

Investigation of the Adsorption Properties of a New Biopolymer Created Using Brown Algae Powder

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ABSTRACT

The objective of this study was to create a new material utilizing a biopolymer (sodium alginate) and the powder of brown algae for the elimination of organic pollutants like dyes by adsorption from a water-based solution. The alginate/algae composite beads used in this study as an adsorbent were created by inotropic gelation of sodium alginate utilizing calcium ions as a cross-linking agent. The beads thus synthesized had been characterized by using different techniques in order to assess their characteristics. The adsorption procedure was studied in a batch mode at room temperature using methyl violet, a cationic dye chosen as an organic pollutant. The influence of beading parameters like contact time, methyl violet concentration, pH, sorbent amount and agitation speed was studied. It was found that the adsorption capacities were notably influenced by the initial dye concentration, pH and bead dose. Indeed, the results found indicated that the equilibrium sorption of methyl violet by this adsorbent was reached in around 3 hours for the different concentrations studied (10 mg/L, 40 mg/L and 70 mg/L) with percentage dye removal of around 80% at the optimum bead amount of 2 g. The kinetic modeling had shown that the model of the pseudo-second-order kinetic governed the adsorption rate of methyl violet on alginate/brown algae composite beads.

Keywords: sodium alginate, brown algae, beads, adsorption, methyl violet.

INTRODUCTION

In recent years, there has been significant interest in utilizing biomaterials as adsorbent in water treatment, primarily because of their cost-effectiveness in preparation and the potential to be produced from renewable sources (Torres-Caban et al., 2019; Wang et al., 2016; De Rossia et al., 2020; Contreras-Cortés et al., 2019). The term “bio-sorbent” designates a wide range of products derived from biological or plant sources capable of fixing organic or inorganic pollutants without undergoing prior transformation. The materials used may be leftovers from

used agricultural production. Algae constitute another widely-studied family of bio-sorbents. These substances possess a notable ability to fix inorganic pollutants, especially heavy metal cations (Dulla et al., 2020; He et al., 2014; Jayakumar et al., 2015; Cid et al., 2015). The efficacy of these materials can be extended to the adsorption of organic molecules with a positive charge (Mahini et al., 2018; Jafari et al., 2020). Derived from brown algae, sodium alginate is a natural polymer composing of α -L-guluronic acid (G) and β -D-mannuronic acid (M) residues (Mohy Eldin et al., 2015). This biopolymer is very interesting due to its capability to create porous

gels, especially in the presence of divalent cations, particularly calcium ions. The fixation of pollutants occurs through ion exchange at the carboxylate functions of the alginate (Esmat et al., 2017; Ren et al., 2021; Wang et al., 2018; Suresh et al., 2022). However, the sodium alginate is soluble in water and presents low stability, which limits its direct use as an adsorbent. The formation of beads by modifying sodium alginate using the ionotropic gelling technique overcomes this problem and offers the possibility of preparing a new adsorbent that has certain advantages in its use and its easy separation from treated water, and will have some potential for its future use in dynamic mode. Moreover, the combination of the adsorption properties of the brown algae and the gelling properties of sodium alginate certainly offers the possibility of developing a new material with good adsorption properties. The main objective of this work was to prepare efficient sorbent, alginate/brown algae composite beads, using an abundantly available low-cost biopolymer, sodium alginate and brown algae powder for the adsorption of methyl violet, a cationic dye, chosen as an organic pollutant from aqueous solution.

MATERIALS AND METHODS

Materials:

- sodium alginate with low viscosity (5.5 ± 2.0 Cps at 25°C) (provided by Biochem Chemopharma);
- hydrochloric acid 37% (Sigma-Aldrich);
- sodium hydroxide tablet (Carlo-Erba);
- the dye methyl violet (Biochem Chemopharma).

The elaboration of alginate/brown algae beads was made according to the following experimental procedure:

- Preparation of a viscous sodium alginate solution – a viscous sodium alginate solution was obtained under magnetic stirring by dissolution of 1 g of this polymer in 25 mL of distilled water. Then, 0.75 g of brown seaweed powder was added to the sodium alginate solution thus prepared. After homogenization, the viscous solution obtained was left to stand for 2 to 3 hours to eliminate any air bubbles formed during stirring.
- Preparation of the alginate/brown algae porous composite beads – the viscous solution

based on sodium alginate and the brown algae powder was poured drop by drop in a calcium chloride solution (0.3 mol/L) and a volume of 400 mL using a 5 mL syringe with a drop height of 4 cm. The alginate/brown algae composite beads elaborated were left in the calcium chloride solution for 24 hours, a time largely sufficient to ensure the complete gelation of the alginate. After this maturation time, the beads were washed in several successive baths of distilled water and then recovered by filtration and attacked again by a solution of HCl(1M) for 48 hours in order to dissolve the carbonates contained in the brown algae and create a porous structure in the various gelled beads obtained. The beads were then recovered by filtration and washed many times with distilled water until the excess acid (HCl) was completely eliminated. Finally, the composite beads obtained were stored in wet form in distilled water until use.

Characterization of alginate/brown algae composite beads

To determine their properties, the composite beads thus obtained were characterized by using physicochemical and spectroscopic methods. The density of the composite beads produced was determined by the gravimetric method using a 10 mL pycnometer and an analytical balance. To determine the water content of the composite beads, the samples of wet beads were weighed and oven dried at 50°C until their weight stabilized. The water content was determined using the following formula:

$$M_w (\%) = \frac{M_w - M_d}{M_w} \times 100 \quad (1)$$

where: M_w and M_d are the amounts (g) of the beads before and after drying.

The diameter of the beads was measured using a digital caliper instrument on a representative sample of beads (134 beads). The average diameter was estimated by modeling the results obtained by a Gaussian distribution (Merakchi et al., 2019). The point of zero charge of beads was established by using the pH drift method (Kragović et al., 2019; Nordine et al., 2016) which consists of placing 50 mL of distilled water in bottles and adjusting the pH of each (values ranging from 2 to 12) by addition of sodium hydroxide or HCl

solution (0.1 mol/L). Subsequently, the beads in a quantity of 0.15 g were introduced into the pH-adjusted solution and the suspensions were allowed at room temperature to equilibrate for 48 hours to establish the final pH. The pH_{pzc} is the point where the curve pH_{final} versus pH_{initial} intercepts the line pH_{final} = pH_{initial}. The IR spectra of the produced composite beads were obtained using an FTIR spectrophotometer (JASCO FT/IR-4200, ATR PRO450-S) with a wavelength range of 400 to 4000 cm⁻¹.

Experimental procedure of the sorption process

The adsorption process was conducted in a batch mode at room temperature by optimizing several parameters, namely the contact time, the adsorbent mass, the initial pollutant concentration, the solution pH and the stirring speed. After each adsorption test, the methyl violet residue concentration was measured using a spectrophotometer at wavelength of 582 nm. The elimination rate (R (%)) and the adsorption capacities (Q_t) of dye at any given time were performed as follows:

$$R (\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

$$Q_t = \frac{(C_0 - C_t) \times V}{W} \quad (3)$$

where: Q_t – adsorption capacity (mg/g); R (%) – elimination rate of methyl violet; C_0 – initial pollutant concentration (mg/L); C_t – residual methyl violet concentration in the solution (mg/L); V – volume of the solution (L); W – mass of the alginate/brown algae composite beads used (g).

Finally, the diverse adsorption kinetics investigated at various initial concentrations were simulated by the pseudo-first-order kinetics model and the pseudo-second-order kinetics model in order to comprehend the adsorption mechanism (Obradovic et al., 2020; Minh et al. 2020). The equation employed for modeling for the pseudo-first-order kinetic model is:

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} t \quad (4)$$

where: Q_e – represents the quantity of methyl violet adsorbed at equilibrium time (mg/g), Q_t – the quantity of methyl violet adsorbed at time t (mg/g), k_1 – the rate constant for pseudo-first-order adsorption (min⁻¹). In the case of the pseudo-second-order kinetic model, the utilized linear equation used is formulated as:

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{k_2 \times Q_e^2} \quad (5)$$

where: k_2 – the rate constant for the second model (g mg⁻¹ min⁻¹).

RESULTS AND DISCUSSIONS

Formation of alginate/brown algae composite beads

The beads employed as adsorbent in this work were prepared by the ionotropic gelation method, following the egg-box model (Rakesh et al., 2015; Kaur et al., 2018) utilizing a blend of sodium alginate and brown algae powder (Figure 1). The latter was added to the composition of the

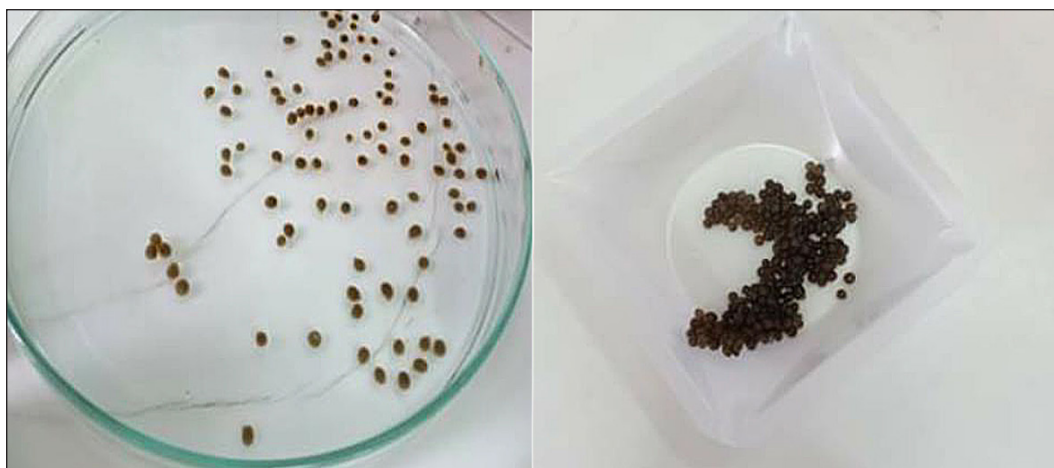


Figure 1. Photographs of wet alginate/brown algae composite beads

beads for two purposes, the first was to minimize the amount of biopolymer used and replace it with a more available raw material and the second objective was to create porosity in the matrix of the beads after their attack with a hydrochloric acid solution. Indeed, the brown algae containing the carbonates react with the acid solutions, releasing CO_2 , which creates a porous structure in the various gelled beads obtained and subsequently improve the adsorption properties.

Characterization of beads

The various characterization results obtained showed that the alginate/brown algae composite beads had a density of 1.08 g/cm^3 , a humidity ration of 94.99% and a pH_{pzc} of the order of 4. After the elaboration, the composite beads obtained were spherical, millimeter-sized and dark brown in color due to the presence of the algae powder.

The average diameter of beads was calculated according to the average by number (Figure 2). The modeling of the results obtained by a Gaussian distribution showed that the distribution of the beads was much more homogenous and follows the logic of the Gaussian curve. The alginate /brown algae composite beads had an average diameter of 3.06 mm. After modification and cross-linking, the main alginate-specific bands appear in the spectra of elaborated beads. In the FTIR spectra of the composite beads, the absorption bands characteristic of the carboxyl group of alginate observed around 1600 cm^{-1} and 1400 cm^{-1} were shifted towards high frequencies (Figure 3). This shift in the absorption bands was certainly due to the bonds formed during the electrostatic interaction between the carboxylate function of sodium alginate and calcium ions, confirming that the alginate/brown algae composite beads were elaborated by ionic gelation, according to the egg-box model (Merakchi et al., 2019).

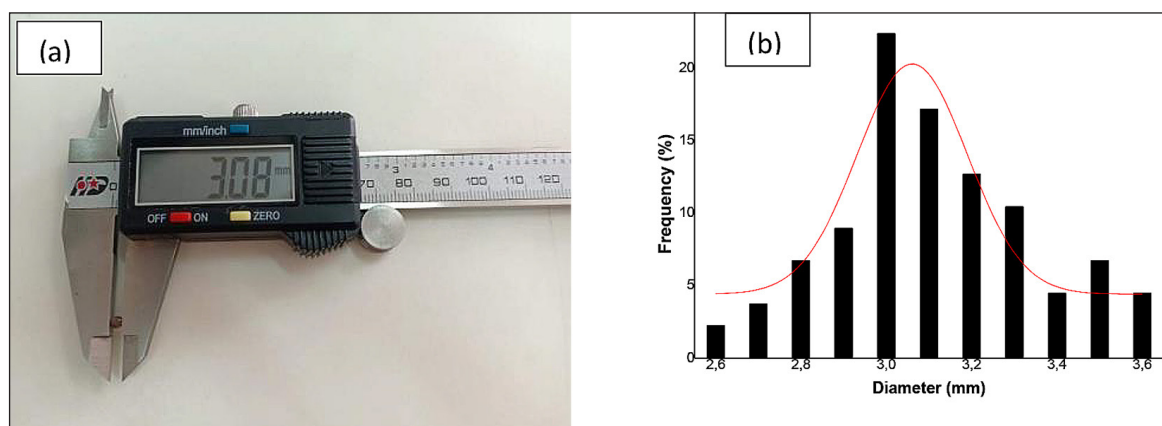


Figure 2. (a) Measurement of beads diameters using a digital caliper and (b) size distribution of alginate/brown algae composite beads

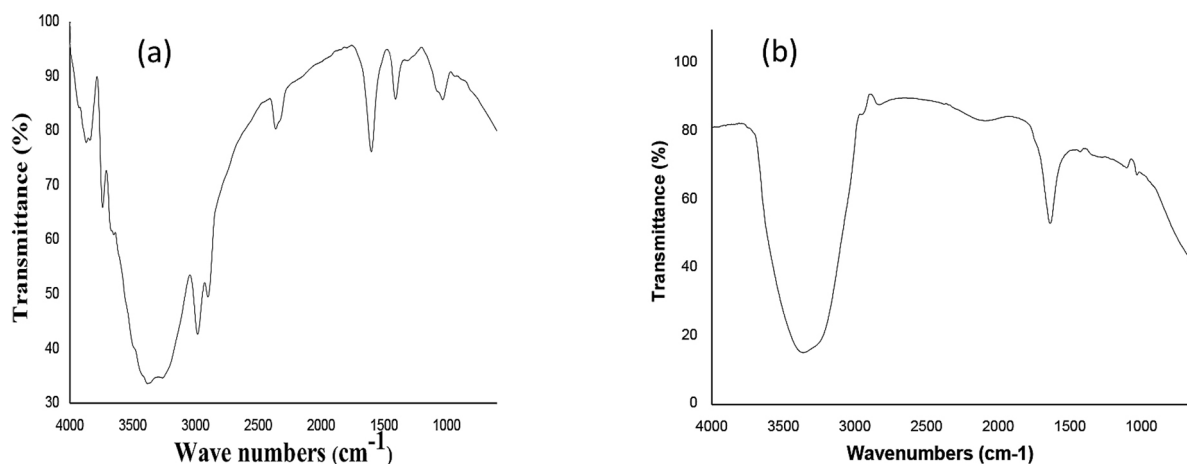


Figure 3. (a) FTIR spectra of sodium alginate (b) FTIR spectra of alginate/brown algae composite beads

Adsorption studies

Influence of initial methyl violet concentration and the contact time

The results found indicated that the rate of adsorption of the dye onto the alginate/brown algae composite beads changed rapidly during the first few minutes of contact, then stabilized as equilibrium approached, which was reached in around 3 hours for the three concentrations studied (10, 40, 70 mg/L) (Figure 4). On the other hand, the adsorbed methyl violet quantity increases along with the initial methyl violet concentration which can be explained by the presence of a strong gradient of dye concentration between the solution and the adsorbent surface (Al-Ghouti et al., 2020; Bhatti et al., 2020; Lim et al., 2014).

Effect of adsorbent amount

It appeared through the results obtained that the removal efficiency of methyl violet increases along with the quantity of adsorbent employed. Indeed, the increase in the amount of the adsorbent increases the number of sites available for the fixation of the dye and there is a rise in electrostatic interaction, which consequently favors the phenomenon of discoloration (Fang et al., 2018; Durmaz et al. 2021; Yaday et al. 2020) (Figure 5).

Influence of stirring speed

The study of the effect of this parameter showed that for moderate values of the stirring speed (50–200 rpm), the dye removal by the

beads was almost independent of the stirring speed. However, by increasing the stirring speed beyond 200 rpm, a vortex phenomenon occurs and the wet alginate beads crumble. As a result, a stirring speed of 200 rpm was selected as optimal for the rest of the study (Figure 6).

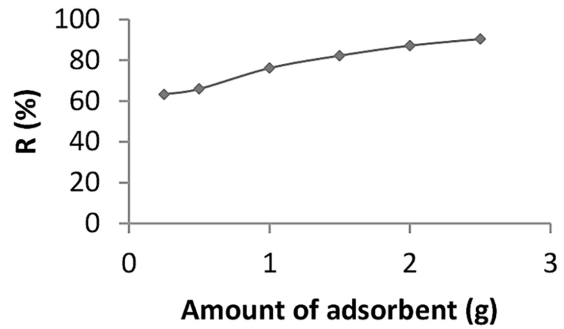


Figure 5. Effects of amount of alginate/brown algae composite beads on the methyl violet percentage removal

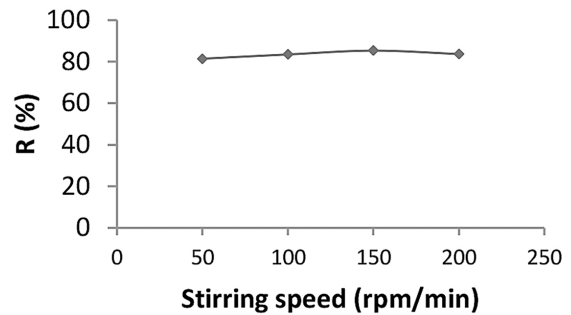


Figure 6. Effect of stirring speed on the methyl violet elimination

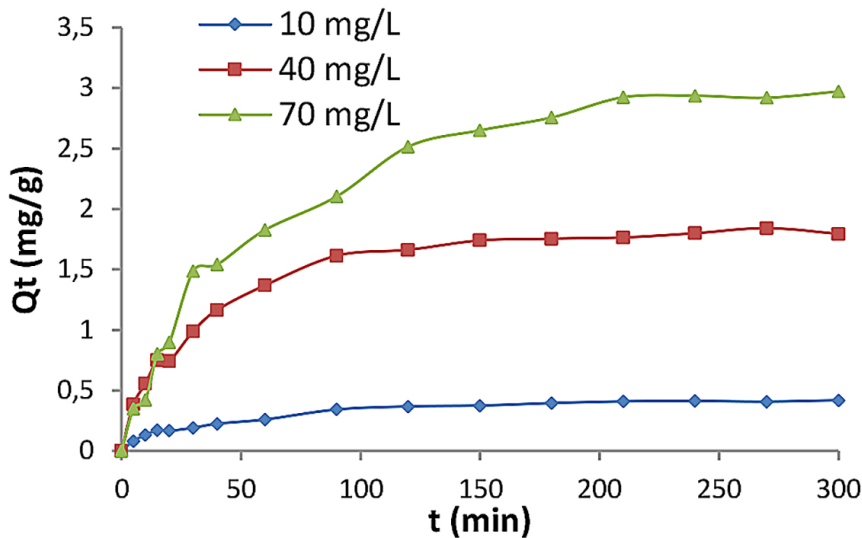


Figure 4. Influence of dye concentration and contact time on sorption of methyl violet by alginate/brown algae composite beads

Influence of pH

The pH of the solution affects the methyl violet sorption capacity of the alginate/brown algae composite beads. Indeed, an increase in pH promotes the sorption of the pollutant (Figure 7). This effect is due to the decrease in the surface charge of the beads, confirmed by the determination of their zero charge point. At acidic pH, the charge

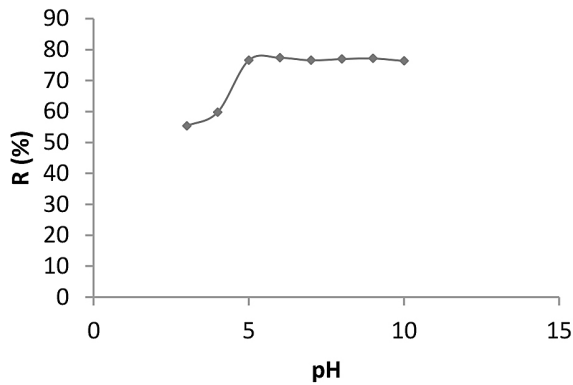


Figure 7. Effect of solution pH on the methyl violet elimination

of the surface becomes less negative, which reduces cationic dye retention. At basic pH, the surface charge becomes increasingly negative, which leads to an increase in adsorption capacity (Parlayici et al., 2022; Abrishamkar et al., 2020).

Batch adsorption kinetic modeling

The analysis of methyl violet adsorption onto alginate/ brown algae composite beads was conducted utilizing the pseudo-first-order and the pseudo-second-order kinetic models. The results obtained are presented in figures 8 and 9. The different kinetic parameters and the corresponding correlation coefficients R^2 calculated for each model and are presented in Table 1.

The modeling of the adsorption kinetics of methyl violet showed that the equilibrium kinetics for the dye studied followed pseudo-second order model, indicating that the chemical sorption constituted the step limiting the rate of the adsorption process (Aoulad El Hadj et al., 2021). Accordingly, it was thought that the methyl violet adsorption on alginate /brown algae composite beads could be chemical sorption. This is in

Table 1. Values of kinetic parameters for methyl violet sorption on alginate/brown algae composite beads

C_0 (mg L ⁻¹)	Experimental result Q_e (mg g ⁻¹)	Pseudo-first-order model			Pseudo-second-order model		
		Q_e (mg g ⁻¹)	k_1 (min ⁻¹)	R^2	Q_e (mg g ⁻¹)	k_2 (g mg ⁻¹ min ⁻¹)	R^2
10	0.4100	0.3427	0.0184	0.983	0.4655	0.0637	0.995
40	1.7650	1.7660	0.0027	0.969	1.9960	0.0192	0.998
70	2.9244	2.7861	0.0184	0.974	3.5714	0.0051	0.993

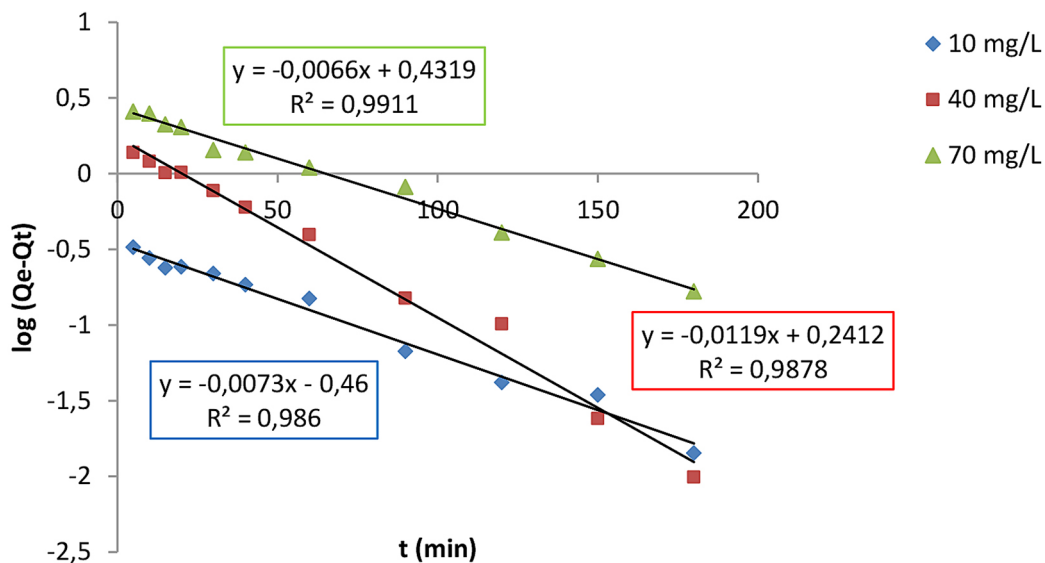


Figure 8. Pseudo-first-order model for batch sorption of methyl violet on alginate / brown algae composite beads

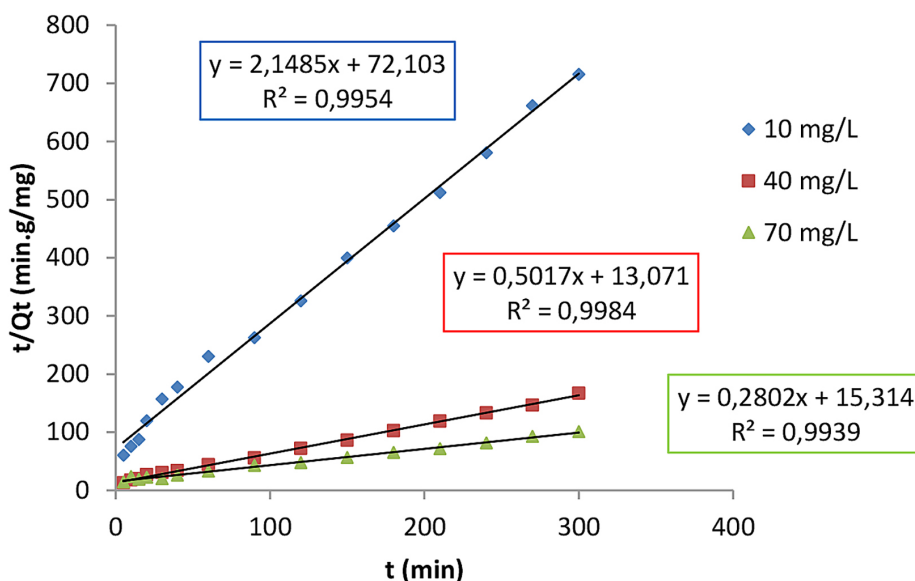


Figure 9. Pseudo-second-order model for batch sorption of methyl violet on alginate / brown algae composite beads

accordance with the previous studies conducted on methyl violet removal by adsorption where the pseudo-second-order model described well the kinetics data (Parlayici et al., 2022; Bonetto et al., 2015; Abrishamkar et al., 2020).

CONCLUSIONS

During this study, the possibility of preparing beads based on a sodium alginate biopolymer was demonstrated. The alginate/brown algae composite beads have been developed to eliminate an organic pollutant (methyl violet) from aqueous solutions by adsorption. These beads were synthesized using the extrusion technique, which is quick and easy to use. Brown algae powder was mixed with sodium alginate to create the beads, with the aim of minimizing the quantity of biopolymer used and further improving the properties of the beads, particularly their structural properties. The various results obtained indicated that the sorption equilibrium of this pollutant (methyl violet) by the alginate composite beads was reached in around three hours for the different concentrations studied. The pH affects the adsorption capacity of methyl violet. Indeed, an increase in pH favors their adsorption. This effect is due to the decrease in surface charge, confirmed by the determination of the zero charge point of the adsorbent. The stirring speed had an insignificant effect on the adsorption of this pollutant. Finally,

the kinetic modeling showed that the adsorption speed of the methyl violet on the alginate/algae composite beads was governed by a pseudo-second order kinetic model. In conclusion, the alginate/brown algae composite beads elaborated in this study were expected to be a good candidate for an excellent adsorbent for cationic dye.

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