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BASIC DYESTUFFS REMOVAL FROM TEXTILE EFFLUENTS USING FEATHERS: EQUILIBRIUM, KINETIC AND COLUMN STUDIES

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ABSTRACT

This research work has been focused in the study of gallinaceous feathers, a waste that may be valorised as sorbent, to remove the Dark Blue Astrazon 2RN (DBA) from Dystar.

This study was focused on the following aspects: optimization of experimental conditions through factorial design methodology, kinetic studies into a continuous stirred tank adsorber (at pH 7 and 20ºC), equilibrium isotherms (at pH 5, 7 and 9 at 20 and 45ºC) and column studies (at 20ºC, at pH 5, 7 and 9). In order to evaluate the influence of the presence of other components in the sorption of the dyestuff, all experiments were performed both for the dyestuff in aqueous solution and in real textile effluent.

The pseudo-first and pseudo-second order kinetic models were fitted to the experimental data, being the latter the best fit for the aqueous solution of dyestuff. For the real effluent both models fit the experimental results and there is no statistical difference between them. The Central Composite Design (CCD) was used to evaluate the effects of temperature (15 - 45ºC) and pH (5 - 9) over the sorption in aqueous solution. The influence of pH was more significant than temperature. The optimal conditions selected were 45ºC and pH 9. Both Langmuir and Freundlich models could fit the equilibrium data. In the concentration range studied, the highest sorbent capacity was obtained for the optimal conditions in aqueous solution, which corresponds to a maximum capacity of 47± 4 mg g^{-1}.

The Yoon-Nelson, Thomas and Yan's models fitted well the column experimental data. The highest breakthrough time for 50% removal, 170 min, was obtained at pH 9 in aqueous solution. The presence of the dyeing agents in the real wastewater decreased the sorption of the dyestuff mostly for pH 9, which is the optimal pH. The effect of pH is less pronounced in the real effluent than in aqueous solution. This work shows that feathers can be used as sorbent in the treatment of textile wastewaters containing DBA.

KEYWORDS: basic dyes, column, equilibrium, kinetics, low cost materials, sorption, wastewater.

1. INTRODUCTION

Textile dyestuffs should be removed from wastewaters because they can cause reduction in the primary production that will affect the aquatic ecosystem, and also for aesthetical reasons. Besides some of them may also be toxic, namely basic dyes (Anliker *et al.*, 1988), which are considered one of the more problematic classes of dyes (El Qada *et al.*, 2008). Their use has been increasing due to the increment of acrylic fibres production (1.4%) in the last decades, which are dyed using basic (cationic) dyes. The 2002 global production was 2.7 million of metric tons (Fiber Economics Bureau, 2003).

Sorption has been considered as one of the most efficient technologies for colour removal (Crini, 2006). Activated carbon is one of the most widely used adsorbents in textile wastewater treatment. However, this treatment presents high operation costs, due to the high price of the activated carbon and to the high volume of effluent involved.

In the last decades research has been directed towards alternative sorbents to replace the costly activated carbon. They are considered low-cost sorbents if they require little processing, are abundant in nature or are by-products or waste materials from industry (Bailey *et al.*, 1999). Certain waste products from industrial and agricultural operations, natural materials and biosorbents represent potentially economical alternative sorbents. Many of them have been tested and proposed for dye removal (Crini, 2006; Gupta and Suhas, 2009; Srinivasan and Viraraghavan, 2010).

Feathers are generated in huge quantities as a waste of the commercial poultry processing plants, which poses a disposal problem (Mittal *et al.*, 2007) and may be valorised as sorbent. Gallinaceous feathers were selected as sorbent for the basic dye Dark Blue Astrazon 2RN (from Dystar), which is a poorly biodegradable dyestuff (less than 10%) and toxic to fish (Dystar, 2002).

This study was focused on the following aspects: optimization of experimental conditions through factorial design methodology, kinetic studies into a continuous stirred tank adsorber, equilibrium isotherms and column studies. In order to evaluate the influence of the presence of other components in the sorption of the dyestuff, all experiments were performed both for the dyestuff in aqueous solution and in real textile effluent.

2. MATERIALS AND METHODS

2.1. Materials

The basic dyestuff Dark Blue Astrazon 2RN (DBA), kindly supplied by Dystar, is a mixture of two basic dyestuffs, 45 – 55% of Basic Green 4 (CI 42000) and 35 – 40% of Basic Red 14 (CI 48016). Dyestuff solutions, at 20 ppm concentration, were prepared with distilled water and were boiled for 30 min for complete dissolution. The real effluent, containing only the selected dyestuff and the auxiliary dyeing agents (Sera Tard A-AS, Evo Soft S-OT, Sera Sperse M-IW, Sera Lube M-UFC and sodium acetate), was also kindly provided by Dystar. The final pH was adjusted to the desired value with chloridric acid or sodium hydroxide.

Gallinaceous feathers from a local poultry processing industry were used. They were washed with water and detergent, then thoroughly rinsed with water and finally dried in the air at room temperature (20ºC) for several days. Feathers were ground in a knives mill.

2.2. Methods

The dyestuff concentration of each sample was obtained by measuring its absorbance in a UV-Vis spectrophotometer (Jenway 6100) at the maximum absorbance wavelength (518 nm). The pH values were evaluated using a Consort C862 multiparameter analyser.

Kinetic studies were performed at pH 7 and 20ºC, using 1 g L^{-1} sorbent concentration (900 mL of total volume). Magnetic stirring (SBS) at 400 rpm was used and samples were taken during the experiments, along 1 day. pH was measured continuously. A centrifuge (Sartorius, Sigma 2-16) was used to separate the feathers and then dyestuff concentration was evaluated.

Factorial planning was used to evaluate the effects of temperature (15-45ºC) and pH (5-9), over the dyestuff sorption in aqueous solution. A set of 100 mL Erlenmeyers (with cap) containing 50.00 mL of solution and 0.05 g of feathers was used. Agitation was performed at 400 rpm using a magnetic stirrer (Velp, Multistirrer 15) into a refrigerated incubator (Lovibond). Replicates and a control test (without sorbent) were made.

Equilibrium isotherms were determined, using the same experimental procedure that was used in factorial design studies, except that different amounts of sorbent were used and no replicates were made. Different experimental conditions were tested for pH (5, 7 and 9) and temperature (20 and 45ºC).

Column experiments were performed using a glass column (Omnifit), with 2.5 cm inside diameter and 15 cm height column. The dyestuff solution was pumped (Gilson, Miniplus 3) downflow at 5 cm^3 min^{-1} flowrate. After weighing 4 g of feathers, they were immersed in distilled water and the air in the adsorbent pores was removed by a vacuum pump, to allow a full contact sorbent/dyestuff. Then they were placed inside the column. The average dyestuff concentration used was of 70 mg L^{-1}. Samples were collected at the column outlet, allowing the determination of the dyestuff concentration and pH.

3. RESULTS

This research includes different steps: kinetic studies, optimization of experimental conditions, equilibrium isotherms and column studies. All experiments were performed both for the dyestuff in aqueous solution and in real textile effluent in order to evaluate the influence of the presence of other components in the sorption of the Dark Blue Astrazon 2RN.

The software Fig.P (version 2.98) was used for the non-linear adjustment to models. The statistic treatment allowed the determination of the confidence intervals at 95% for each parameter of the model, the variance (s^2) and the determination factor (r^2) for each model. The Fisher's test was used to compare models based on the F value for each model (F_{calc}) and F critical value (F_c) for a probability of 95%.

3.1. Kinetics

The kinetic studies were performed at pH 7 and 20ºC both for the dyestuff in aqueous solution and for the real effluent (Figure 1), respectively with initial concentrations of 20 and 73 mg L^{-1}. The equilibrium times obtained were 2 and 3 h, respectively for the dyestuff in aqueous solution and in the real effluent. For convenience a contact period of 24 h was adopted in further experiments. The pH showed a slight decreased in the dyestuff aqueous solution (from 7.0 to 6.2) and it had no variation in the textile effluent, which might be explained by the buffer capacity given by the dyeing agents present in the wastewater.

The Lagergren's (1898) pseudo-first and Ho's (1995) pseudo-second order models were fitted to the experimental data. The parameters of the models and their statistics are presented in Table 1. Accordingly to Fisher's test the best fit for the aqueous solution of dyestuff was the pseudo-second order model; both models could fit the experimental results of the real effluent and there was no statistical difference between them, although the pseudo-second order model adjusts better to the shape of the experimental data.

3.2. Optimization

The optimization of experimental conditions was performed through factorial design methodology using JMP "The Statistic Software (version 5)". The Central Composite Design (CCD) was used to evaluate the effects of temperature and pH over the sorption in aqueous solution. They were evaluated at three levels (-1, 0, +1) for temperature (15, 30, 45ºC) and pH (5, 7, 9), respectively, which are possible working ranges for this kind of effluent. The analysis of variance (ANOVA) of the quadratic model for dyestuff sorption by feathers show high significance of the model (Table 2) and has a determination factor of 0.946. The mathematical model that represents the influence of variables, their interactions and the statistics of the regression are presented in Table 3. The linear effects of pH and temperature, their interaction and the quadratic effect of temperature are significant, being the influence of pH more significant than temperature. The optimal conditions selected were 45ºC and pH 9.

Sorption of the cationic dye DBA is enhanced at higher pH values. This might be explained by the attraction between the dyestuff (positively charged) and the feathers negatively charged (Mittal, 2006b) when the pH value of the solution is higher than the point of zero charge (Noh and Schwarz, 1991).

Temperature rise has a favourable effect on adsorption rate, which might be related to swelling of the porous structure of feathers allowing a further penetration of the large dyestuff molecule, as observed in chitin by McKay *et al.* (1982).

3.3. Equilibrium

The equilibrium studies were performed using the optimal conditions, pH 9 and 45ºC. However both the correction of pH from 5 (the original pH of the effluent) to 9 (the optimal pH value) and the warming up of the effluent from 20ºC (usually the temperature of the effluent) to 45ºC (the optimal temperature) would have costs. Therefore isotherms at pH 5 and 20ºC were performed in order to compare it with the optimal conditions. They were also compared with the ones obtained at pH 7, at 20ºC, which correspond to the characteristics expected after a biological treatment and before the sorption polishing treatment. The experimental results of the equilibrium isotherms both for the aqueous dyestuff solution and for the effluent are presented in Figure 2, together with the corresponding fits to Langmuir and Freundlich models. Their parameters and statistics are presented in Tables 4 and 5, respectively for 20 and 45ºC. Both Langmuir and Freundlich models could fit the experimental results owing that Fisher's test shows that there is no statistical difference between them. The highest sorbent capacity was obtained for the optimal conditions in aqueous solution, for the concentration range studied (0-70 mg L^{-1}).

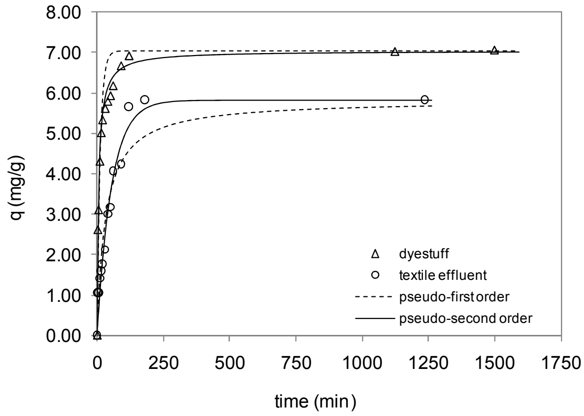

Figure 1. Kinetic studies in DBA dyestuff solution and in the textile effluent; pseudo-first and pseudo-second order models fits, at pH 7 and 20ºC

Table 1. Parameters of the kinetic models for the sorption by feathers of the DBA dyestuff in aqueous solution and in the textile effluent, at pH 7 and 20ºC

Model	Parameters	Dyestuff	Textile effluent
Pseudo-1st order	k_1 (min^{-1})	0.084 ± 0.03	0.018 ± 0.003
	q_e (mg g^{-1})	7.05	5.83
	s^2	0.513	0.153
	r^2	0.939	0.968
Pseudo-2nd order	k_2 (g (mg min)$^{-1}$)	0.023 ± 0.004	0.005 ± 0.002
	q_e (mg g^{-1})	7.05	5.83
	s^2	0.089	0.272
	r^2	0.982	0.934

Table 2. ANOVA of the quadratic model for DBA dyestuff sorption by feathers

Sources of variation	Degrees of freedom	Sum of squares	Mean square	F-ratio	Prob > F
Model	5	133.127	26.626		
Error	14	7.531	0.538	49.497	<0.0001
Corrected total	19	140.658			

Table 3. Regression model results for DBA dyestuff sorption by feathers

Term	Coefficient	Standard error	t-ratio	Prob > |t|
Intercept	4.751	0.310	15.33	<0.0001
pH	2.409	0.212	11.38	<0.0001
T	1.634	0.212	7.72	<0.0001
pH * T	1.365	0.259	5.26	0.0001
pH^2	-0.483	0.340	-1.42	0.1765
T^2	1.875	0.340	5.52	<0.0001

The capacities here obtained might also be compared with the ones obtained for other classes of dyestuffs using hen feathers pre-treated by 30% (m/v) hydrogen peroxide during 24 h (0.1 mm average grain size). Isotherms at 50ºC were determined for this material. The capacities presented for Acid red 41 (Gupta *et al*., 2006), Malachite green (Mittal, 2006a) and Brilliant Blue FCF (Mittal, 2006b), respectively 20.8, 27.1 and 30.9 mg g^{-1}, are lower than the maximum (optimal conditions) obtained in this work, 47± 4 mg g^{-1}.

The pH showed a slight decrease during the experiments. The maximum variation was observed for the dyestuff aqueous solution (from 5.0 to 4.5).

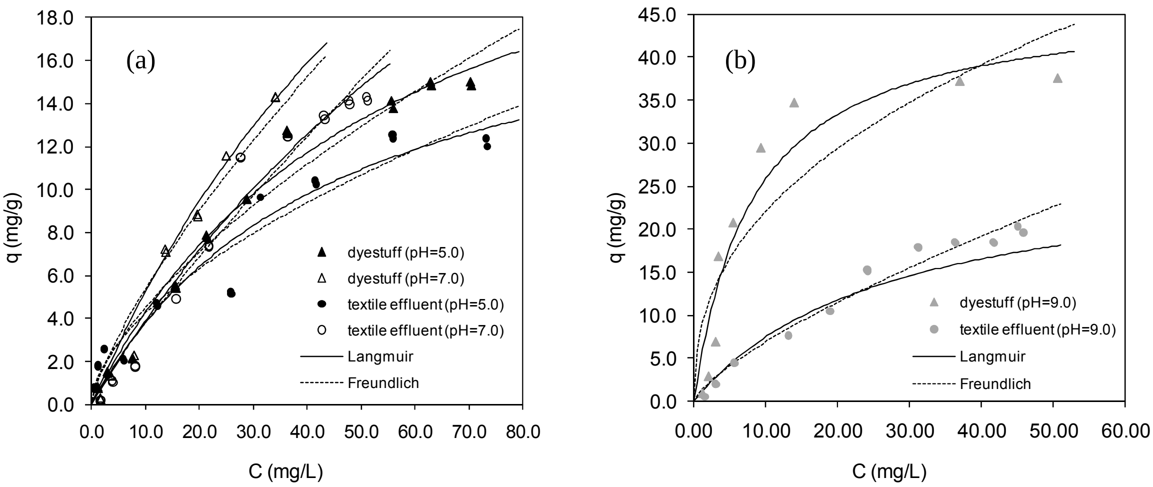

Figure 2. Equilibrium studies for feathers in DBA dyestuff solution and in the textile effluent at 20ºC (a) and 45ºC (b); Langmuir and Freundlich models fits

3.4. Column studies

The fixed bed column experiments were performed at 20ºC, at pH 5, 7 and 9. The experimental results for the dyestuff both in aqueous solution and in textile effluent are presented in Figure 3, together with Yoon-Nelson (1984), Thomas (1944) and Yan's (Yan *et al.*, 2001) model fits. Their parameters and statistics are presented in Tables 6 and 7, respectively for the dyestuff in aqueous solution and in the real effluent. In general, both models fitted well the experimental results. According to Fisher's test there is no statistical difference between them, expect for the real effluent at pH 9 for which Yan's model is the best fit. The highest breakthrough time for 50% removal, 170 min (estimated by Yoon-Nelson's model), and the highest sorbent capacity, 15 ± 1 mg g^{-1} (estimated by Thomas's model), were obtained at pH 9 for the aqueous solution. As expected this capacity, at 20ºC, is lower than in equilibrium studies performed at the optimal temperature, 45ºC.

Table 4. Parameters of the Langmuir and Freundlich models for the sorption of feathers in DBA dyestuff solution and in the textile effluent, at 20ºC

	Dyestuff		Textile effluent	
Parameters	pH = 5.0	pH = 7.0	pH = 5.0	pH = 7.0
q_m (mg g^{-1})	28 ± 5	50 ± 19	21 ± 7	50 ± 34
K_L (L mg^{-1})	0.018 ± 0.006	0.012 ± 0.007	0.02 ± 0.02	0.008 ± 0.007
s^2	0.5822	2.203	1.429	1.030
r^2	0.982	0.969	0.941	0.973
K_F ((mg g^{-1})(L $mg^{-1})^{1/n}$)	1.0 ± 0.4	0.9 ± 0.5	1.1 ± 0.5	0.5 ± 0.3
n	1.5 ± 0.3	1.3 ± 0.3	1.7 ± 0.4	1.2 ± 0.2
s^2	1.151	3.3166	1.2868	1.3040
r^2	0.966	0.951	0.938	0.963

3.5. Comparison with the real effluent

Equilibrium studies (Figure 2) show that the presence of the dyeing agents in the real effluent decreased the sorption of the dyestuff mostly for pH 9 and 45ºC (optimal conditions); this difference is not so marked at 20ºC, for pH 5 and 7.

Table 5. Parameters of the Langmuir and Freundlich models for the sorption of feathers in DBA dyestuff solution and in the textile effluent, at pH 9 and 45ºC

	Dyestuff	Textile effluent
q_m (mg g^{-1})	47 ± 8	28 ± 10
K_L (L mg^{-1})	0.13 ± 0.06	0.04 ± 0.03
s^2	20.9	3.822
r^2	0.920	0.979
K_F ((mg g^{-1})(L mg^{-1})$^{1/n}$)	9 ± 4	1.3 ± 0.5
n	2.4 ± 0.8	1.4 ± 0.2
s^2	48.49	1.587
r^2	0.787	0.973

The breakthrough curves (Figure 3) at 20ºC for pH 5 and 7 do not show significant differences for the dyestuff both in aqueous solution and in the real effluent. Only at pH 9 a significant difference is observed for the dyestuff solution. Since there is no significant effect of the pH, the real effluent could be treated in a more economical way at the original pH (or pH 7, if there is a biological treatment), without pH adjustment. Given that the optimization studies show that temperature has a minor effect than pH, then it would also have little influence in the treatment the textile effluent.

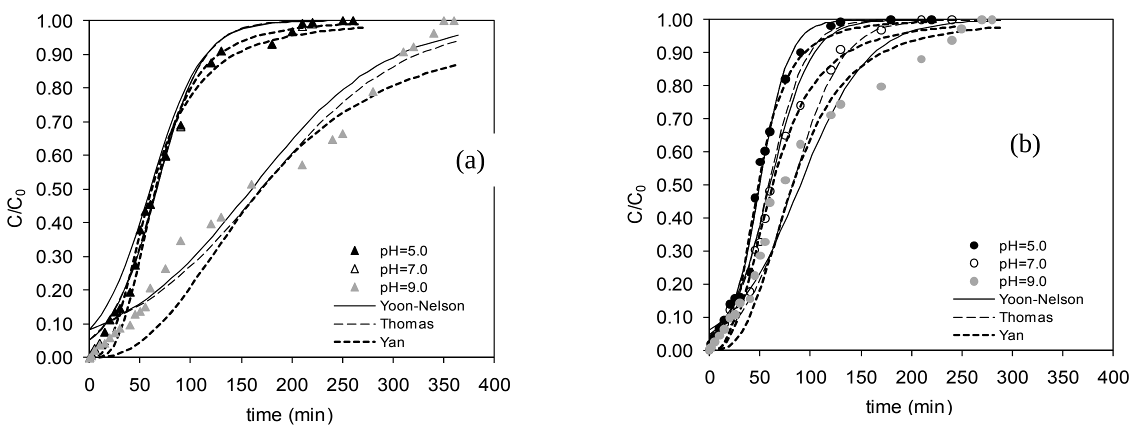

Figure 3. Column studies, at 20ºC, for DBA dyestuff sorption by feathers in aqueous solution (a) and in the textile effluent (b); Yoon-Nelson, Thomas and Yan's model fits

Table 6. Parameters of the column models for the sorption by feathers in DBA dyestuff aqueous solution, at 20ºC

Model	Parameters	pH = 5	pH = 7	pH = 9
Yoon-Nelson	k_{YN} (min^{-1})	0.044 ± 0.005	0.044 ± 0.005	0.015 ± 0.002
(YN)	τ_{YN} (min)	66 ± 3	67 ± 3	170 ± 12
	s^2	0.0012	0.0013	0.0036
	r^2	0.994	0.993	0.974
Thomas	k_{TH} (mL(mg min)$^{-1}$)	0.62 ± 0.07	0.62 ± 0.07	0.21 ± 0.03
(T)	q_{TH} (mg g^{-1})	5.9 ± 0.2	5.9 ± 0.3	15 ± 1
	s^2	0.0012	0.0013	0.0035
	r^2	0.994	0.993	0.974
Yan	a_Y	2.6 ± 0.3	2.6 ± 0.3	2.0 ± 0.4
(Y)	q_Y (mg g^{-1})	5.5 ± 0.1	5.5 ± 0.3	12 ± 2
	s^2	0.0011	0.0011	0.0047
	r^2	0.995	0.995	0.967

Table 7. Parameters of the column models for the sorption by feathers of the DBA dyestuff in the textile effluent, at 20ºC

Model	Parameters	pH = 5	pH = 7	pH = 9
Yoon-Nelson	k_{YN} (min^{-1})	0.070 ± 0.009	0.046 ± 0.006	0.031 ± 0.006
(YN)	τ_{YN} (min)	50 ± 2	65 ± 3	83 ± 8
	s^2	0.0013	0.0011	0.0042
	r^2	0.992	0.993	0.975
Thomas	k_{TH} (mL(mg min)$^{-1}$)	1.0 ± 0.2	0.68 ± 0.08	0.45 ± 0.09
(T)	q_{TH} (mg g^{-1})	4.6 ± 0.2	5.6 ± 0.3	7.1 ± 0.7
	s^2	0.0013	0.0011	0.0042
	r^2	0.992	0.993	0.975
Yan	a_Y	3.3 ± 0.6	2.7 ± 0.4	2.1 ± 0.2
(Y)	q_Y (mg g^{-1})	4.4 ± 0.3	5.3 ± 0.3	6.3 ± 0.4
	s^2	0.0022	0.0015	0.0013
	r^2	0.989	0.992	0.992

4. CONCLUSIONS

The effects over the sorption in aqueous solution of the basic dyestuff Dark Blue Astrazon 2RN by gallinaceous feathers were evaluated for temperature (15-45ºC) and pH (5-9). The influence of pH is more significant than temperature and the optimal conditions selected were 45ºC and pH 9.

Equilibrium studies in the concentration range selected (0-70 mg L^{-1}) show that the highest sorbent capacity was obtained at the optimal conditions for the dyestuff in aqueous solution, which corresponds to a maximum capacity of 47 ± 4 mg g^{-1}.

In column studies the highest breakthrough time for 50% removal, 170 min, and the highest sorbent capacity, 15 ± 1 mg g^{-1}, were obtained at pH 9 and 20ºC for the aqueous solution.

One of challenges in the treatment of real industrial wastewater is their complexity. The presence of the dyeing agents in the real wastewater decreased the sorption of the dyestuff mostly for pH 9, which is the optimal pH. The effect of pH is less pronounced in the real effluent than in aqueous solution of the dyestuff and not significant in column experiments. Given that temperature had also shown minor effect than pH the effluent may be treated more economically at its original pH and temperature. This work shows that feathers are a promising sorbent for DBA effluents.

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