ADSORPTION STUDIES FOR THE REMOVAL OF AMARANTH DYE FROM AQUEOUS SOLUTION USING LOW COST AGRICULTURAL RESIDUE

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RESUMO: Sementes de mamão Papaya foram usadas com adsorvente para remover o corante amaranto em soluções aquosas sintéticas. Os efeitos do pH, concentração inicial do corante e tempo de contato foram investigados. Os dados de equilíbrio de adsorção foram analisados pelas isotermas de Langmuir, Freundlich e Temkin. A cinética de adsorção foi testada utilizando os modelos de pseudo-primeira e segunda ordem e Elovich. O modelo de Langmuir foi o mais adequado para representar o processo de adsorção, onde se obteve uma capacidade máxima de adsorção de 37.4 mg g^{-1}. Observou-se uma rápida cinética e os dados seguiram o modelo de pseudo-segunda ordem. Os resultados demonstraram que as sementes de mamão é um adsorvente alternativo e de baixo custo para remover o corante amaranto em soluções aquosas.

PALAVRAS-CHAVE: semenstes de mamão, adsorção, corante, amaranto.

ABSTRACT: Papaya (*Carica papaya L.*) seeds were used as adsorbent to remove amaranth dye from synthetic wastewaters. The effects of pH, initial dye concentration and contact time were investigated. The equilibrium data were analyzed by Langmuir, Freundlich and Temkin isotherm models. Adsorption kinetic data were fitted with the pseudo-first order, pseudo second-order and Elovich models. It was found that the Langmuir model was the most suitable to represent the adsorption process, being the maximum adsorption capacity of 37.4 mg g^{-1}. A fast kinetic was observed and the data followed the pseudo second-order model. In summary, these results demonstrated that the papaya seeds are a low cost and alternative adsorbent to remove amaranth dye from aqueous solutions.

KEYWORDS: papaya seeds, adsorption, dyes, amaranth.

1. INTRODUCTION

Several industries such as pharmaceutical, textile and tanneries, generate dye containing effluents. These, when disposed into the environment, can cause adverse effects to the aquatic ecosystem and human life (Gupta and Suhas, 2009). Adsorption process using activated carbon has been widely used to treat dye containing wastewater (Foletto *et al.*, 2012; Ioannou and Simitzis, 2013; Zhang and Ou, 2013), but, it is relatively expensive. Therefore, low-cost materials from industrial or vegetable wastes may be used as alternative adsorbents for dye removal (Crini and Badot, 2008; Gupta and Suhas, 2009; Srinivasan and Viraraghavan, 2010; Yang et al. 2013) in order to make the adsorption process less expensive.

The use of papaya seed as adsorbent is very interesting because it is a low cost agricultural residue. Some recent studies reported that papaya seeds were satisfactory for dyes adsorption. Papaya seeds were effective to adsorb methylene blue (Hameed, 2009; Paz *et al.*, 2013), leather (Weber *et al.*, 2013) and textile (Foletto *et al.*, 2013) dyes. However, the use of papaya seeds for the adsorption of toxic pharmaceutical dyes is rarely reported. Amaranth is an anionic dye extensively used in food, cosmetic and pharmaceutical industries (Adii Ali *et al.*, 2011). This dye has a complex, aromatic and non-biodegradable structure. It is a recalcitrant molecule, and so, conventional physicochemical and biological treatment methods were not effective for its removal (Rêgo *et al.*, 2013).

In this context, the aim of this work was to evaluate the use of papaya seeds for the removal of amaranth from aqueous solution. The pH effect was evaluated; equilibrium and kinetics studies were carried out in order elucidate the adsorption process.

2. EXPERIMENTAL

2.1. Adsorbent and Adsorbate

Papaya seeds were prepared and characterized according our previous work (Foletto *et al.*, 2013). Papaya fruits were collected at a local farm. The seeds were removed from the fruit and dried at 85 ºC in an oven for 12 h followed by crushing in a knife-mill. The resulting material was sieved, and a portion with particle diameter between 350 and 450 μm was used in the experiments. The sample presented specific surface area (BET) of 0.23 m^2 g^{-1} and pore diameter of 332 Å. The SEM image showed a papaya seed particle containing a heterogeneous, irregular and rough surface (Foletto *et al.*, 2013).

Amaranth (molecular weight 604.5 g mol^{-1}; C.I. 16,185; $\lambda_{max} = 521$ nm) was supplied by a local manufacturer (Duas Rodas Ind.) and used without further purification. The optimized-three dimensional structural formula of Amaranth (obtained from ChemBio 3D 11.0.1 software (Cambridge Soft, USA)) is shown in Figure 1. All solutions were prepared using distilled water and reagents were of analytical-grade.

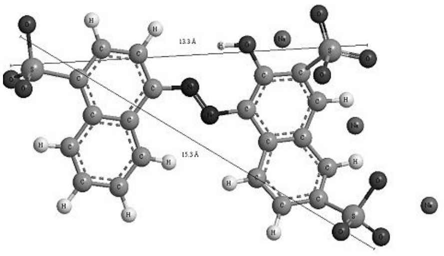

Figure 1. Three-dimensional chemical structure of amaranth.

2.2. Adsorption Assays

For the adsorption tests, 0.05 g of adsorbent was added into 100 mL of dye aqueous solution at different initial concentrations (20 to 70 mg L^{-1}). The adsorption tests were carried out in various pH (2.5 to 8.5), which were adjusted using H_2SO_4 and NaOH. The resulting solution was continuously stirred using a thermostatic orbital shaker (Tecnal, Brazil) until equilibrium, at constant temperature (25 ^{o}C). An aliquot of the aqueous solution was taken at various time intervals, centrifuged and filtered before analysis. The dye concentrations in aqueous solution were determined by spectrometry (Spectrovision model T6-UV). The adsorption capacities at any time (q_t) and at equilibrium (q_e) were calculated by the Equations 1 and 2, respectively:

$$q_t = \frac{V(C_0 - C_t)}{W} \tag{1}$$

$$q_e = \frac{V(C_0 - C_e)}{W} \tag{2}$$

where, C_o (mg L^{-1}) is the initial dye concentration, C_t (mg L^{-1}) is the dye concentration at any time (t), C_e (mg L^{-1}) is the equilibrium dye concentration W (g) is the adsorbent amount and V (L) is the volume of the solution. All adsorption experiments were carried out in duplicate and only the mean values were reported. The maximum deviation observed was about 6.5 %.

2.3. Equilibrium and Kinetic Models

In order to evaluate the adsorption equilibrium, the models nominated, Langmuir, Freundlich and Temkin were applied (Liu and Liu, 2008). These models are given by the Equations 3, 4 and 5:

$$q_e = \frac{q_m k_L C_e}{1 + (k_L C_e)} \tag{3}$$

$$q_e = k_F C_e^{1/n_F} \tag{4}$$

$$q_e = \frac{RT}{B} \ln(A_T C_e) \tag{5}$$

where, q_m is the maximum adsorption capacity (mg g^{-1}), k_L is the Langmuir constant (L mg^{-1}), k_F is the Freundlich constant (mg g^{-1})(mg L^{-1})$^{-1/nF}$, $1/n_F$ is the heterogeneity factor, R is the universal gas constant (kJ mol^{-1} K^{-1}), T is the temperature (K), B is related to the adsorption heat and A_T is the Temkin constant (L mg^{-1}).

The kinetic curves were obtained under different initial concentrations, ranging from 20 to 70 mg L^{-1}. Pseudo first-order, pseudo second-order and Elovich models (Qiu *et al.*, 2009) were fitted to the experimental data. These models are shown in Equations 6, 7 and 8:

$$q_t = q_1(1 - \exp(-k_1 t)) \tag{6}$$

$$q_t = \frac{t}{(1/k_2 q_2{}^2) + (t/q_2)} \tag{7}$$

$$q_t = \frac{1}{a}\ln(1 + abt) \tag{8}$$

where, k_1 and k_2 are the rate constants of pseudo first-order and pseudo second-order models, respectively in (min^{-1}) and (g mg^{-1} min^{-1}), q_1 and q_2 are the theoretical values for the adsorption capacity (mg g^{-1}), a is the initial velocity due to dq/dt with q_t=0 (mg g^{-1} min^{-1}), b is the desorption constant of the Elovich model (g mg^{-1}) and t is the time (min).

The kinetic and isotherm parameters were found by nonlinear regression using the software Statistica 6.0 (Statsoft, USA). The fit quality was measured according to the coefficient of determination (R^2) and average relative error (ARE) (El-Khaiary and Malash, 2011).

3. RESULTS AND DISCUSSION

3.1. pH Effect

The effect of pH was evaluated under the following fixed conditions: initial dye concentration of 20 mg L^{-1}, temperature of 298 K, 0.05 g of adsorbent and volume of solution 0.1 L. The results are shown in Figure 2.

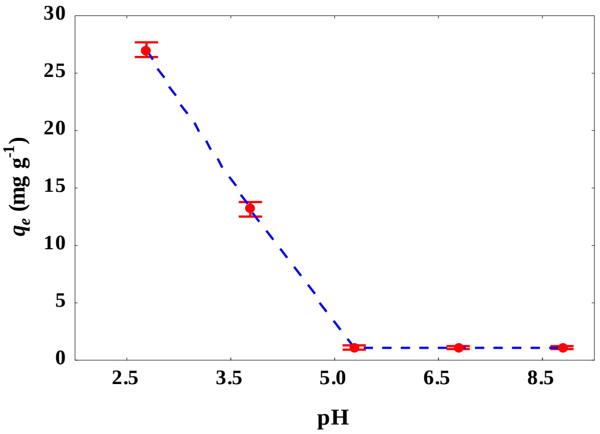

Figure 2. Effect of pH on the adsorption (C$_o$=20 mg L^{-1}, T=298 K).

The pH increase from 2.5 to 8.5 caused a strong decrease in adsorption capacity (Figure 2). The point of zero charge of the papaya seeds is pH$_{pzc}$=6.25 (Unuabonah *et al.*, 2009). So, when pH>pH$_{pzc}$, the surface charge of papaya seeds is negative, leading to an electrostatic repulsion of the anionic dyes (see Figure 1). On the contrary, when pH<pH$_{pzc}$, the hydrogen atoms (H$^+$) in solution tends to protonate the papaya seeds surface, facilitating the electrostatic interactions with the anionic dyes (Dotto and Pinto, 2011). The more adequate pH for the adsorption of Amaranth was 2.5 and this pH was then selected for the sequence of the study.

3.2. Equilibrium Study

The equilibrium curve was obtained at 298 K, using 0.05 g of adsorbent at pH of 2.5. The isotherm curve is shown in Figure 3. Table 1 shows the equilibrium parameters.

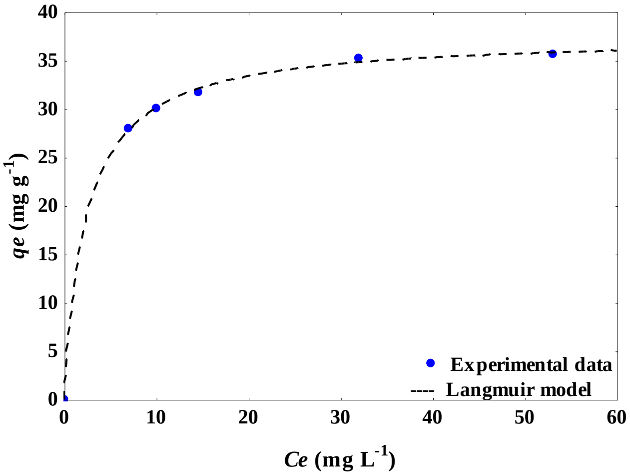

Figure 3. Equilibrium curve for the adsorption of Amaranth onto papaya seeds.

Table 1. Equilibrium parameters.

Model	
Langmuir	
q_m (mg g^{-1})	37.4
k_L (L mg^{-1})	0.4098
R^2	0.9994
ARE (%)	1.52
Freundlich	
k_F (mg g^{-1})(mg L^{-1})$^{-1/nF}$	22.7
$1/n_F$	0.119
R^2	0.9329
ARE (%)	9.76
Temkin	
A_T (L mg^{-1})	214.3
B	0.63
R^2	0.8145
ARE (%)	15.82

The adsorption isotherm curve was characterized by an initial step with increase in adsorption capacity followed by a convex shape (Figure 3). The initial step indicates a great papaya seeds-amaranth affinity and numerous readily accessible sites. The convex shape suggests the formation of a monomolecular layer of amaranth on the papaya seeds surface (Dotto *et al.*, 2012). The higher values of the coefficient of determination and the lower values of the average relative error (Table 1), indicated that the Langmuir model was the more appropriate to represent the adsorption of amaranth on papaya seeds. The maximum adsorption capacity was 37.4 mg g^{-1} (Table 1). Comparing these values with the literature cited in this work, it can be affirmed that papaya seeds are an alternative adsorbent to remove amaranth dye from aqueous solutions.

3.3. Kinetic Study

Kinetic curves were obtained at pH 2.5 and temperature of 298 K. The effect of initial dye concentration (20-70 mg L^{-1}) was evaluated. The kinetic curves are shown in Figure 4.

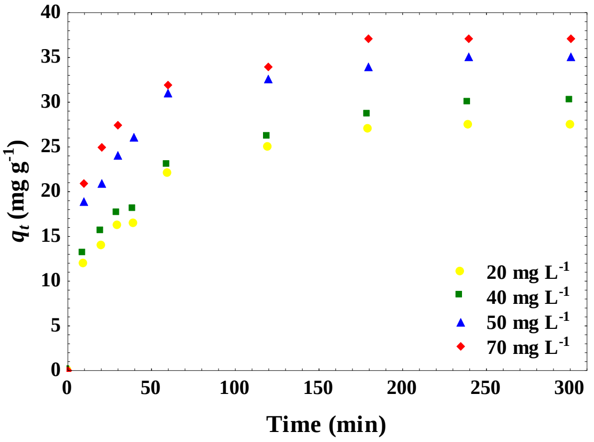

Figure 4. Kinetic curves for the adsorption of amaranth onto papaya seeds (pH 2.5 and 298 K).

The kinetic curves revealed a fast adsorption process, where about 80-90% of saturation was attained at 80 min. Later, adsorption rate decreased considerably, being the equilibrium attained at about 180-200 min. It was found that the q_t values increased as a function of C_0 increase (Figure 4). Similar behavior was verified by Weber *et al.* (2013) in the adsorption of Direct Black 38 onto papaya seeds. Table 2 shows the kinetic parameters for the adsorption of amaranth onto papaya seeds.

The high values of the coefficient of determination and the low values of the average relative error (Table 2) demonstrated that the pseudo second-order model was the more adequate to represent the adsorption kinetics of the amaranth dye onto papaya seeds. The values of q_2 and k_2 increased as a function of the C_0 increase (Table 2). This shows that more dye was adsorbed and the process was faster at high concentrations.

Table 2. Kinetic parameters.

Model	**C_0 (mg L^{-1})**			
	20	**40**	**50**	**70**
Pseudo first-order				
q_1 (mg g^{-1})	24.2	25.3	33.4	34.8
k_1 (min^{-1})	0.015	0.017	0.029	0.036
R^2	0.941	0.965	0.969	0.971
ARE (%)	9.69	7.67	10.0	5.45
Pseudo second-order				
q_2 (mg g^{-1})	21.2	22.1	31.5	32.8
k_2 (g mg^{-1} min^{-1})	0.002	0.002	0.003	0.003
R^2	0.999	0.999	0.995	0.997
ARE (%)	7.88	1.05	7.50	8.41
Elovich				
a (mg g^{-1} min^{-1})	0.196	0.193	0.160	0.163
b (g mg^{-1})	7.67	8.02	11.34	12.54
R^2	0.961	0.956	0.952	0.978
ARE (%)	8.19	10.15	10.03	7.58

4. CONCLUSIONS

In this study, papaya seeds were applied successfully for the removal of Amaranth dye from aqueous solution. pH of 2.5 was the more adequate for the amaranth adsorption onto papaya seeds. The Langmuir model was the most suitable to represent the equilibrium data, being the maximum adsorption capacity of 37.4 mg g^{-1}. The kinetic studies revealed that about 80-90% of saturation was attained at 80 min, being the equilibrium attained at about 180-200 min. Pseudo second-order model was suitable to represent the adsorption kinetics.

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