

Removal of hazardous pharmaceutical dyes by adsorption onto papaya seeds

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ABSTRACT

Papaya (*Carica papaya* L.) seeds were used as adsorbent to remove toxic pharmaceutical dyes (tartrazine and amaranth) from aqueous solutions, in order to extend application range. The effects of pH, initial dye concentration, contact time and temperature were investigated. The kinetic data were evaluated by the pseudo first-order, pseudo second-order and Elovich models. The equilibrium was evaluated by the Langmuir, Freundlich and Temkin isotherm models. It was found that adsorption favored a pH of 2.5, temperature of 298 K and equilibrium was attained at 180–200 min. The adsorption kinetics followed the pseudo second-order model, and the equilibrium was well represented by the Langmuir model. The maximum adsorption capacities were 51.0 and 37.4 mg g⁻¹ for tartrazine and amaranth, respectively. These results revealed that papaya seeds can be used as an alternative adsorbent to remove pharmaceutical dyes from aqueous solutions.

Key words | adsorption, amaranth, dyes, papaya seeds, tartrazine

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INTRODUCTION

Several industries, such as pharmaceuticals, textiles and tanneries generate dye containing effluents. The inadequate release of these effluents into the environment can cause adverse effects on the aquatic ecosystem and on human life (Gupta & Suhas 2009). Specifically, tartrazine and amaranth are toxic pharmaceutical azo dyes and can be degraded into aromatic amines, which are very harmful. These dyes are carcinogenic, mutagenic, cause hyperactivity in children, hypersensitivity and allergic reactions (Kobylewski & Jacobson 2010). Accordingly, the search for alternatives to remove these dyes is necessary.

Many techniques have been used to treat dye containing effluents (Gupta & Suhas 2009). Among these, adsorption with activated carbon is one of the most commonly employed methods for the removal of synthetic dyes from aqueous effluents, due its simplicity and high efficiency (Foletto *et al.* 2012; Zhang & Ou 2013). However, the costs of production and regeneration of activated carbon are high (Gupta & Suhas 2009). Therefore, low-cost materials from industrial or vegetable wastes may be used as promising adsorbents in order to make the

adsorption process less expensive (Weng *et al.* 2001; Yang *et al.* 2013).

Some studies reported that papaya seeds were adequate for the removal of dyes from aqueous solutions. Papaya seeds were effective for removing methylene blue (Hameed 2009), from leather (Weber *et al.* 2013) and textile (Foletto *et al.* 2013) dyes. However, an adsorbent should be adequate for a wide range of dyes, and the use of papaya seeds for the adsorption of hazardous pharmaceutical dyes has not been reported yet. The use of papaya seeds as adsorbent is very interesting because it is a widely available and low-cost agricultural residue (Hameed 2009).

In this context, the aim of this work was to investigate the use of papaya seeds as an alternative adsorbent for the removal of tartrazine and amaranth from aqueous solutions. First, the effect of pH was investigated. Next, kinetic studies were carried out under different initial dye concentrations and the pseudo first-order, pseudo second-order and Elovich models were fitted to the experimental data. Finally, the equilibrium was evaluated under different temperatures by the Langmuir, Freundlich and Temkin models.

MATERIALS AND METHODS

Adsorbent and dyes

Papaya seeds were prepared and characterized according our previously published work (Foletto *et al.* 2013). Papaya fruits were collected at a local farm. The seeds were removed from the fruit, washed, oven dried at 85 °C for 12 h and ground in a knife-mill (Wiley Mill Standard, 03, USA). The resulting material was sieved, and a portion with a particle diameter between 350 and 450 μm was used in the experiments. The seeds presented a specific surface area of 0.23 $\text{m}^2 \text{g}^{-1}$ and pore diameter of 332 Å. The scanning electron microscopy image showed papaya seeds containing a heterogeneous, irregular and rough surface.

Tartrazine (molecular weight 534.4 g mol^{-1} ; color index 19140; and $\lambda_{\text{max}} = 426 \text{ nm}$) and amaranth (molecular weight 604.5 g mol^{-1} ; color index 16185; and $\lambda_{\text{max}} = 521 \text{ nm}$) with purity higher than 85% were supplied by a local manufacturer (Duas Rodas Ind.). The chemical structure of the dyes is presented in Figure 1. All solutions were prepared using distilled water and the reagents were of analytical grade.

Adsorption assays

The adsorption assays were carried out in a batch system using a thermostated orbital shaker (Tecnal, TE-141, Brazil). The effects of pH (2.5–8.5) (which were adjusted using H_2SO_4 and NaOH), initial dye concentration (20–70 mg L^{-1}), contact time (0–300 min) and temperature (298–328 K) were investigated. These conditions were determined by preliminary tests. 0.05 g of adsorbent was added into 100 mL of dye aqueous solution in determined experimental conditions. The resulting solution was continuously stirred at 100 rpm until the equilibrium was reached. Aliquots were taken at various time intervals, centrifuged at 4,000 rpm for 20 min (Centribio, 80-2B, Brazil)

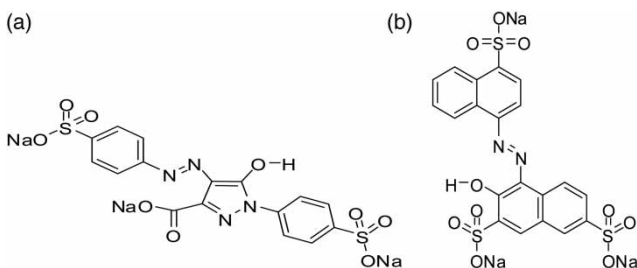


Figure 1 | Chemical structure of the dyes: (a) tartrazine and (b) amaranth.

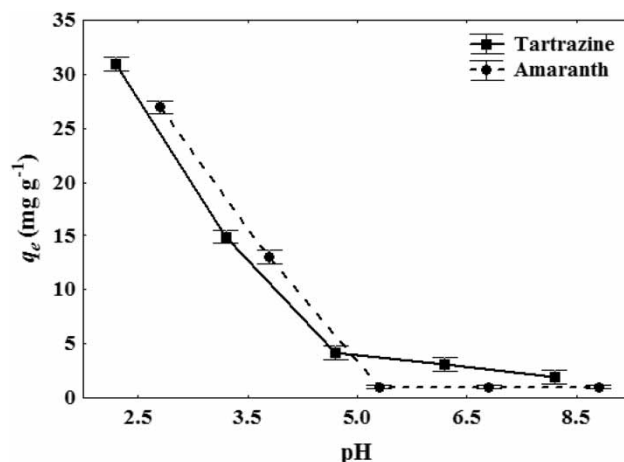


Figure 2 | Effect of pH on the adsorption of pharmaceutical dyes onto papaya seeds ($C_0 = 20 \text{ mg L}^{-1}$ and $T = 298 \text{ K}$).

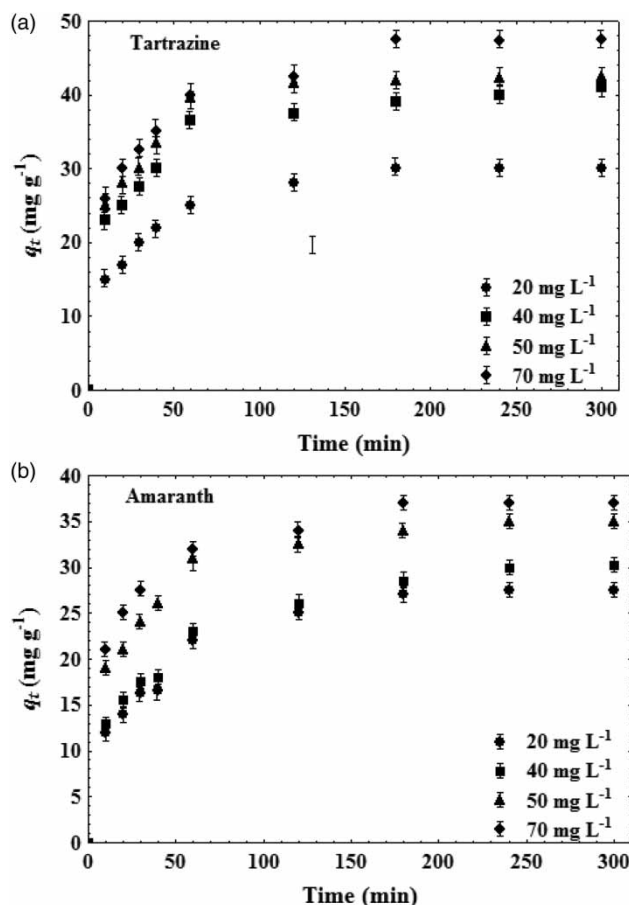


Figure 3 | Kinetic curves for the adsorption of tartrazine (a) and amaranth (b) onto papaya seeds (pH 2.5 and 298 K).

and filtered (Whatman No. 40) before analysis. The dye concentration was determined by spectrometry (Spectro Vision, T6-UV, Brazil). The mass of dye adsorbed per gram of

adsorbent at any time (q_t (mg g⁻¹)) and at equilibrium (q_e (mg g⁻¹)) were calculated as follows (Crini & Badot 2008):

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

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

where C_0 , C_t and C_e (mg L⁻¹) are the dye concentrations at $t = 0$, at any time and at equilibrium, respectively, W (g) is the adsorbent amount and V (L) is the volume of the solution.

Kinetic and equilibrium models

For both dyes, kinetic curves were obtained under different initial concentrations, ranging from 20 to 70 mg L⁻¹. Pseudo first-order (Lagergren 1898), pseudo second-order (Ho & McKay 1998) and Elovich models (Zeldowitsch 1934) were fitted to the experimental data in order to investigate the adsorption kinetics. These models are given by the following equations:

$$q_t = q_1(1 - \exp(-k_1 t)) \quad (3)$$

$$q_t = \frac{t}{(1/k_2 q_2^2) + (t/q_2)} \quad (4)$$

$$q_t = \frac{1}{a} \ln(1 + abt) \quad (5)$$

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 equilibrium curves were obtained at different temperatures (298, 308, 318 and 328 K). In order to fit the experimental equilibrium data, Langmuir (Langmuir 1918), Freundlich (Freundlich 1906) and Temkin (Temkin 1941) isotherm models were applied. These models are given by the following equations:

$$q_e = \frac{q_m k_L C_e}{1 + (k_L C_e)} \quad (6)$$

$$q_e = k_F C_e^{1/n_F} \quad (7)$$

Table 1 | Kinetic parameters for the adsorption of tartrazine and amaranth onto papaya seeds

Models	Tartrazine				Amaranth			
	20 (mg L ⁻¹)	40 (mg L ⁻¹)	50 (mg L ⁻¹)	70 (mg L ⁻¹)	20 (mg L ⁻¹)	40 (mg L ⁻¹)	50 (mg L ⁻¹)	70 (mg L ⁻¹)
Pseudo first-order								
q_1	27.7	38.3	40.4	41.1	24.2	25.3	33.4	34.8
k_1	0.024	0.018	0.020	0.016	0.015	0.017	0.029	0.036
R^2	0.923	0.943	0.951	0.973	0.941	0.965	0.969	0.971
ARE (%)	14.5	8.93	9.61	8.12	9.69	7.67	10.0	5.45
Pseudo second-order								
q_2	27.8	40.0	41.9	45.4	21.2	22.1	31.5	32.8
k_2	0.0020	0.0027	0.0029	0.0030	0.0020	0.0022	0.0028	0.0030
R^2	0.993	0.995	0.991	0.998	0.999	0.999	0.995	0.997
ARE (%)	5.22	3.45	8.93	8.51	7.88	1.05	7.50	8.41
Elovich								
a	0.160	0.140	0.138	0.134	0.196	0.193	0.160	0.163
b	20.66	20.07	20.87	20.01	7.67	8.02	11.34	12.54
R^2	0.958	0.971	0.965	0.980	0.961	0.956	0.952	0.978
ARE (%)	9.38	8.26	7.97	6.11	8.19	10.15	10.03	7.58
q_e (exp)	33.3	42.8	44.8	46.0	28.0	31.6	35.3	35.6

$$q_e = \frac{RT}{B} \ln(A_T C_e) \quad (8)$$

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}) $^{-1/n_F}$, $1/n_F$ is the heterogeneity factor, R is the universal gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$), T is the temperature (K), B is related to the adsorption heat and A_T is the Temkin constant (L mg^{-1}).

The kinetic and isotherm parameters were found by non-linear 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).

RESULTS AND DISCUSSION

Effect of pH

The effect of pH was evaluated under the following 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.

For both dyes, it can be seen (Figure 2) that the pH increase from 2.5 to 8.5 caused a strong decrease in adsorption capacity. This behavior can be explained on the basis of the point of zero charge of the papaya seeds ($\text{pH}_{\text{pzc}} = 6.25$) (Unuabonah *et al.* 2009). Under basic conditions ($\text{pH} > \text{pH}_{\text{pzc}}$) the surface charge of papaya seeds is negative, leading to an electrostatic repulsion of the anionic dyes (see Figure 1). However, under acid conditions ($\text{pH} < \text{pH}_{\text{pzc}}$) the hydrogen atoms (H^+) in the solution tend to protonate the papaya seeds' surface, facilitating electrostatic interactions with the anionic dyes. A similar trend was obtained by Rêgo *et al.* (2013) in the adsorption of tartrazine and amaranth on chitosan films. In this work, the more adequate pH for the adsorption of tartrazine and amaranth was 2.5, and so this pH was selected for the study sequence.

Kinetic study

Kinetic curves were obtained at pH 2.5 and a temperature of 298 K. The effect of the initial dye concentration ($20\text{--}70 \text{ mg L}^{-1}$) was evaluated. The kinetic curves are shown in Figure 3.

The kinetic curves revealed a fast adsorption process, where about 80–90% of saturation was attained at 80 min.

Later, the adsorption rate decreased considerably, with equilibrium being attained at 180–200 min. It was found that the q_t values increased as a function of C_0 increase (Figure 3). This behavior can be explained by two facts: (1) at higher values of C_0 , the concentration gradient between the bulk solution and the adsorbent external surface is higher, facilitating the external mass transfer; and (2) at higher values of C_0 , the mass flux of dye by surface diffusion is increased. Similar behavior was verified by Weber *et al.* (2013) in the adsorption of Direct Black 38 onto papaya seeds. Table 1 shows the kinetic parameters for the adsorption of tartrazine and amaranth onto papaya seeds.

The high values of the coefficient of determination ($R^2 > 0.99$) and the low values of the ARE (ARE < 10.0%) demonstrated that the pseudo second-order model was the more adequate to represent the adsorption kinetics of the pharmaceutical dyes onto papaya seeds. The values of q_2 and k_2 increased as a function of the C_0 increase

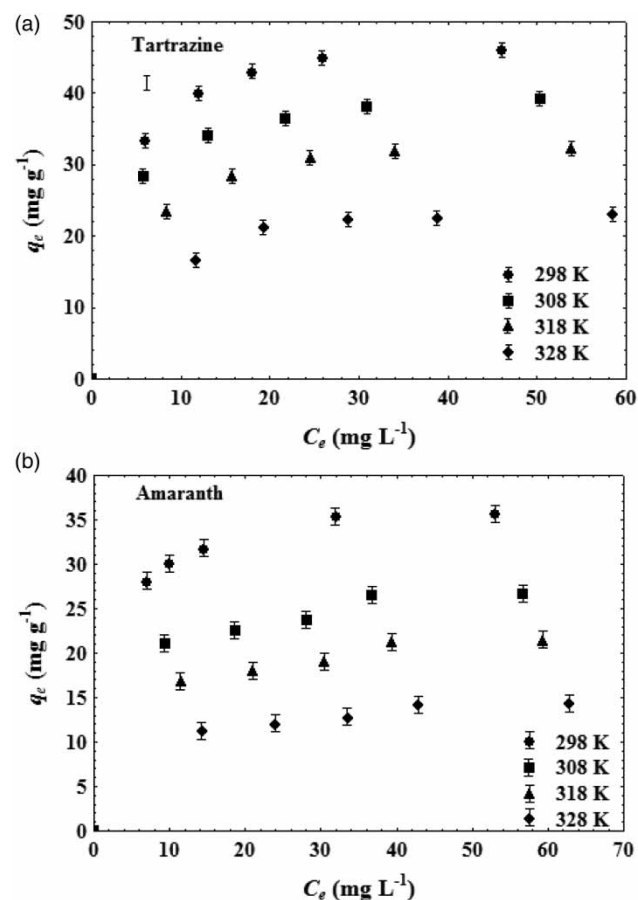


Figure 4 | Equilibrium curves for the adsorption of tartrazine (a) and amaranth (b) onto papaya seeds (pH 2.5).

Table 2 | Isotherm parameters for the adsorption of tartrazine and amaranth onto papaya seeds

Models	Tartrazine				Amaranth			
	298 K	308 K	318 K	328 K	298 K	308 K	318 K	328 K
Langmuir								
q_m	51.0	41.1	35.3	25.8	37.4	28.0	22.8	15.6
k_L	0.373	0.353	0.245	0.182	0.410	0.279	0.215	0.161
R^2	0.999	0.999	0.998	0.999	0.996	0.997	0.999	0.995
ARE (%)	1.12	1.71	3.45	4.32	2.78	4.00	2.95	3.61
Freundlich								
k_F	26.9	22.8	17.6	12.0	22.7	14.9	11.2	6.9
$1/n_F$	0.144	0.149	0.162	0.169	0.119	0.148	0.161	0.178
R^2	0.951	0.943	0.948	0.963	0.970	0.972	0.941	0.958
ARE (%)	7.89	9.38	9.47	7.05	6.29	8.51	12.69	8.43
Temkin								
A_T	40.4	52.4	18.4	11.1	214.3	39.0	19.2	9.2
B	0.39	0.51	0.54	0.74	0.63	0.75	0.86	1.21
R^2	0.901	0.889	0.898	0.891	0.931	0.877	0.907	0.904
ARE (%)	11.28	10.18	13.40	13.21	10.12	15.07	11.50	12.11
$q_e(\text{exp})$	46.0	39.1	32.2	23.0	35.6	26.7	21.4	14.2

(Table 1). This shows that more dye was adsorbed and the process was faster at high concentrations.

Equilibrium study

The equilibrium curves were obtained at 298, 308, 318 and 328 K, using 0.05 g of adsorbent at pH 2.5. The curves are shown in Figure 4.

Figure 4 shows that the adsorption isotherm curves were characterized by an initial step with an increase in the adsorption capacity followed by a convex shape. The initial step indicates a great papaya seeds–dyes affinity and numerous readily accessible sites. The convex shape suggests the formation of a monomolecular layer of the dyes on the papaya seeds' surface (Dotto *et al.* 2012). The adsorption capacity increased with temperature decrease reaching maximum values at 298 K (Figure 4). Similar behavior was verified by Dotto *et al.* (2012) in the adsorption of Acid Blue 9 and FD&C red 40 on *Spirulina platensis*. The experimental equilibrium curves were fitted with Langmuir, Freundlich and Temkin models. These results are shown in Table 2.

The higher values of the coefficient of determination ($R^2 > 0.99$) and the lower values of the ARE (ARE < 5.0%) were found for the Langmuir model. In this way, the

Langmuir model was the more appropriate to represent the adsorption of pharmaceutical dyes on papaya seeds. The k_L values increased as a function of the temperature decrease, indicating that the papaya seeds–dyes affinity was higher at 298 K. A similar trend was verified for the q_m parameter, being the maximum adsorption capacities 51.0 and 37.4 mg g⁻¹, for tartrazine and amaranth, respectively, obtained at 298 K. Comparing these values with the literature cited in this work, it can be affirmed that papaya seeds are an alternative adsorbent to remove pharmaceutical dyes from aqueous solutions.

CONCLUSIONS

Papaya seeds were tested as adsorbent to remove tartrazine and amaranth from aqueous solutions. The adsorption favored high concentrations, pH of 2.5, temperature of 298 K; equilibrium was attained at 180–200 min. The adsorption kinetics followed the pseudo second-order model and equilibrium was well represented by the Langmuir model. The maximum adsorption capacities were 51.0 and 37.4 mg g⁻¹, for tartrazine and amaranth, respectively. These results revealed that papaya seeds can be used as an alternative adsorbent to remove pharmaceutical dyes from aqueous solutions.

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First received 8 October 2013; accepted in revised form 10 April 2014. Available online 23 April 2014