Sorption kinetics and isotherms, trisacrylamide blue by poly [(MAA-co-NVP)-cross-BAA] hydrogels network

N. DIB¹, F.Z. SEBAA¹, H. SEBTI¹,²* and S. OULD KADA¹

¹Laboratoire de Chimie Physique Macromoléculaire, Faculté des Sciences Exactes et Appliquées, Université Oran and ²Ecole Nationale Polytechnique Oran

Abstract

Hydrogels were prepared based on methacrylic acid (MAA) and N-Vinylpyrrolidone (NVP) to the NVP percent molar composition of 10, 47.5 and 85. These new hydrogels were then used to adsorb and remove the cationic dye trisacrylamide blue (TB) at temperature 25°C, were studied using two kinetics models of sorption intra-particle diffusion and the pseudo-second order model, result of the kinetic are in a good correlation with the intra-particle. Sorption isotherm results showed that the isotherm was correlated reasonably by the Freundlich isotherm.

(pH=6.8; C₀=20mg/l), m_hydrogen=30mg, poly[(MAA-co-10%NVP)-cross-BAA]:photo A-T=25°C et photo D-T=37°C, poly[(MAA-co-47.5%NVP)-cross-BAA]:photo B-T=25°C et photo E-T=37°C poly[(MAA-co-85%NVP)-cross-BAA]: photo C-T=25°C et photo F-T=37°C

Key words: Methacrylic acid, Cationic dye, Hydrogel network, Sorption and Sorption isotherm

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1. Introduction

Nine million tonnes of dyes are produced annually, and there are more than one hundred thousand kinds of dyes [1] and the contaminant to be recognized in wastewater [2]. The present amount of dyes in water (less than 1 ppm for dyes) is visible and unwanted [3]. Different pollution problems arise as a result of increasing industries. In particular, water cycles throughout the industrial world are contaminated with organic dyes emitted from liquid wastewater from textile, leather, paper, printing, dyestuff, plastic and pharmaceutical industries [4, 5]. Methyl orange (MO) has been widely used in textile, printing, paper, food and pharmaceutical industries and research laboratories. Methyl blue (MB) is one of the most commonly dying materials for wood, silk and cotton. The removal of dyes from water is very important because of its toxicity [6, 7]. It is difficult to dispose of this wastewater, the high content of organic pollutants, complex composition and high biological toxicity, by traditional methods. Over a decade, it has been shown that adsorption is now an effective and economical way to remove dyes from sewage from many ways to remove dyes including coagulation and occultation [8], membrane separation [9], oxidation or coronation [10], electro-coagulation [11] and adsorption [12]. Polymerization novel adsorbent can selectively adsorb toxic organic compounds from aqueous solution, also this adsorbent are not easy to be separated from water [13, 14]. Hydrogel is
one of the important methods for removal of dyes. Hydrogel are superior to other absorbents due to their characteristic properties like adsorption, regeneration and environmental friendly behavior [15]. Functional groups such as carboxylic acid and sulfonic acid can absorb ionic dyes and heavy metals [16, 17].

2. Material and Methods

2.1. Materials

Methacrylic acid, vinylpyrrolidone and bisacrylamide (Sigma–Aldrich)

2.2. Methods

Adsorption experiments: Aqueous solutions of dyes were prepared by individually dissolving blue trisacrylamide in distilled water with different concentrations of blue trisacrylamide (150–1200 ppm) were prepared by serial dilution of solution with distilled water. Blue trisacrylamide concentrations were determined using an absorbance (at 440 and 700 nm, respectively) of the solutions after getting the UV spectrum of solution. In the adsorption procedure, 0.01 g of the individual synthesized adsorbent was added to 10 ml of dye solution from initial concentration under stirring at 25°C, at predetermined time intervals, a supernatant solution was obtained. The residual dye concentration in the supernatant solution was determined using WFZ UV-2000 at wavelength 440 and 700 nm, respectively. The amount of dye adsorbed per unit mass of the adsorbent was evaluated by using the mass balance equation (1):

$$q_t = \frac{(C_0 - C_t) \cdot V}{m} \ldots (1)$$

Where $q_t$ (mg/g) is the amount adsorbed per gram of adsorbent, $C_0$ and $C_t$ are the initial and concentrations at time of dye in the solution (mg/L), respectively, $m$ is mass of the absorbent (g) and $V$ (L) is the initial volume of the dye solution.

2.3. Evaluation of adsorption kinetics

Pseudo-Second-Order Model: Kinetic model is pseudo-second-order model, $K_2$ is equilibrium rate constant of pseudo-second-order adsorption (g/g min) which is expressed by [18].

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 \cdot q_e^2} \ldots (2)$$

Intra-Particle Diffusion: The kinetic model to investigate intra-particle diffusion is a step limiting the rate is given by (Weber and Morris) [19]

$$q_t = k_d t^{0.5} \ldots (3)$$

Where, $K_d$ is the intra-particle diffusion rate constant and was calculated for different initial concentrations of dye by plotting $q_t$ vs. $t^{0.5}$.

2.4. Adsorption isotherm analysis

Langmuir equation can be linearized as shown in Equation (4) [20].

$$\frac{C_e}{q_e} = \frac{1}{K_l \cdot q_m} + \frac{1}{q_m} \cdot C_e \ldots (4)$$

Where $C_e$ is the concentration of trisacrylamide (milligram per liter) at equilibrium, $q_e$ is the amount of adsorbed dye per unit mass of adsorbent (milligram per gram), $q_m$ the maximum monolayer capacity (milligram per gram) and $K_l$ is Langmuir adsorption constant indicating the adsorption energy (liter per milligram).

The Freundlich isotherm is model the multilayer adsorption and for the adsorption on heterogeneous surfaces. The Freundlich model is formulated in Eq [20].

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \ldots (5)$$

Where $K_F$ is the sorption capacity (milligram per gram) and $n$ is an empirical parameter which is an indicator of adsorption intensity.

3. Results and Discussions

Sorption kinetics of dyes by poly [(MAA-co-NVP)-cross-BAA]: Sorption capacity of blue trisacrylamide by poly [(MAA-co-NVP)-cross-BAA] hydrogels were obtained with NVP percent molar composition of 10, 47.5 and 85 in the pH 6.6 in distilled water, at temperature 25°C sorption kinetics (intra-particle diffusion and pseudo-second-order) of the hydrogels shown in Fig.1 and table1. We observe, in this case, correlation coefficients vary from 0.970 to 0.986, we can confirm that the sorption of trisacrylamide blue follows the intra particle diffusion.
We are studied pseudo-order 2 of trisacrylamide blue by poly [(MAA-co-NVP)-cross-BAA] hydrogels shown in Fig. 2 and table 2. We are find that the correlation coefficients are around [0.870-0.918], also experimental sorption capacity are different to those theoretical sorption capacity. sorption of trisacrylamide blue (TB), probably does not follow the pseudo second order kinetic model.

Sorption Isotherm: We studied the Langmuir isotherm of hydrogels at temperature 25°C, the results obtained are illustrated by the figure 3 and table 3. We notice that the correlation coefficients vary from 0.56 to 0.71. We also find negative values of maximum sorption capacities and Langmuir constant these results lead us to conclude that the sorption of trisacrylamide probably does not follow the Langmuir isotherm.
We are studied the Freundlich isotherm of hydrogels at temperature 25°C the results obtained are presented by the figure 4 and table 4. We observe, in this case, the correlation coefficients vary from 0.980 to 0.982. Freundlich constants and values of heterogeneity factors are inversely proportional to NVP.

Table 3: Adsorption isotherm parameters at temperature 25°C

<table>
<thead>
<tr>
<th>Hydrogels</th>
<th>NVP%</th>
<th>T(°C)</th>
<th>Kf (L/g)</th>
<th>qo (mg/g)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly[(MAA-co-10% NVP)-cross-BAA]</td>
<td>10</td>
<td>25</td>
<td>-6.600</td>
<td>-0.170</td>
<td>0.560</td>
</tr>
<tr>
<td>Poly[(MAA-co-47.5% NVP)-cross-BAA]</td>
<td>47.5</td>
<td>25</td>
<td>-7.280</td>
<td>-0.140</td>
<td>0.610</td>
</tr>
<tr>
<td>Poly[(MAA-co-85% NVP)-cross-BAA]</td>
<td>85</td>
<td>25</td>
<td>-0.0015</td>
<td>-500</td>
<td>0.710</td>
</tr>
</tbody>
</table>

Figure 4: Linearized plot for Freundlich isotherm evaluation for adsorption of TB on Poly[(MAA-co-NVP)-cross-BAA] at temperature 25°C

Table 4: Adsorption isotherm parameters at temperature 25°C

<table>
<thead>
<tr>
<th>Hydrogel</th>
<th>NVP%</th>
<th>°C</th>
<th>Kf</th>
<th>n</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly[(MAA-co-NVP)-cross-BAA]</td>
<td>10</td>
<td>25</td>
<td>12.21</td>
<td>4.87</td>
<td>0.980</td>
</tr>
<tr>
<td>Poly[(MAA-co-47.5% NVP)-cross-BAA]</td>
<td>47.5</td>
<td>25</td>
<td>10.25</td>
<td>3.45</td>
<td>0.981</td>
</tr>
<tr>
<td>Poly[(MAA-co-85% NVP)-cross-BAA]</td>
<td>85</td>
<td>25</td>
<td>08.20</td>
<td>3.14</td>
<td>0.982</td>
</tr>
</tbody>
</table>

4. Conclusion

We studied sorption kinetics such as pseudo second order sorption and intra-particle diffusion, also the sorption isotherms by Langmuir and Freundlich model of dye trisacylamide blue. The variations of quantities of molecules adsorbed as a function of time by hydrogels are in very good agreement with the kinetic model intra-particle diffusion. Sorption isotherms were analyzed using Langmuir and Freundlich models. Experimental results confirm that the sorption isotherms were correlated by the Freundlich isotherm.

References


