $m^2/g$. The applicability of the aerogel as an adsorbent was examined in methylene blue removal. Adsorption isotherms, kinetics, and thermodynamic studies of Removal of MB from aqueous solutions were conducted in a batch system. The effect of pH and adsorbent dosage on the adsorption of MB was investigated. The equilibrium data were best fitted to Langmuir model with a maximum adsorption capacity of 70.42 mg/g. The adsorption kinetics of MB followed the pseudo-first-order models. Thermodynamic analysis of the results indicated that adsorption is a physical process and is in agreement with data obtained from the Dubinin−Radushkevich isotherm model. The removal of the MB process was spontaneous and endothermic.*

**KEYWORDS:** *Carbonaceous aerogel; Methylene blue; Adsorption model; Kinetics.*

## INTRODUCTION

Dyes are resistant molecules, that are hardly biodegradable [1-5]. By increasing the excessive use of dyes, pollution by dyes wastewater is becoming increasingly alarming which causes eye burns, methemoglobinemia, cyanosis, convulsions, tachycardia, dyspnea and irritation to the skin [1, 6, 7].

Methylene Blue (MB) ($(CH_3)_2$ N ($C_6H_3$) $NS^+(C_6H_3)N(CH_3)_2Cl^-$), is one of the monovalent cationic dyes with S and N linkage, has wide application in paper coloring, plastics and printing, temporary hair colorant, food processing, dying cottons and wools [1, 4, 6]. It appears as a solid, odorless, dark-green powder that yields a blue solution when dissolved in water at room temperature. This dye is stable and incompatible with bases, reducing agents, and strong oxidizing agents. During a chemical or biological reaction pathway,

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these dye compounds not only deplete the dissolved oxygen in water bodies but also release some toxic compounds to endanger aquatic life. The evacuation of MB from the textile industry to the receiving waters leads to a decrease in the influence of sunlight, emergence of interference in the ecology of the receiving waters, and by decreasing the photosynthesis rate of aquatic plants and algae in environments Blue, causing damage to the environment. Color removal from effluents is a major environmental problem, because of difficulty of treating such streams by conventional physicochemical and biological treatment methods. Heretofore various biological, physical and chemical methods have been used to remediate dye contaminated wastewater such as membrane filtration, adsorption, coagulation/flocculation, ion exchange, reverse osmosis, chemical oxidation and photocatalytic degradation [8-11]. The biological methods are not effective due to structure complexity, artificial origin, low biodegradability and xenobiotic nature of dyes. Most of the other methods have some restrictions like high cost, high energy supplies and production of hazardous and toxic residues [6]. Among these mentioned methods, adsorption is one of the most effective and favorable techniques for water and waste water treatment due to economic feasibility, easy operation, possible reusability of the adsorbent and nonexistence of secondary harmful substance production [12-14].

There are a lot of adsorbents such as carbon nanostructure, activated carbon, natural materials, mineral materials, biosorbents, agricultural and industrial wastes which are capable for water remediation and methylene blue removal [4, 15-16]. Activated carbon due to its vast surface area, porous structure, large adsorption capacity, adjustable surface chemistry and activity [3, 17], is one of the most effective adsorbents, which can be used for other various applications like oil refining, petro chemistry, municipal and industrial wastewater treatment, organic synthesis, catalyst…etc. [6]. However, the activated carbon has high adsorption capacity and the fast removal rate because of their higher specific surface area and surface reactivity, but it is prohibitively expensive.

*A. Rodríguez et al.* [18] investigated adsorption of dyes on carbon nanomaterials from aqueous solutions using MultiWall Carbon NanoTubes (MWCNTs) and Crbon NanoFibers (CNFs) as adsorbents to remove MB and orange II. They found that the adsorption capacity of CNFs was higher than for MWCNTs. Also, they investigated significant role of the pH of the solution in influencing the capacity of both adsorbents within 2 dyes. Optimum adsorption of MB and Orange II on MWCNTs was 7.0 and 3.0, respectively, and on CNF was 5.0 and 9.0, respectively. It was found that the adsorption of MB and OII increase in the range of 60-70 mg/g with the decrease of temperature in the range of 30–65 °C. *N.S. Tabrizi et al.* [19] investigated the Removal of MB ability of the carbon nanotubes-based aerogels. Their results showed that the MB adsorption capacity of the adsorbent at ambient temperature was 62.5 mg/g, which is in accordance with the above mentioned study. Also, other adsorbents including Ca-alginate/activated carbon beads and Ca-alginate beads have been reported by [20].

In this investigation we have selected carbon aerogel with high porosity and specific surface, prepared from sodium alginate for removal of MB dye.

Sodium alginate ($C_6H_9NaO_7$) is a natural polysaccharide product (molecular weight =216.1 $gmol^{-1}$) extracted from brown seaweed. It is soluble in cold and hot water with strong agitation, forming a viscous solution and can thicken and bind to divalent cations [21, 22]. Alginate is polysaccharides, which are widely adopted in several fields (pharmacy, cosmetics, medicine, agriculture and biotechnology). Due to their noncytotoxicity, stability, availability, renewability and well-studied gelation chemistry, they are attractive candidates for aerogel production. Materials based on pure alginate often have high hydrophilicity properties.

The objective of this work was to apply sodium alginate as a precursor with biocompatibility, biodegradability, and nontoxicity properties. Our mesoporose carbon aerogel can be utilized as an inexpensive, highly surface rea and highly effective adsorbent for the removal of MB from an aqueous solution.

## EXPERIMENTAL SECTION

### *Materials and methods*

Methylene blue ($C_{16}H_{18}N_3SCl$), hydrochloric acid (HCl, analytically pure) and ethanol ($C_2H_6O$, analytically pure) were purchased from Merck. Sodium alginate

($NaC_6H_7O_6$) with purity 99.8% was supplied from Aldrich and calcium chloride was purchased from BDH.

***Adsorbent preparation***

1 g of Sodium alginate was slowly added to 100 mL DI water under stirring (700 rpm) at 50°C, to obtain a homogeneous mixture. The mixture was kept at 50°C under stirring for an additional time of 30 min and was added drop-wise into an aqueous (500 mL) of $CaCl_2$ (3 wt.%) at room temperature without stirring [23]. The resulted spherical gels were moved to ethanol for 2 days. The gels were then transferred in to freeze dryer for 48 h and then carbonized by calcination up to 600°C under argon flow gas for 3 hours. The resulted aerogels were treated with 0.2M HCl solution for 3 hours at room temperature in order to remove the remaining sodium and calcium species from the material and then were washed with DI water several times until pH of the washing water showed no change [19]. The product of each stage is shown in Fig. 1.

***Characterization***

Morphology of the synthesized aerogels was studied by a Stereo Scan S360 scanning electron microscope (SEM, MIRA3 TESCAN) operated at an accelerating voltage of 100KV. The nitrogen adsorption and desorption isotherms were measured at 77 K (Micromeritics Gimini III 2375 instrument). The specific surface area was calculated by Brunauer–Emmett– Teller (BET) method. Elemental analysis and chemical characterization of the aerogels were conducted by Energy-Dispersive X-ray Spectroscopy (EDS). The pH was measured by a Metrohm 827 pH lab meter. The concentration of dye solutions was measured using T80+UV-Vis PG Instruments spectrophotometer. FT-IR spectra in KBr pellets were recorded using a PerkinElmer.

***Dye removal experimental***

Methylene blue was applied as a model pollutant. For Kinetic studies of the adsorption, 200 mL of 10 mg/L Methylene blue solution was prepared. Then 42 mg adsorbent was placed in the solution and samples were taken from the solution at certain time intervals. The removal percentage of methylene blue was calculated using the following relation [19]:

$$\%\, Removal = 100 \times \frac{A^{\circ} - A}{A^{\circ}} \quad (1)$$

Where $A$ is absorbance at $\lambda_{max}$ (665 nm for MB) at time t, and $A^o$ is the absorbance of the initial MB solution.

In order to determine the adsorption isotherm, 6 solutions with a volume of 25 mL and concentrations in the range of 10-60 mg/L were prepared. Then 10 mg of adsorbent was added to each solution and the equilibrium concentrations were measured.

For studying the effect of initial pH on MB uptake, solutions with volume of 25 mL and concentration of 10 mg/L were prepared. The solutions pH was adjusted with addition of 0.1M HCl or 0.1M NaOH solutions. 5 mg absorbent was added to each solution. After reaching the equilibrium, concentration of each solution was determined by spectrophotometer.

In order to determine the effect of adsorbent dosage, 5 solutions with a concentration of 20 mg/L and volumes of 25 mL were prepared. Then 4, 8, 12, 16, 20 mg of adsorbent was added to the solutions. Concentration of each solution was then determined by spectrophotometer.

***Thermodynamic analysis***

6 solutions with a volume of 25 mL and concentrations of 10-60 mg/L were prepared. The amount of 10 mg absorbent was added to each solution. Prepared samples were placed at 20°C to reach equilibrium. The same steps were repeated at 30°C and 40°C. After reaching equilibrium, the final concentration of MB in each solution was determined using the spectrophotometer.

## RESULTS AND DISCUSSION

***Characterization of Adsorbent***

Scanning electron microscopy images obtained from the carbon aerogel can be seen in Fig. 2. The SEM images were taken at different magnifications, showing high porosity and many cavities in the morphology with wide pore size distribution. The porous structure of the carbon aerogel provides sufficient space for the storage of absorbed dye solvents, so that its absorption ability is greatly enhanced. As shown in the EDS element mapping (Fig. 3), the atomic content of C and O is 88.29% and 10.11%, respectively. The presence of the carbon element signal demonstrated that the carbonization treatment was done, which is in good agreement with XRD and FT-IR results can be found in the supplementary data.

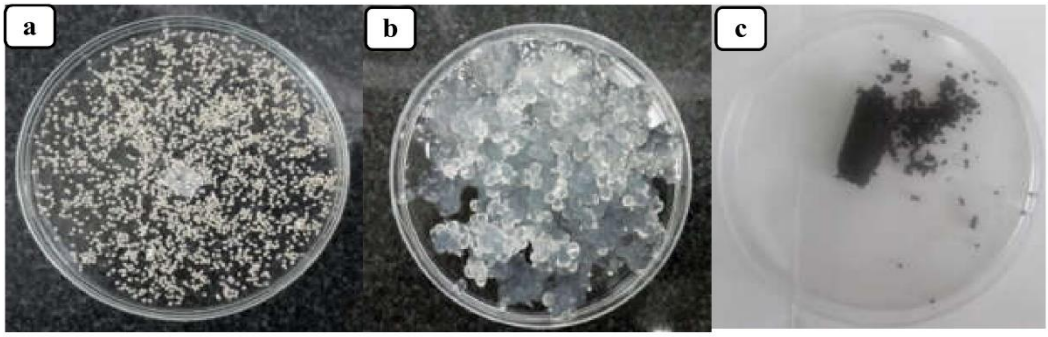


*Fig. 1: Product of each stage: a) after gelation b) after freeze dryer c) after carbonization.*

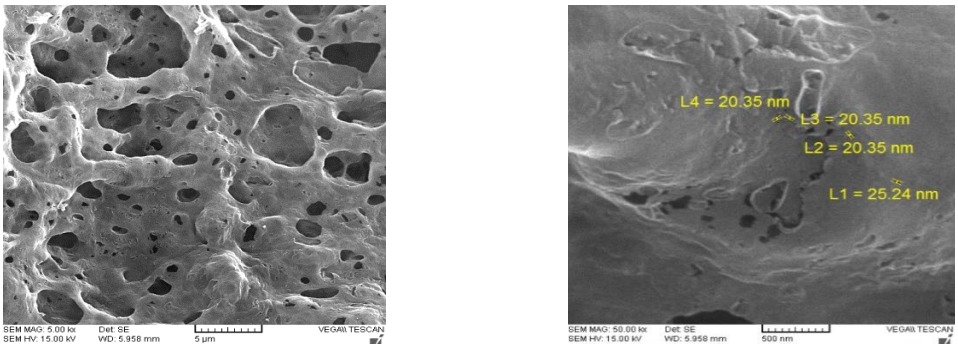


*Fig. 2: SEM images of synthesized carbon aerogel.*

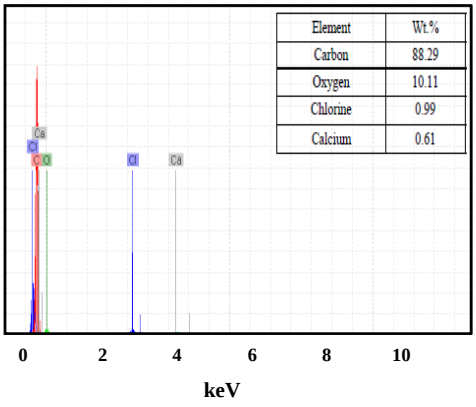


*Fig. 3: EDS spectrum of the carbon aerogel*

Specific surface area and pore size distributions are the effective parameters in adsorption capacity. Nitrogen adsorption-desorption isotherms (77 K) of the carbon aerogel are shown in Fig. 4. According to the IUPAC classification, this isotherm is similar to type (IV) and indicates multilayer absorption at the surface of mesoporous materials with irregular cavities. It is noted that the mesopores are often the major contributor to the adsorption capacity for adsorbate molecules small enough to penetrate. Specific surface area of the sample, which was obtained from BET model, is about 470 $m^2/g$, this value is 2 times more than surface area of carbon nanotube (surface area of the MWCNTs ~ 118.9 $m^2/g$) [24].

The average size of pores and pore volume measured by the BJH method, as well as density of the aerogel can be found in Table 1.

### *Adsorption Kinetics*

Kinetics of adsorption has important role in the adsorption efficiency. According to Fig. 5, in the initial hours of the adsorption process, the concentration of MB is significantly reduced. Some of the effective parameters in the adsorption process are specific surface area and pore volume of the adsorbent [25, 26]. Electrostatic interactions, hydrogen bonding, and the Van der Waals forces are likely the major mechanisms of the adsorption of MB molecules on the surface [27]. The dimensions of MB molecule allow diffusion of MB molecules into the structure of the aerogel and the cavities [28].

***Table 1: Structural properties of the Carbon aerogel.***

| $d_{av.}$ (nm) | $S_{BET}$ ($m^2/g$) | $V_T$ ($cm^3/g$) | Density±5% ($g/cm^3$) |
|---|---|---|---|
| 10.32 | 470 | 1.2 | 0.05 |

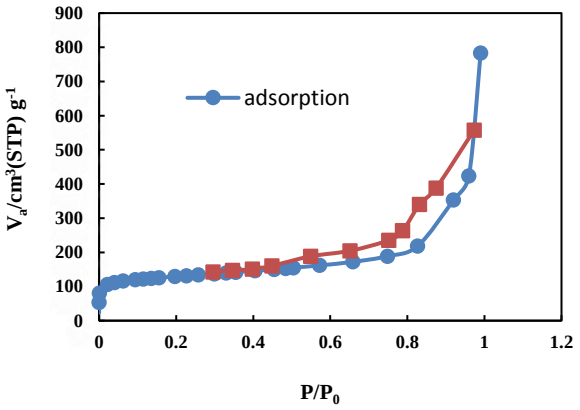


***Fig. 4: Nitrogen adsorption-desorption isotherms of the carbon aerogel.***

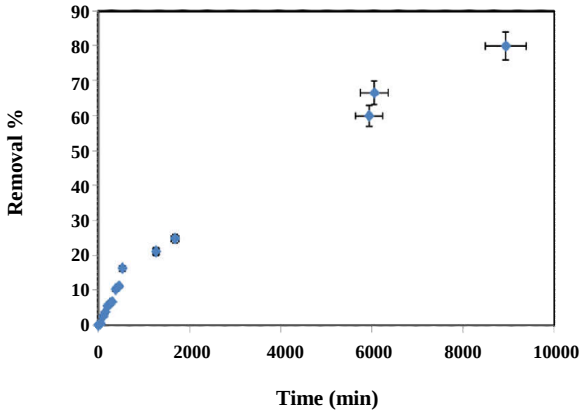


***Fig. 5: Removal of the MB initial solution vs time.***

researchers. One of the simple kinetics models is the pseudo-first order kinetics model which is expressed by [25, 26]:

$$\boldsymbol{log(q_e - q_t) = log\, q_e - \frac{k_1 t}{2.303}} \quad (2)$$

$$q_e = \left(\frac{C_0 - C_e}{m}\right) V \quad (3)$$

Where $q_e$ is the amount of dye adsorbed at equilibrium, mg/g; $q_t$ is the amount of dye adsorbed at time t, mg/g; $k_1$ is the equilibrium rate constant of pseudo-first order sorption, $min^{-1}$ and $C_e$ is the equilibrium adsorbate concentrations in solution mg/L.

Second-order kinetic model is expressed by [24]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

Whereas k is the equilibrium rate constant of pseudo-second order sorption, g $mg^{-1}min^{-1}$.

The intraparticle diffusion rate constant ($k_i$), mg/g $min^{0.5}$ is calculated by following equation [26]:

$$q_t = k_i t^{\frac{1}{2}} \quad (5)$$

Constants calculated from pseudo-first order, pseudo-second order and intraparticle diffusion kinetic models have been illustrated in Table 2.

### *Effect of initial pH and Adsorbent dosage*

The effect of pH parameter on the adsorption of methylene blue by the aerogel is investigated. As seen in the Fig. 6, with increasing of pH, concentration of methylene blue in solution was decreased and bleaching was increased. It can be due to increasing electrostatic interaction between negative surface of the adsorbent and the cationic dye (MB) with increasing pH of the solution. In addition, for small quantities of pH, concentration of protons is high, so there is more competition to achieve the surface of absorbent and therefore bleaching is lower. On the other hand, the number of positively charged sites decreases and the number of negatively charged sites increases as the pH increases. This can be ascribed to the hydrogen bond interaction between cationic dyes and aerogel, which is stronger than that of an electrostatic interaction Therefore, the higher adsorption capacity of MB onto carbon aerogel at higher pH can be explained.

Effect of adsorbent dosage on the removal of MB is shown in Fig. 7. It can be seen that by increasing the amount of adsorbent, the concentration of methylene blue in solution is decreased. By increasing the amount of absorbent in a fixed concentration of solution, more active sites for absorption are provided, thus absorption of methylene blue is increased.

### *Adsorption Isotherm*

It is apparent that determination coefficient of first order and second order models are higher and close to

***Table 2: Parameters of kinetic models for MB adsorption by the carbon aerogel.***

| kinetic models | constants | $q_e$ ($mgg^{-1}$) | $R^2$ |
|---|---|---|---|
| Pseudo-first order | $K_1$ ($min^{-1}$) 0.00023 | 24.02 | 0.975 |
| Pseudo-second order | $K_2$ (g/mg.min) 0.0000312 | 23.98 | 0.971 |
| Intraparticle diffusion | $K_i$($mg/g.min^{0/5}$) 0.3473 | - | 0.938 |

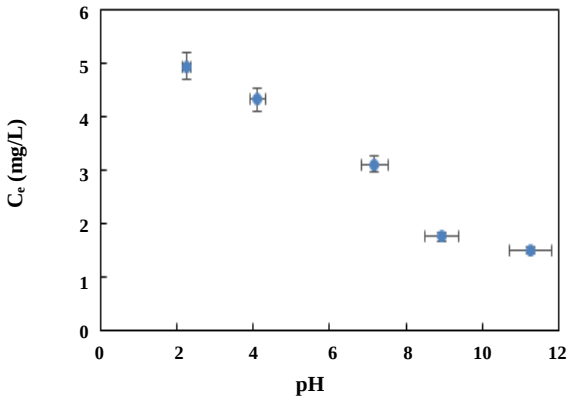


***Fig. 6: Initial pH effect on the adsorption of methylene blue by the carbon aerogel.***

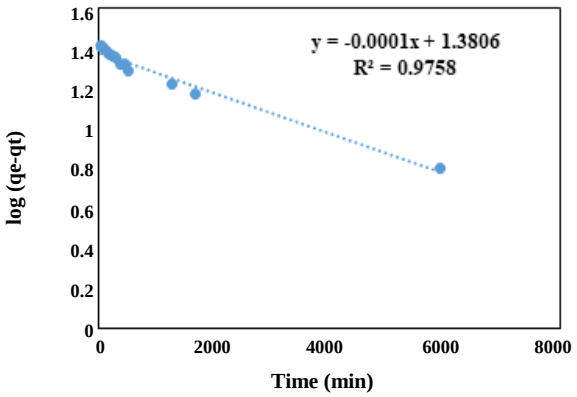


***Fig. 8: The plot of pseudo-first order model for adsorption of methylene blue by the carbon aerogel.***

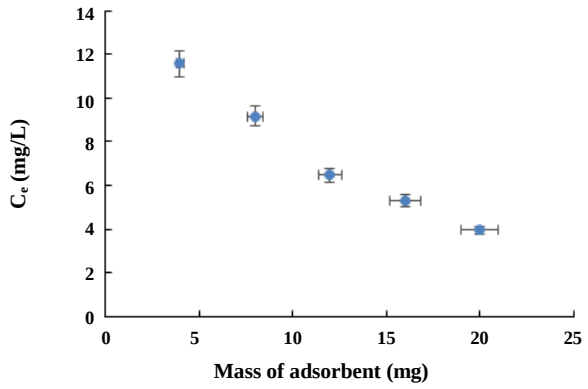


***Fig. 7: Effect of adsorbent dosage on the absorption of methylene blue by the carbon aerogel.***

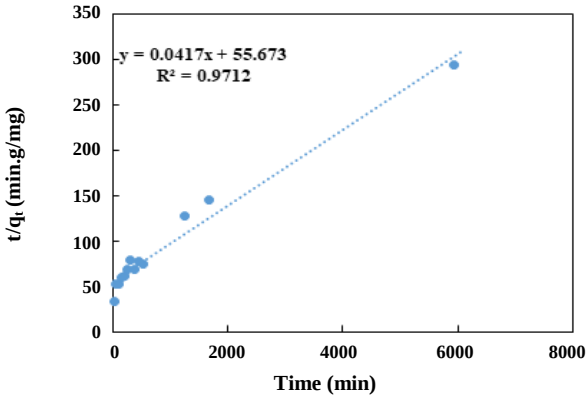


***Fig. 9: The plot of pseudo-second order model for adsorption of methylene blue by the carbon aerogel.***

each other. Hence, calculated $q_e$, the amount of dye adsorbed at equilibrium, close to theory show that MB adsorption on carbon aerogel can be described by pseudo-first-order model. Plots of pseudo-first and second order models are given in Fig. 8 and Fig. 9.

Three consecutive mass transport steps are associated with the adsorption from solution by porous adsorbent. First, film diffusion, followed by solute movement from particle surface into interior site by pore diffusion and finally the adsorbent is absorbed into the active sites at the interior of the adsorbed particle. This process takes relatively long contact time [29].

The equilibrium relationship between the amounts of adsorbates per unit mass of adsorbent and the equilibrium concentration in the liquid phase, at constant temperature, is called adsorption isotherm. Adsorption isotherms are one of the most important parameters to understand the absorption mechanism [30].

Langmuir model shows monolayer adsorption on the homogeneous surface without interaction between

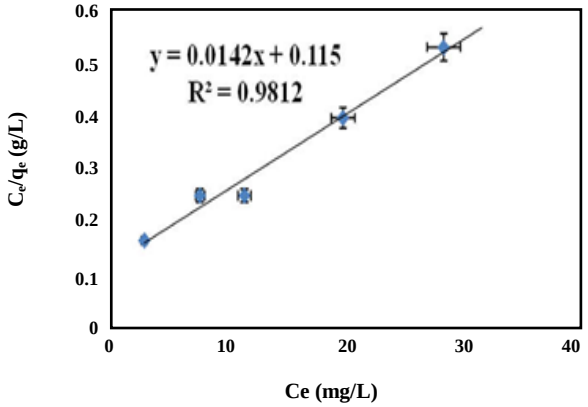


*Fig. 10: Langmuir isotherm chart for adsorption of methylene blue by the carbon aerogel.*

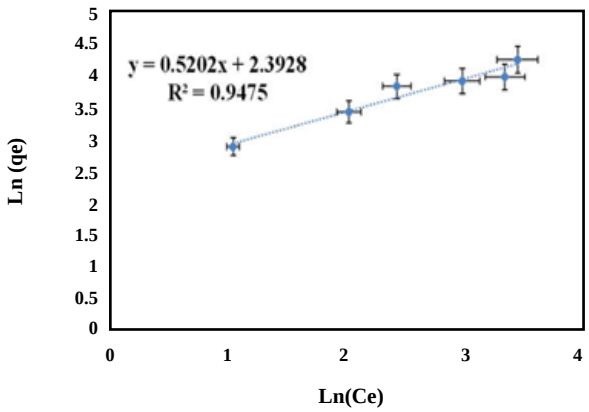


*Fig. 11: Freundlich isotherm chart for adsorption of methylene blue by the carbon aerogel.*

molecules. Linear form of the Langmuir model is as follows [31]:

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

Where $q_e$ is equilibrium concentration of MB on adsorbent, mg/g; $C_e$ is equilibrium concentration of MB in solution, mg/L; $K_L$ is Langmuir constant, L/g; $a_L$ is Langmuir constant too, L/mg.

Freundlich isotherm model is an empirical model to explain multi-layer adsorption with heterogeneous active sites. Linear form of the Freundlich model is as follows [32]:

$$\mathbf{\ln q_e = \ln K_F + \frac{1}{n} \ln C_e} \quad (7)$$

In this equation, $K_F$ is isotherm constant linked to the absorption capacity, L/g; *1/n* is the absorption intensity which changes with non-uniformity of the materials. 1/n is related to the heterogeneity of absorption surface. Values of 0.1<1/n<1 represent the favorable absorption of adsorbates on the adsorbent [33].

Langmuir and Freundlich adsorption isotherm charts and table of coefficients are given in Fig. 10, Fig. 11 and Table 3, respectively.

The results indicate compliance with the Langmuir isotherm with determination coefficient about 0.98. Therefore, the Langmuir model suggested that pollutant removal from the aqueous phase occurred on homogeneous surfaces by monolayer sorption without interactions between adsorbed molecules.

To estimate the energy of adsorption and indication of chemical or physical adsorption, the linear Dubinin−Radushkevich (D-R) isotherm model was used:

$$\ln q_e = \ln q_m - K'\varepsilon^2 \quad (8)$$

where ε, the Polanyi potential, is equal to :

$$\varepsilon = RT ln(1 + {}^{1}/_{C_e}) \quad (9)$$

where $q_m$ signifies the monolayer saturation capacity (L/g) and K′ the constant of adsorption energy, which gives the mean free energy (E) of adsorption per molecule of adsorbate, when it is transferred to the surface of the solid from the solution and can be calculated from the following relationship:

$$E = {}^{1}/_{(2K')^{1/2}} \quad (10)$$

Based on our data, we have obtained free energy of adsorption is about 9.926 kJ/mol. Due to value of E in the range of 8−16 kJ/mol, indicates the MB are favorably physisorbed on to the adsorbent surface [34].

The maximum adsorption capacity was comparable to the adsorption capacities of some other adsorbents for MB (Table 4). A comparative study shows that the carbon aerogel (our work) has high adsorption capacity as well as other desirable properties. So the carbon aerogel with facile separation from the solutions is an efficient adsorbent with high performance for methylene blue removal from aqueous solutions.

***Thermodynamic Analysis***

The thermodynamic parameters, including changes in standard enthalpy (ΔHº), standard entropy (ΔSº) and standard Gibbs free energy (ΔGº) are calculated using the following equation:

***Table 3: Coefficients of Langmuir and Freundlich isotherms for MB adsorption by the carbon aerogel.***

| Adsorption isotherms | constants | values |
|---|---|---|
| Langmuir model | $q_{max} = [K_L/a_L]$ (mg/g)<br>$a_L$ (L/mg)<br>$K_L$ (L/g)<br>$R^2$ | 70.42<br>0.123<br>8.66<br>0.981 |
| Freundlich model | $K_F$ ((mg/g) (L/mg) $^{1/n}$)<br>1/n<br>$R^2$ | 10.94<br>0.5202<br>0.947 |

***Table 4: Methylene blue adsorption capacities of different adsorbents given in the literature.***

| Adsorbent | Adsorption capacity (mg/g) | References |
|---|---|---|
| Glass fibers | 2.24 | [35] |
| Fly ash | 5.57 | [36] |
| Clay | 6.3 | [37] |
| PANI NTs | 9.21 | [38] |
| PANI nanotube base/silica | 10.3 | [39] |
| PProDOT/MnO2 | 13.94 | [3] |
| Orange peel | 18 | [40] |
| Rice husk | 40.6 | [41] |
| Palm kernel | 80.3 | [41] |
| Waste tea | 85.2 | [43] |
| Carbon nanotubes | 64.70 | [44] |
| Magnetic graphene–carbon nanotube composite | 65.79 | [45] |
| Oxalic acid modified rice husk | 53.21 | [46] |
| Alginate-Derived Aerogels | 70.42 | This work |

$$\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (11)$$

Where R = 8.314 J/mol K is the universal gas constant, $T$ is the temperature in K and $K_d$ is the distribution coefficient with the following calculation:

$$K_d = \frac{a_s}{a_e} = \frac{v_s}{v_e}\frac{C_{Ae}}{C_e} \quad (12)$$

Where $C_e$ (mg/L) is equilibrium concentration, $C_{Ae}$ (mg/L) is the amount adsorbed on the solid at equilibrium. $a_s$ is activity and $v_s$ is activity coefficient of the dye absorbed by the absorbent, $a_e$ is activity and $v_e$ is activity coefficient of solute in equilibration solution. When the concentration of solute tends zero, the activity coefficient tends unity. To calculate $K_d$, the theoretical values of $C_{Ae}$ and $C_e$ can be obtained from suitable isotherm models at different temperatures.

The values of ΔG° can be calculated from the following equation:

$$\Delta G^o = -RT \ln K_d \quad (13)$$

ΔSº and ΔHº values are calculated from the intercept and the slope of the linear graph (ln $K_d$) versus 1/T (Van't Hoff curve), respectively [47, 48].

As shown in Fig. 12. Positive values of ΔHº, indicates that the process of absorption of methylene blue by the carbon aerogel is an endothermic reaction. Endothermic adsorption suggests that the adsorbate and adsorbent are not strongly interacting on the surface and that the energy required to first displace the water molecules already adsorbed on the adsorbent is larger than the energy being produced by adsorbent/adsorbate interaction [49]. Positive changes in the values of standard entropy represent an increase of irregularities in the solid-liquid interface in the adsorption process. According to Table 5, the negative values of ΔGº a t different temperatures indicate that

***Table 5: Thermodynamic parameters of adsorption of methylene blue at 296 K, 306 K, and 316K.***

| T (K) | ln K | ΔG° (KJ/mol) | ΔH° (KJ/mol K) | ΔS° (J/mol K) |
|---|---|---|---|---|
| 296 | 1.8719 | -4.606 | 2.7427 | 108.373 |
| 306 | 2.2909 | -5.828 | | |
| 316 | 2.5761 | -6.767 | | |

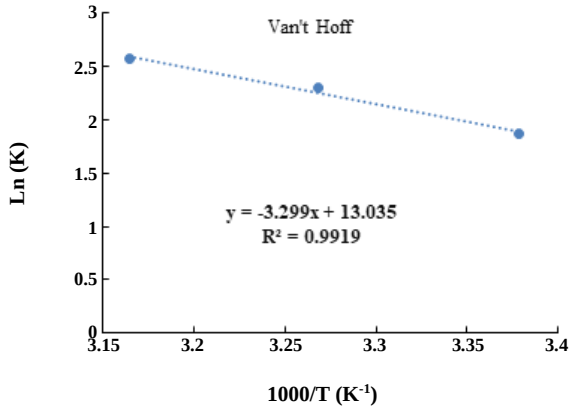


***Fig. 12: Van't Hoff diagram for the adsorption of methylene blue.***

the adsorption process is spontaneous. Reduction in the amount of ΔG° with increasing temperature indicates the desirability of the adsorption process at higher temperatures [7].

## CONCLUSIONS

In this study MB adsorption on carbon aerogel prepared from sodium alginate, was studied. The synthesized aerogel has high surface area, low density and porous structure. It was experimentally shown that MB adsorption increases with increase in dosage of adsorbent. The results of adsorption isotherms followed the Langmuir model with maximum adsorption capacity of 70.42 mg $g^{-1}$. Kinetics of MB adsorption on the carbon aerogel was described by Pseudo-first-order model. The mean adsorption energy E calculated from the D-R isotherm indicated that MB were undergoing physical adsorption. Thermodynamic studies revealed that MB adsorption process was endothermic and spontaneous. The synthesized carbon aerogel is economical, environmentally friendly and an appropriate adsorbent for environmental applications such as methylene blue removal from aqueous solutions and wastewater.

### *Supplementary data*

Supplementary data related to this article can be found, in the online version, at www.ijcce.ac.ir

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