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

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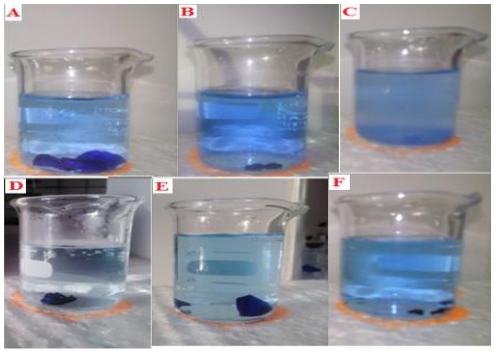
Abstract

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; C_0=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

Full length article **Corresponding Author*, e-mail: sebti.houari@yahoo.fr

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 adsorbents 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 bisarcylmide (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 700nm, 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):

$$\mathbf{q_t = \frac{(C_0 - C_t)V}{m}} \dots (\mathbf{1})$$

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].

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

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

$$\mathbf{q_t = k_i t^{0.5}} \dots (\mathbf{3})$$

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].

$$\mathbf{\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e} \dots (\mathbf{4})$$

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).

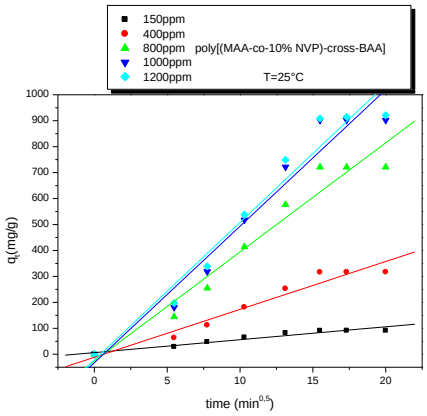
The Freundlich isotherm is model the multilayer adsorption and for the adsorption on heterogeneous surfaces. The Freundlich model is formulated in Eq [20].

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

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.



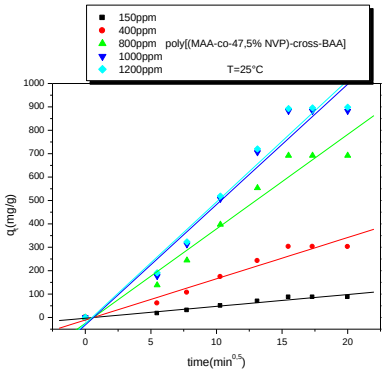
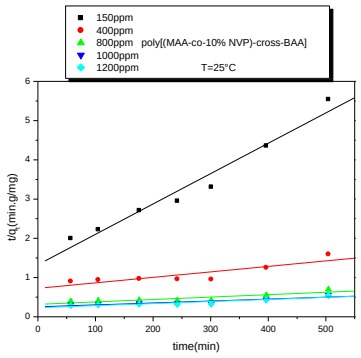


Figure 1: Intra particle diffusion for different initial concentration of dye plot of hydrogels on blue trisacrylamide

Table 1: Intra particle diffusion rate constants at 25°C

Hydrogels	NVP	C_0 mg/L	T	K_d	R^2
Poly[(MAA-co-NVP)-cross-BAA]	10	150	25	5.06	0.970
		400		18.45	0.980
		800		42.03	0.975
		1000		52.60	0.982
		1200		53.06	0.977
	47.5	150		4.88	0.986
		400		17.62	0.979
		800		40.35	0.978
		1000		51.43	0.974
		1200		51.99	0.977
	85	150		4.76	0.976
		400		17.27	0.975
		800		39.73	0.977
		1000		51.05	0.976
		1200		51.35	0.977

We are studied pseudo-order 2 of trisacrylamide blue by poly [(MAA-co-NVP)-cross-BAA hydrogels shown in Fig.2 and table2. 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.



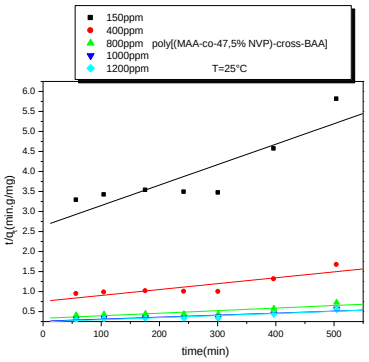


Figure 2: Pseudo-first-order model for different initial concentration of dye

Table 2: Rate constants, sorption capacity calculated q_{cal} and experimental q_e

Hydrogels	NVP	C_0mg/L	T°C	K_2 g.mg^{-1}.min^{-1}	$q_{e,exp}$ mg/g	q_{cal} mg/g	R^2
Poly[(MAA-co-NVP)-cross-BAA]	10	150	25	0.00583	91.050	129.87	0.918
		400		0.00194	316.550	714.28	0.872
		800		0.00197	721.021	1639.34	0.874
		1000		523.28	902.221	03.90	0.872
		1200		0.00226	920.960	1923.07	0.910
	47.5	150		0.00191	86.820	195.70	0.871
		400		0.00194	302.150	680.27	0.876
		800		0.00188	692.120	1562.50	0.876
		1000		0.00193	882.200	2000	0.862
		1200		0.00218	898.624	1886.79	0.903
	85	150		0.00193	81.820	184.84	0.882
		400		0.00194	296.280	666.66	0.872
		800		0.00197	681.550	1538.46	0.89
		1000		0.00192	876.020	2000	0.882
		1200		0.00221	886.289	1886.79	0.902

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.

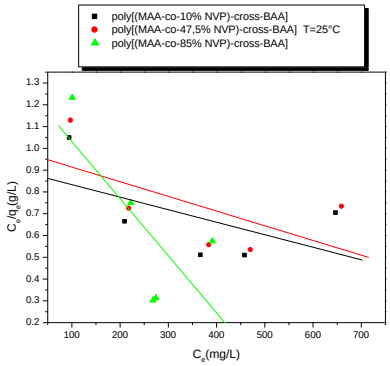


Figure3: Linearized plot for Langmuir isotherm evaluation for adsorption of TB on Poly[(MAA-co-NVP)-cross-BAA] at temperature 25°C

Table 3: Adsorption isotherm parameters at temperature 25°C

Hydrogels	NVP%	T(°C)	K_L (L/g)	q_m(mg/g)	R^2
Poly[(MAA-co-NVP)-cross-BAA]	10	25	-6.600	-0.170	0.560
	47.5		-7.280	-0.140	0.610
	85		-0.0015	-500	0.710

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.

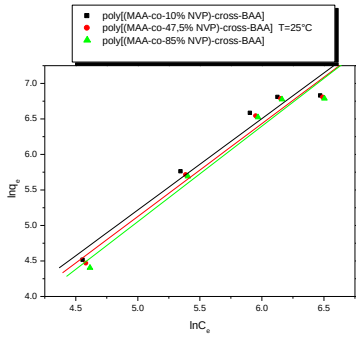


Figure 4: Linearized plot for Freundlich isotherm evaluation for adsorption of TB on Poly[(MAA-co-NVP)-cross-BAA] at temperature 25°C

Table 4: Adsorption isotherm parameters at temperature 25°C

Hydrogel	NVP % mol	T°C	K_F	n	R^2
Poly[(MAA-co-NVP)-cross-BAA]	10	25	12.21	4.87	0.980
	47.5		10.25	3.45	0.981
	85		08.20	3.14	0.982

4. Conclusion

We studied sorption kinetics such as pseudo second order sorption and intra-particular diffusion, also the sorption isotherms by Langmuir and Freundlich model of dye trisacrylamide 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.

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