

Adsorption Studies of Astrozon Blue Dye onto Acrylic Resin

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Abstract: In this study an acrylic resin, CC₁-P₁₀, is used as sorbent for Astrazone Blue basic dye (Basic Blue 3 or BB3), from aqueous solutions. Factors affecting the adsorption process: pH, contact time, initial dye concentration (30 – 200 mg L⁻¹), adsorbent doses (0.05 – 0.3 g) and temperature (290-323 K) were investigated. The sorption isotherm followed both the Langmuir and Freundlich models within concentration and temperature range employed in this study. Pseudo-first order, pseudo-second order kinetic and intraparticle diffusion models were used to analyze the kinetic data obtained at different concentrations. The kinetic data corresponded well with the pseudo-second order kinetic model. CC₁-P₁₀ resin was shown to be a promising material for adsorption of BB3 from aqueous solutions.

Keywords: Dye; Basic Blue3; Acrylic Resin; Adsorption isotherms; Adsorption kinetics.

Introduction

The wastewater contains a variety of organic compounds and toxic substances which are harmful to fish and other aquatic organisms.¹ The

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coloured wastewater damages the aesthetic nature of water and reduces the light penetration through the water's surface and also the photosynthetic activity of aquatic organisms.²

Dyes have been extensively used in many industries, such as textile, paper production, food technology, etc. The discharge of dyes in the environment is worrying for both toxicological and esthetical reasons.³ Various methods including chemical and electrochemical oxidation,⁴ coagulation,⁵ photo catalysis⁶ and adsorption techniques have been examined. In comparison with other techniques, adsorption can use a large number of suitable adsorbents as activated carbon, polymeric resins or various low cost adsorbents.⁷ Adsorption has been found to be superior to other techniques for wastewater treatment in terms of cost, simplicity of design, ease of operation and insensitivity to toxic substances.⁸

The aim of this work was to determine the efficiency of the removal of basic dye, namely Astrazon Blue BG (BB3), from water solution using an acrylic copolymer functionalized with - COOH, namely CC1- P10 resin.

Batch studies are carried out involving process parameters such as solution pH, the initial dye concentration and temperature, contact time, adsorbent doses. Equilibrium and kinetic analysis were conducted to understand the sorption process and optimization of various parameters in dye recovery.

Experimental

Adsorbent

Sorption experiments of basic dye were tested on four weak acid exchange resins as adsorbents (Table 1).

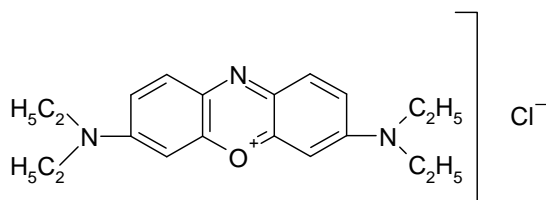
Table 1. The structural characteristics of resins tested for BB3 sorption.

Adsorbent Notation and matrix	Active group	Sorption capacity (mEq g ⁻¹)
CM 60: 10% DVB, 5% AN, 85% AE,	-CH ₂ -COONa	4.026
CC1-P10: 15% DVB, 20% AN, 65% AE,	-COONa	7.679
CC 42: 6% DVB, 20% AN, 74% AE,	-COONa	1.272
AS 80: 10% DVB, 5% AN, 85% AE,	TETA	6.782

DVB-divinylbenzene; AN-acrylonitrile; AE-ethylacrilate ; TETA-triethylenetetramine

Adsorbate, BB3

The basic dye BB3, (C₂₀H₂₆N₃OCl) (Scheme 1), 95% dye content, M.W. = 359.9) was used without further purification, as commercial salt.

**Scheme 1**

The stock solution of 1000 mg L⁻¹ was prepared by dissolving BB3 textile dye in double distilled water. The experimental solution, in concentration from 30 to 200 mg L⁻¹, was prepared by diluting the stock with double distilled water when necessary.

The dye concentration in solution was spectrophotometrically measured by using an UV-1700 Pharma Spec – spectrophotometer, (Shimadzu). The wavelength was selected, from the absorption spectra, so as to obtain the maximum absorbance; $\lambda_{\text{max}} = 654 \text{ nm}$.

Methods

In a series of kinetic and equilibrium experiments was investigated the effect of important parameters such as pH, contact time, initial dye concentration, adsorbent dose and temperature on the adsorptive removal of BB3.

Equilibrium studies

The sorption experiments were performed by batch method when the sample of 0.05 g CC₁-P₁₀ resin was equilibrated with 25 mL of solution containing various amounts of BB3. The solutions were kept in a thermostatic bath and stirred at a controlled speed (mechanic stirrer S-420) The adsorption isotherms were taken in the temperature range of 291 ÷ 323 K.

The pH was varied from 1.0 to 7.0 and was adjusted by using diluted solution of HCl and NaOH and measured with a RADELKIS pH - meter, OP 211/2.

Kinetic studies

The effect of contact time on the removal of colour was studied by adding 0.15 g of adsorbent to 75 mL of double distilled water containing 30 ÷ 200 mg L⁻¹ of BB3 at constant temperature and controlled stirring speed. After regular intervals of time (15 minutes to 12 hours), volumes of 1.0 mL supernatant were taken and the concentration of the adsorbed dye was determined by difference between the initial and final concentrations spectrophotometrically measured. These experiments were used to establish

the equilibrium time between the adsorbent and the dye solutions. This equilibrium time was used as contact time in the isotherms experiments.

Dye uptake

The sorption capacity of CC₁-P₁₀ resin was evaluated by the amount of dye adsorbent:

$$q_e = (C_o - C_e) V 10^{-3} / m \quad (1)$$

by percent of dye removal:

$$R \% = (C_o - C_e) 100 / C_o \quad (2)$$

and by the distribution constant (or saturation constant):

$$K_d = q_e / C_e \quad (3)$$

where: q_e is the amount of the solute sorbed per unit weight of sorbent at equilibrium, mg g^{-1} ; C_o and C_e are initial and equilibrium concentration of dye in solution, mg L^{-1} ; m is the amount of adsorbent, g; V is the volume of solution, mL; K_d is the distribution constant, $(\text{mg g}^{-1})/(\text{mg L}^{-1})$.

Results and discussions

Equilibrium studies

Effect of pH

The sorption capacity of four resins, for basic dye BB3, was determined at different values of pH (1 ÷ 7) and the same initial dye concentration. The quantity of adsorbent was kept constant, 0.05 g respectively.

Figure 1 shows the comparative data on the pH effect. CC₁-P₁₀ resin was selected for this study.

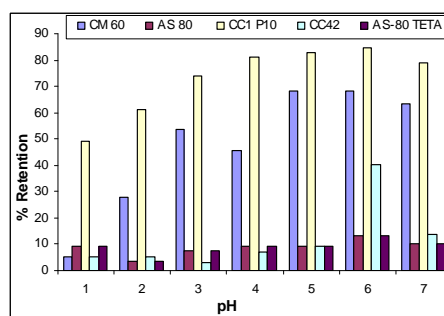


Figure 1 .The pH influence of the BB3 adsorption for different sorbents.

It was observed that the amount of BB3 onto CC₁-P₁₀ resin increases with increasing pH until pH = 5 ÷ 6, after that the sorption has an insignificant variation in the range 6 ÷ 7. For this reason, the following experiments were made at pH = 5.5 (without pH adjustment of the dye solutions).

The higher values of pH were not tested because the textile wastewater is weakly acid. At lower pH, the H⁺ ions compete with dye cations justifying the decrease in the percent of retention.

Effect of contact time and initial dye concentrations

It was studied the effect of contact time and initial dye concentration. The sorption capacity of CC₁-P₁₀ resin for basic dye BB3 was determined at different initial dye concentrations (from 30 to 200 mg L⁻¹) and the same quantity of adsorbent for all determinations.

Figure 2 shows the comparative data on the effect of contact time on the extent of BB3 sorption on CC₁-P₁₀. All the experiments were conducted at pH = 5.5 and T = 291 K.

The sorption rate is high at the beginning of adsorption and saturation levels were completely reached at 120 minutes, in all the experiments and were independent on the dye concentration. After

equilibrium is reached the amount of BB3 does not significantly change in time.

Figure 2 also shows that q increases from 17.25 to 115 mg g^{-1} when the concentration of dye increases from 30 to 200 mg L^{-1} .

The plots are single and continuous, leading to saturation, and suggesting the possible monolayer coverage of dye on the surface of the adsorbent; this confirms the applicability of the Langmuir model.

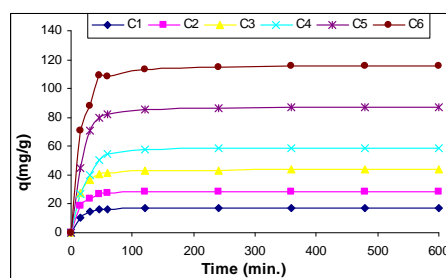


Figure 2. Effect of contact time and initial dye concentrations.

$C(\text{mg L}^{-1})$: C₁ - 30; C₂ - 50; C₃ - 75; C₄ - 100; C₅ - 150; C₆ - 200.

When the initial dye concentration increases, the adsorbed amount of dye on adsorbent increases until equilibrium.

The amount of the adsorbed dye increased with contact time and this confirmed strong interactions between the dye and the material driven by electrostatic interactions between the cationic dye and the carboxylic groups ($-\text{COO}^-$) of CC₁-P₁₀ resin as well as was reported in literature.⁹

Effect of adsorbent mass

To determine the effect of adsorbent dose, different amounts (0.05 ÷ 0.30 g adsorbent) were suspended in 25 mL dye solution (400 mg L^{-1}) under optimized conditions of pH and contact time. The amount of adsorbent significantly influenced the dye sorption.

The dye uptake increased from 36.88 to 97.91 mg g⁻¹ for an increase in adsorbent mass from 0.05 g to 0.3 g.

The percent of colour removal increases with increasing adsorbent dose (from 97.68 to 99.66% for an increase in adsorbent mass from 0.05 g to 0.3 g). Thus, for efficiency reason, the dose of 0.05 g sorbent was selected for all the further studies.

Effect of temperature

The effect of temperature on BB3 sorption onto CC₁-P₁₀ resin has been investigated at three different temperatures, 291, 308 and 323 K respectively, using a constant amount of adsorbent (0.05 g) and contact time 120 min.

The results show that with increase in reaction temperature from 291 to 323 K the maximum percentage of dye removal after 120 min of contact increased for the investigated dye concentrations (Figure 3). The fact that the percentage dye removal is favoured by temperature indicates that the mobility of the dye molecules increases at higher temperatures, according with other reports.¹⁰

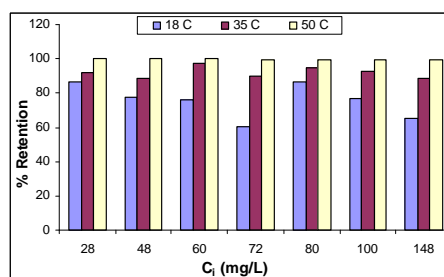


Figure 3. The temperature influence on the BB3 adsorption. The basic dye sorption onto CC₁-P₁₀ is temperature dependent.

Adsorption isotherms

Adsorption isotherm study was carried out based on two isotherm models: Langmuir and Freundlich.

The applicability of the isotherm models was compared based on the correlation coefficients, R^2 .

The model parameters for both isotherms are presented in Table 2. In order to assess the different isotherms and their ability to correlate with experimental results, the theoretical plots from each isotherm have been plotted with experimental data for sorption of BB3 on CC₁-P₁₀ resin, at 291 K.

The Langmuir model assumes that the uptake of adsorbate occurs on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions.

The Langmuir equation can be expressed in a mathematical form as shown in the equation:

$$C_e/q_e = 1/Q_0b + C_e/Q_0 \quad (4)$$

The maximum adsorption capacity and Langmuir constant were calculated from the slope and intercept of the linear plots C_e/q_e vs. C_e and the results are summarized in Table 2.

Table 2. Characteristic Langmuir and Freundlich isotherms parameters at 291 K.

Langmuir			Freundlich				
K_L $L g^{-1}$	q_0 $mg g^{-1}$	b $L mg^{-1}$	R_L	R^2	K_f $L g^{-1}$	n	R^2
4.719	72.99	0.0646	0.0718	0.999	0.817	1.874	0.991

The essential characteristic of Langmuir isotherm, expressed in terms of a dimensionless separation factor, R_L ,¹¹ can be calculated with the relation:

$$R_L = 1 / (1 + K_L C_o) \quad (5)$$

where: K_L is the Langmuir constant, $L \text{ mol}^{-1}$; C_o is the highest initial dye concentration, mg L^{-1} .

The calculated values of R_L , in the range $(0 \div 1)$, confirmed that the adsorption behaviour of $\text{CC}_1\text{-P}_{10}$ resin was favourable for BB3.

The adsorption capacity and correlation coefficient values (Table 2) indicate that the BB3 – $\text{CC}_1\text{-P}_{10}$ resin sorption data closely follow the Langmuir model of sorption.

The Freundlich isotherm describes equilibrium on heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface.¹²

The application of Freundlich equation suggests that sorption energy exponentially decreases on completion of the active sites of an adsorbent.

The linear form of Freundlich model is represented by the equation:

$$\log q_e = \log K_f + (1/n) \log C_e \quad (6)$$

where: K_f ($L \text{ g}^{-1}$) and n are the Freundlich constants that point to relative capacity and adsorption intensity, respectively.

The Freundlich constants were calculated from the slope and intercept of the Freundlich plots (Table 2).

The Freundlich equation presents the poorest fit for the experimental data compared to other equations although the value of $n > 1$ reflects the favourable adsorption. It is an empirical equation employed to describe heterogeneous systems and multilayer sites.

Kinetic studies

Three simplified kinetic models were adopted to examine the mechanism of the adsorption process: pseudo-first-order model, pseudo-second-order model and intraparticle diffusion model.

Pseudo-first-order kinetics

The kinetics of adsorption was firstly analyzed by the pseudo-first-order equation given by Lagergren as:

$$\log (q_e - q) = \log (q_e) - (k_1/2.303)t \quad (7)$$

where: q_e and q - are the amount of BB3 adsorbed on resin at equilibrium and at time t , mg g^{-1} ; k_1 is the rate constant of adsorption, min^{-1} .

The k_1 values were calculated from the plots of $\log (q_e - q)$ vs. t , for different concentrations of the basic dye BB3 (Table 3).

Table 3. Kinetic parameters for BB3 sorption on CC₁-P₁₀.

C_o mg L^{-1}	q_{exp} mg g^{-1}	Lagergren			Ho			
		k_1 min^{-1}	q_e mg g^{-1}	R^2	k_2 $\text{g mg}^{-1}\text{min}^{-1}$	q_e mg g^{-1}	h $\text{g mg}^{-1}\text{min}$	R^2
30	17.21	0.0451	85.96	0.835	0.0033	17.39	3.467	0.999
50	28.88	0.0476	11.91	0.979	0.0011	29.15	5.727	0.999
75	43.67	0.0469	20.51	0.976	0.0005	44.05	9.057	0.999
100	58.77	0.0490	31.32	0.989	0.00028	60.24	5.685	0.999
150	87.02	0.0444	64.93	0.992	0.00013	88.49	13.021	0.999
200	115.85	0.0502	80.13	0.973	7.23E-05	117.64	18.348	0.999

The experimental q_e values did not agree with the calculated values obtained from the linear plots.

Pseudo-second order kinetics

The pseudo-second-order model proposed by Ho and McKay¹³ can be represented in the following linear form:

$$(t/q) = (1/k_2 q_e^2) + (1/q_e) t \quad (8)$$

where: k_2 is the rate constant of pseudo-second-order adsorption, $\text{g mg}^{-1} \text{min}^{-1}$.

The second order rate constant, k_2 , was used to calculate the initial sorption rate, respectively

$$h = k_2 q_e^2 \quad (9)$$

Values of k_2 and q_e were calculated from intercept and slope of the linear plots of t/q vs. t (Figure 4).

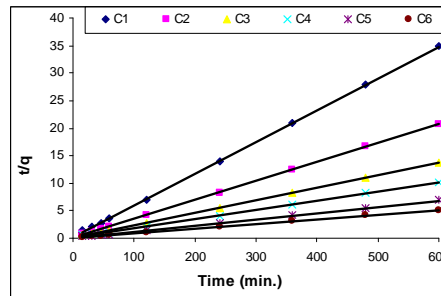


Figure 4. Pseudo-second order kinetics, Ho; $C_0(\text{mg L}^{-1})$: $C_1 - 30$; $C_2 - 50$; $C_3 - 75$; $C_4 - 100$; $C_5 - 150$; $C_6 - 200$.

The experimental and the calculated q_e values are in good agreement (Table 3), indicating the applicability of pseudo-first order model (at low concentrations), pseudo-second order model (at all concentrations), to describe the adsorption process of BB3 on $\text{CC}_1\text{-P}_{10}$ resin.

The kinetics of BB3 adsorption on $\text{CC}_1\text{-P}_{10}$ resin followed the pseudo-second order model suggesting that chemisorption might be the rate – limiting step that controls the adsorption process.

Intraparticle diffusion

Intraparticle diffusion model based on the theory proposed by Weber and Morris¹⁴ was tested to identify the diffusion mechanism. The rate constant for intraparticle diffusion, k_{id} , is calculated by the following equation:

$$q = k_{id} t^{1/2} \quad (10)$$

where: q is the amount of BB3 adsorbed on resin, mg g^{-1} , at time t , min; k_{id} is the rate constant for intraparticle diffusion, $\text{mg g}^{-1} \text{min}^{-1/2}$.

The k_{id} values were calculated from the slope of the linear plots of q vs. $t^{1/2}$ (Figure 5 and Table 4).

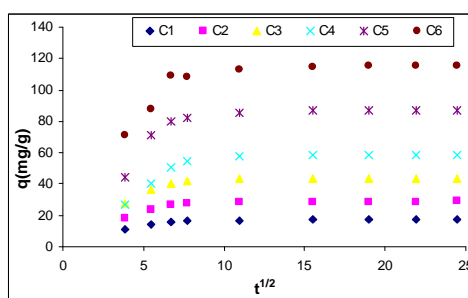


Figure 5. Intraparticle diffusion. $C_0(\text{mg L}^{-1})$: $C_1 - 30$; $C_2 - 50$; $C_3 - 75$; $C_4 - 100$; $C_5 - 150$; $C_6 - 200$.

The first, sharper part corresponds to the instantaneous adsorption or external surface adsorption. The second part represents the gradual adsorption stage where intraparticle diffusion is the rate-limiting step.

In some cases, the third part exists, that corresponds to the final equilibrium stage when intraparticle diffusion starts to slow down due to the extremely low adsorbate concentrations left in solution.¹⁵

Table 4. Intraparticle diffusion parameters for BB3 sorption on CC₁-P₁₀.

C ₀ (mg L ⁻¹)	k _{id} (mg g ⁻¹ min ^{-1/2})	R ²
30	1.8494	0.976
50	2.94	0.999
75	4.5113	0.986
100	8.4603	0.999
150	12.735	0.962
200	13.413	0.978

Conclusions

CC₁-P₁₀ resin is a copolymer that can be used as adsorbent material for removal of Basic Blue 3 from aqueous solution. In batch studies, the adsorption process was dependent on pH, contact time, initial dye concentration, adsorbent dosage and temperature.

The equilibrium is reached within about 120 minutes at optimum pH (5-6).

Langmuir isotherm was found to fit the experimental data better than Freundlich isotherm.

The adsorption of the BB3 on the resin was a multi-step process that involves adsorption at the external surface, diffusion into the bulk and chemical reaction (adsorption of dye at an active site via ion-exchange).

The basic dye removal technique using a polyacrylic resin as adsorbent material could be an alternative method for the treatment of textile wastewaters.

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References

1. Ramakrishna, K. R. and Viraraghavan, T., *Water Sci. Technol.*, **36**, 189 (1997).
2. Marungrueng, K. and Pavasant, P., *J. Environ. Manag.*, **78**, 268 (2006).
3. Tan, I. A. W., Hameed, B. P., and Ahmad, A. L., *Chem. Eng. J.*, **127**, 111 (2007).
4. Rao, N. N., Somasekhar, K. M., Kaul, S. N., and Szpyrkowicz, L., *J. Chem. Technol. Biotechnol.*, **76**, 1124 (2001); Malik, P. K. and Saha, S. K., *Sep. Purif. Technol.*, **31**, 241 (2003).
5. Stephenson, R. J. and Sheldon, J. B., *Water Res.*, **30**, 781 (1996); Sarasa, J., Roche, M. P., Ormad, M. P., Gimeno, E., Puig, A., and Ovelleiro, L., *Water Res.*, **32**, 2721 (1998).
6. Bukallah, S. B., Rauf, M. A., and Salman, A. S., *Dyes Pigments*, **72**, 353 (2007).
7. Allen, S. J. and Koumanova, B., *J. of the University of Chemical Technology and Metallurgy*, **40**, 175 (2005).
8. Garg, V. K., Kumar, R., and Gupta, R., *Dyes Pigments*, **62**, 1 (2005).
9. Crini, G., *Bioresour. Technol.*, **90**, 193 (2003).
10. Ofomaja, A. E., *Chem. Eng. J.*, **126**, 35 (2007).

11. Hall, K. R., Eagleton, L. C., Acrivos, A., and Vermeulen, T., *Ind. Eng. Chem. Fundam.*, **5**, 212 (1966).
12. Freundlich, H. M. F., *J. Phys. Chem.*, **57**, 385 (1906).
13. Ho, Y. S. and McKay, G., *Process Biochem.*, **34**, 451 (1999).
14. Weber, W. J. and Morris, J. C., *J. Sanit. Eng. Div. Am. Soc. Civ. Eng.*, **89**, 31 (1963).
15. Wu F. C., Tseng R. L., and Juang R. S, *J. Colloid Interface Sci.*, **283**, 49 (2005).