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# Preparation of carboxymethylcellulose-based hydrogel beads and their used as bioadsorbent of dye from aqueous solutions

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**Abstract ━** Sodium carboxymethylcellulose (MC)-based hydrogels beads were synthesized using sodium dodecyl sulfate (SDS) as foaming agent, NaCl as porogen agent and $Al^{3+}$ as crosslinker without and in presence of diatomite (Di) as inorganic additive at various contents. The beads were by Fourier Transform Infrared spectroscopy-Attenuated transmittance spectroscopy (FTIR-ATR) and X-Ray Diffraction (XRD) analysis and Scanning Electron Microscopy (SEM). The swelling properties were investigated in deionized water. The application of CMC-based beads as biosorbents was prospected by examining the effect of Al and Di contents on the remove efficiency of Methylene Blue (MB) dye from aqueous solutions. Batch studies were conducted for various parameters: initial MB concentration, biosorbent dose, and contact time. The adsorption capacity increases as the pollutant concentration and contact time increase, and also as the biosorbent dose and crosslinker content decrease. Furthermore, the addition of inorganic Di has not improved the capacity of CMC beads. Isotherm adsorption data were modeled according to Langmuir and Freundlich models. The experimental data have the best fit to Langmuir isotherm model. The adsorption kinetics obeys well to pseudo-second-order model.

***Keywords**: CMC, beads, composite, methylene blue, adsorption*

## Introduction

Hydrogels are cross-linked polymers that can absorb, swell, and retain aqueous solutions up to hundred times their own weight. Their use for removal of heavy metal ions and dyes from wastewaters has become the subject of great interest owing to their absorption capacity, selectivity and reusability [1]. The presence of functional groups in network helps in binding the pollutants via formation of complex structures. Natural polymer-based hydrogels are promising biosorbents since they are less expensive than usual adsorbents, such as ion-exchange resins or activated carbon.

The sodium carboxymethyl cellulose (CMC) salt is a water-soluble cellulose derivative, which is renewable, non-toxic, biodegradable and biocompatible. The presence of carboxylic $COO^-$ ions groups allowed making electrostatic interactions with multivalent metal cations like $Fe^{3+}$ and $Al^{3+}$ to form stabilized ionotropic hydrogels [2]. The presence of $COO^-$ ions groups opens potential application in removal of pollutants from wastewaters. The porosity of hydrogels can be enhancing the water uptake of hydrogels and their ability for pollutant adsorption. Using a self-assembled micelle of surfactants as templating porogen is an effective approach to improve the porosity of hydrogels [3,4]. The aim of this work is to prepare crosslinked CMC beads and its Di-loaded CMC composites and to evaluate their potential as alternative low-cost bio-adsorbents for removal of cationic dye, namely meythlene blue (MB), which is selected as a model pollutant, from

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aqueous solutions. The ionotropic gelation method used for the preparation of these adsorbents has the benefit of lower temperature, short time and inexpensive raw materials, and hence reduce the production and application cost.

# I. Experimental

## *I.1.Materials*

Carboxymethylcellulose sodium salt (CMC) 400-800 cp was purchased from Sigma-Aldrich, sodium n-dodecyl sulfate (SDS), aluminum nitrate $Al(NO_3)_3.9H_20$, Sodium chloride (NaCl), methylene blue (MB). All chemicals (analytical grade) were used as received. The diatomite (Di), from Algerian type, was kindly supplied by ENOF chemical Ltd, Algeria. Doubly distilled water (DDW) was used in this study, Fig.1.

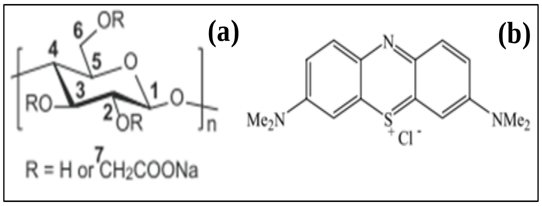

Fig. 1 Structures of (a) NaCMC, (b) MB dye.

## *I.2.Preparation of CMC-based beads*

The synthesis of CMC beads is given below. Aqueous mixture of 1.5 % NaCMC and 0.2 % of SDS was prepared in NaCl solution under vigorous stirring, and then added dropwise to $Al(NO_3)_3$ solution under gentle stirring. The obtained CMC beads were left overnight, and then washed with DDW and ethanol/water, dehydrated in ethanol, and finally dried in oven. Composite beads were prepared as above in where the diatomite was ultrasonically treated before addition to the CMC solution.

## *I.3.Characterization*

ATR-FTIR spectra were performed on Bio-Rad spectrometer model FTS-162. XRD analysis was performed on D8 Advance diffractometer (CuKα radiation, $\lambda = 0.1541$ nm). The surface of beads was observed using SEM microscope type Quanta 250. For adsorption studies, the change in MB concentration was monitored periodically using a UV-visible spectrophotometer (Shimadzu UV-1650, Japan) at λ max 664 nm of MB.

## *I.4. Adsorption experiments.*

The isotherm adsorption studies were carried out by varying the parameters: concentration of MB, biosorbent dose and contact time. All the adsorption experiments were examined through a batch method. Briefly, required amount of beads was contacted with MB solution at 25 °C under magnetically stirring at 300 rpm for 24 h until complete equilibrium. The beads were removed by filtering, and the filtrate was analyzed to evaluate the dye amount adsorbed by the beads at equilibrium. The MB concentrations ranged from 25 to 400 mg/L. The adsorption capacity ($q_e$, $mg.g^{-1}$) and sorption efficiency S (%) were calculated using Eq.1 and Eq. 2, respectively.

$$q_e = \frac{(C_0-C_e)}{m}.V \qquad (1)$$

$$S = \frac{(C_0-C_e)}{C_0}.100 \qquad (2)$$

Where, $C_0$ and $C_e$ (mg/L) are the initial and the equilibrium dye concentrations, respectively. V is the volume of MB solution (L), and m is the dry weight of beads sample (g).

Adsorption kinetics were conducted at 23 °C by immersing 0.8 g of beads into 200 mL of MB solution (50 mg/L) and stirring at 300 rpm. A required volume was collected from solution at desired time t and the residual dye concentration ($C_t$) was monitored periodically by UV-visible analysis until the MB removal equilibrium is reached. The adsorption capacity at any t was calculated, using Eq. 1. In this equation, the $C_e$ and $q_e$ are replaced with $C_t$ and qt, respectively.

# II. Results and discussion

## II.1. *Structural characterization*

Beads were formed instantly when NaCMC solution was extruded though the needle into solution containing $Al^{3+}$ cations. Research works have reported [5] on gelling process. The $Al^{3+}$ form ionic crosslinks between two CMC chains. The exchange of $Na^+$ occurs with $Al^{3+}$ that is ionically substituted at the $COO^-$ site, Thus, $Al^{3+}$ is attached to three CMC strands together.

Fig. 2 regroups the ATR-FTIR spectra of diatomite, CMC and Di powders, CMC beads and its typical Di-loaded composites. The CMC spectrum exhibits mainly bands at 3300 $cm^{-1}$ due to $\nu_{O\text{-}H}$, at 1587 $cm^{-1}$ and 1414 $cm^{-1}$ ascribed to $\nu_{C=O}$ asymmetric and symmetric of $COO^-$ groups, respectively, at 1040 cm$^{-1}$ due to $\nu_{C\text{-}O\text{-}C}$ skeletal units. The cross linking of CMC is evidenced by an extra peak at 1730 cm$^{-1}$ due to electrostatic interactions between COO$^{-}$ groups and Al $^{3+}$.[6]. Also, the asymmetric $\nu_{C=O}$ shifts to 1612 cm$^{-1}$.

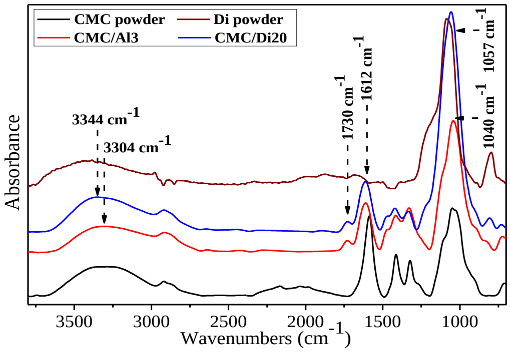

Fig. 2 ATR-FTIR spectra of CMC, Di, crosslinked free CMC, and its composite CMC/Di20.

Besides, the main chemical composition of the natural or calcinated diatomite contain Si and Al oxides ($SiO_2$~76%, $Al_2O_3$~15%). Hence, the spectrum of Di shows intense band at 1080 cm$^{-1}$ due to $\nu_{Si\text{-}O}$ of $SiO_2$ groups and another at 798 cm$^{-1}$ related to $\nu_{Al\text{-}O}$ in $Al_2O_3$. From CMC/Di20 spectrum, all bands are ascribed to CMC. The presence of Di is highlighted by the shift to higher values and intensification of the bands of $\nu_{O\text{-}H}$ from hydroxyls and of $\nu_{C\text{–}O}$ by about 44 and 17 cm$^{-1}$, respectively.

From Fig.3, the XRD pattern of the composite depicted clearly the highly crystalline peaks of silica, and quartz originated from diatomite, beside the amorphous peak of the CMC matrix.

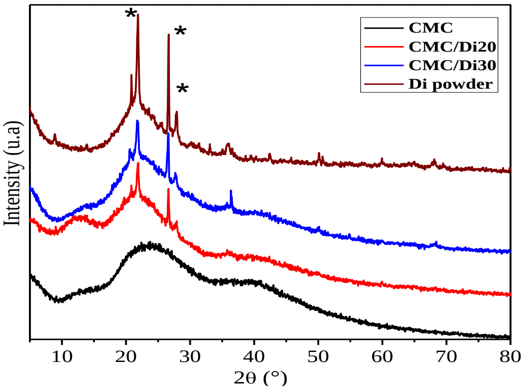

Fig. 3 XRD patterns of Di, crosslinked free-CMC, and its composites.

Fig.4 shows SEM images of beads crosslinked at Al3, Al5 and CMC/Al3/Di20 composite. The beads were spherical in shape and they fell in the size ranges of 1.056-1.11 and 1.23-2 mm for CMC/Al3 and CMC/Al5. Indeed, the increase in Al$^{3+}$ produces smaller beads. At higher crosslink densities, the hydrogel might have undergone rapid shrinking during crosslinking, leading to the formation of smaller and rigid bead. Also, the addition of 20 wt. % of Di in CMC/Al3 increases the size bead (1.46-1.52 mm) since it occupied the interstitial spaces. The surfaces of beads are rather rough and dense with crease-shaped scales and high porosity, essentially for CMC/Al3 bead.

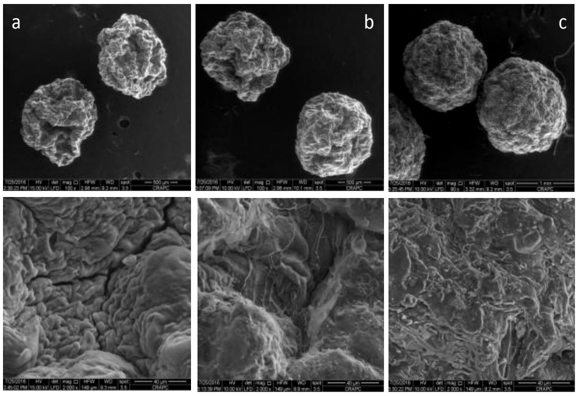

Fig. 4 SEM micrographs of CMC beads where (a) CMC/Al3 (b) CMC/Al5 and (c) CMC/Al3/Di20.

### *II.2. Dye adsorption studies*

The isotherms adsorption data are obtained at 25 °C and by varying $C_0$ of MB. As it can be seen in Fig. 5, the adsorption, increase with an increase of $C_0$, notably for CMC/Al3, until the equilibrium is reached. It indicates a relatively high affinity between MB and adsorbent.

Also, the sorption efficiency (%) is gradually deceases. The higher $C_0$ led to stronger driving force resulting from the concentration gradient, this increased the diffusion of MB molecules into the adsorbent. Beyond 300 mg/L, the adsorption kept nearly constant owing to saturation of the adsorption sites. Also, the increase of Al contents reduced adsorption due to the beads pores size. Indeed, for higher Al content, the narrow pore sizes delay training of MB into beads. Also, the addition of Di has not improved adsorption, yet CMC/Di20 data closer with those of free beads.

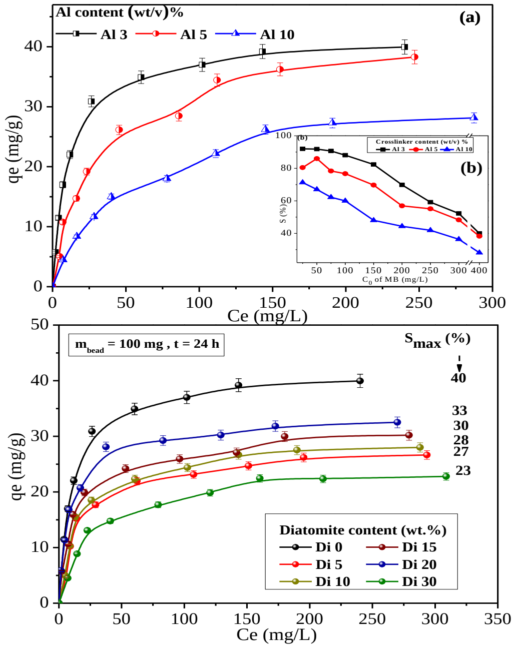

Fig. 5 Effect of initial MB concentration on adsorption of free CMC beads and its Di composites.

## II.3. Adsorbent dose

From Fig. 6, the removal efficiency increases by increasing the adsorbent dose. MB was almost completely removed about 94 % with 0.15g of CMC/Al3. At fixed MB concentration, some of adsorbent sites remain free, so the quantity of adsorbed MB per gram beads decreases.

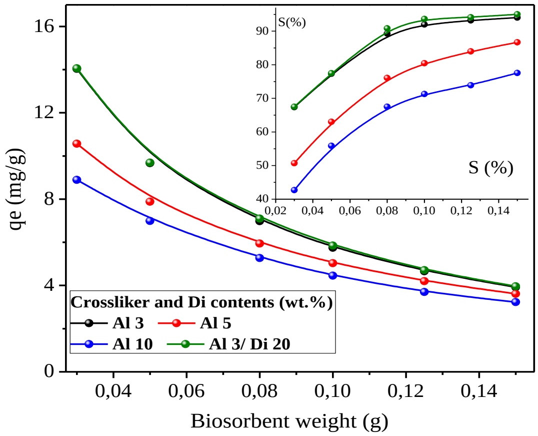

Fig. 6 Effect of adsorbent dosage on MB adsorption capacity, and sorption efficiency of CMC beads.

## II.4. Isotherm Models

Freundlich and Langmuir isotherm models have been widely used to describe the interaction between dye and adsorbents. Langmuir isotherm model deals with homogeneous adsorption at monolayer surface within the adsorbents. [7] The linear Langmuir equation is given in Eq. (3).

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \qquad (3)$$

Where, $q_m$ ($mg.g^{-1}$) is theoretical adsorption limit, and $K_L$ is Langmuir adsorption constant (L/mg). The interaction between dye and biosorbent is also evaluated by separation factor ($R_L$) in Eq.4 [8]. It reveals the isotherm type be either favorable ($0<R_L<1$), unfavorable ($R_L>1$), linear ($R_L=1$) or irreversible ($R_L=0$).

$$R_L = \frac{1}{(1 + K_L C_0)} \qquad (4)$$

Freundlich isotherm is an empirical model [9] based on heterogeneous multilayer surface adsorption. The linear form equation is below.

$$Lnq_e = LnK_F + \frac{1}{n} LnC_e \qquad (5)$$

n is dimensionless Freundlich constant (0-1) and. $K_F$ ($mg.g^{-1}$) is the equilibrium adsorption. The results are shown in Fig.7 and in Table 1. The adsorption is correlated well with Langmuir, suggesting monolayer favorable process.

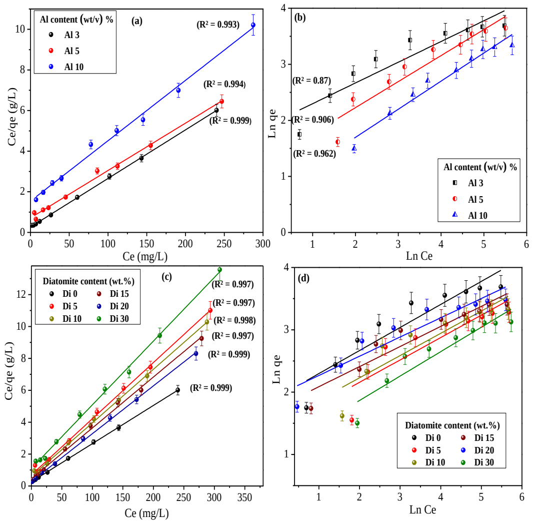

Fig. 7 The linearized form of (a,c) Langmuir and (b,d) Freundlich isotherms models for the adsorption of MB on (a,b) CMC beads at different Al and Di contents.

*Table 1.Freundlich and Langmuir parameters*

| **Bead** | ***Langmuir model*** | | | |
|---|---|---|---|---|
| | ***$q_m$ (mg/g)*** | ***$K_L$(L/mg)*** | ***$R^2$*** | ***$R_L$*** |
| Al 3 | 43.48 | 0,087 | 0.999 | 0.31 |
| Al 5 | 42.72 | 0,032 | 0.994 | 0.55 |
| Al 10 | 34.48 | 0,019 | 0.993 | 0.68 |
| Di 5 | 28.57 | 0,050 | 0.997 | 0.44 |
| Di 10 | 30.30 | 0,055 | 0.998 | 0.42 |
| Di 15 | 32.26 | 0,069 | 0.997 | 0.36 |
| Di 20 | 33.33 | 0,105 | 0.999 | 0.27 |
| Di 30 | 24.39 | 0,051 | 0.997 | 0.44 |

| **Bead** | ***Freundlich model*** | | |
|---|---|---|---|
| | ***$K_F$ (mg/g)*** | ***n*** | ***$R^2$*** |
| Al 3 | 6.875 | 2.710 | 0.873 |
| Al 5 | 3.665 | 2.155 | 0.906 |
| Al 10 | 1.999 | 1.996 | 0.962 |
| Di 5 | 4.216 | 2.785 | 0.795 |
| Di 10 | 4.549 | 2.801 | 0.835 |
| Di 15 | 5.841 | 3.105 | 0.911 |
| Di 20 | 7.085 | 3.246 | 0.886 |
| Di 30 | 3.811 | 2.881 | 0.827 |

### *II.5. Adsorption kinetics*

The effect of time contact on MB adsorption is shown in Fig. 5. The adsorption occurs in three stages. The first stage exhibits a sharp initial rise due to the availability of abundant vacant active sorption sites, and so a rapid diffusion and adsorption of MB to adsorbent surface occurred. In second one, the process is delayed and is close to equilibrium at 300 min. In the third stage, adsorption reaches equilibrium due complete saturation of adsorbent sites. The experimental data were fitted by pseudo first-order (Eq. 6) [10] and pseudo-second order models (Eq. 7) [11].

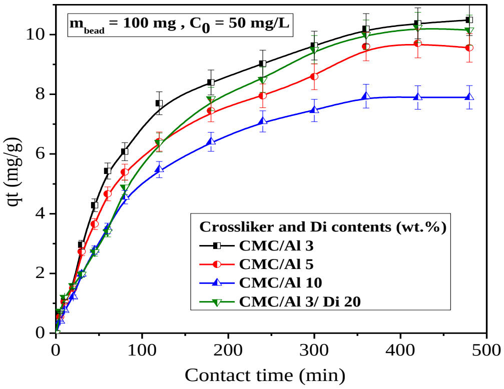

Fig. 5 Effect of contact time on the adsorption of MB on free and Di-loaded CMC beads

$$Ln(q_e - q_t) = Ln\, q_{e_1} - k_1 t \qquad (6)$$

$$\frac{1}{q_t} = \frac{1}{k_2\, q^2_{e2}} + \frac{t}{q_{e2}} \qquad (7)$$

Where, $q_{1e}$, $q_{2e}$, and $q_t$ (mg.g$^{-1}$) are theoretical equilibrium adsorption and adsorption at any time t, respectively. The parameters $k_1$(min$^{-1}$) and $k_2$ (g.mg$^{-1}$.min$^{-1}$) are the rate constants of pseudo-first and pseudo second-order models, respectively. The related parameters are given in Table 2. The values of $q_{2e}$ are mostly close to $q_e$ exp, so the adsorption process fitted the pseudo-second-order kinetic model.

*Table 2. Kinetics models parameters*

| **Bead** | ***Pseudo-first -order model*** | | | |
|---|---|---|---|---|
| | ***$q_{1e}$ (mg/g)*** | ***$k_1$(min$^{-1}$)*** | ***$R^2$*** | ***$q_{e\ exp}$*** |
| Al 3 | 9.318 | 0.009 | 0.987 | 10.50 |
| Al 5 | 8.482 | 0.007 | 0.984 | 9.55 |
| Al 10 | 7.683 | 0.009 | 0.987 | 7.90 |
| Di 20 | 10.762 | 0.009 | 0.968 | 10.14 |

| **Bead** | ***Pseudo-second-order model*** | | |
|---|---|---|---|
| | ***$q_{2e}$ (mg/g)*** | ***$k_2$ (g.mg$^1$.min$^{-1}$)*** | ***$R^2$*** |
| Al 3 | 12.987 | 0.00077 | 0.990 |
| Al 5 | 12.048 | 0.00077 | 0.993 |
| Al 10 | 10.101 | 0.00082 | 0.991 |
| Di 20 | 13.699 | 0.00049 | 0.972 |

## Conclusions

Porous CMC-based beads with a spherical shape were prepared and characterized. Their performance as an adsorbent to remove MB was examined. Experimental data were better fitted with Langmuir isotherm model. The kinetic data were obeyed to pseudo-second-order model.

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