A study of Adsorption of Azure B and C from Aqueous Solutions on Poly (Acrylamide-co-Crotonic acid) Hydrogels Surface

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ABSTRACT

This study is concerned with the adsorption of azure B and C from solution on the surface of poly(AAm-co-CA) . The hydrogels have the ability to remove these dyes from aqueous solution, though not very efficient. UV-Visible-spectrophotometric technique has been used to produce quantitative adsorption data at different conditions of ionic strength and temperature. The adsorption isotherms are of S-curve type according to Giles classification and the experimental data were best fitted to Langmuir and Freundlich isotherm models. The results obtained show greater adsorption uptake of dyes on hydrogels. The adsorption phenomenon was examined as a function of temperature (**15, 20, 25, 30 ^{o}C**). The extent of adsorption of azure B and C on poly(AAm-co-CA) was found to decrease with increasing temperature (**exothermic process**). The basic thermodynamic functions have also been calculated. The adsorption of all adsorbates on this surface has increased with the increase of the ionic strength of solution.

Keywords: Adsorption, Azure B, Azure C, Hydrogels

1- INTRODUCTION

Adsorption is an important surface phenomenon usually describes the concentrating of a particular component at an interface relative to an adjacent solution or other bulk phase (Glasstone 1962). It is a phenomenon in which the available surface is the determining factor (Ladd 1998). Adsorption is a spontaneous process and hence is attained by a decrease in free energy change and entropy of the system. This process is influenced by a number of factors: concentration of adsorbate (Ladd 1998), surface area of adsorbent (Kiselev *et al.* 1969) solubility of adsorbate, temperature, pH, ionic strength (Kapoor 1994, Gerasimov 1974, Sorby *et al.* 1966, Olphen 1977, Adamson & Gast 1997 & Camazano *et al.* 1980), and the chemical state of adsorbate and adsorbent molecules (Davis *et al.* 1973).

The molecular and thermodynamic characteristics of adsorption (i.e. capacity, affinity, isotherm shape and enthalpy) are essential to understanding binding processes and providing mechanistic evidence for the selection and ranking of adsorbents that have application in reducing water pollution (Patil *et al.* 2011). Polymeric hydrogels play an important role in the treatment of waste water. Over the past several decades, polymeric hydrogels have attracted much scientific interest and have found uses in many fields, such as molecular filters and super absorbents (Rao *et al.* 2002, Guilherme *et al.* 2003 & Liu *et al.* 2003). The aim of present work is to explore the feasibility utilizing Polymeric hydrogels as adsorbent for dye. Equilibrium analysis were conducted to investigate the mechanism of dye adsorption and optimization of various parameters in dye recovery.

2- MATERIALS AND METHODS:

2.1- INSTROUMENT:

1. UV-Visible spectrophotometer, Double Beam, Shimadzu. PC 1650, Japan.
2. Dunboff metabolic shaking Incubater GCA/ precision Scientific.
3. Centrifuge tubes., Hettich Universal (D-7200).
4. Electronic Balance, Sartorius Lab. L420 B, +0.0001.

2.2- MATERIALS:

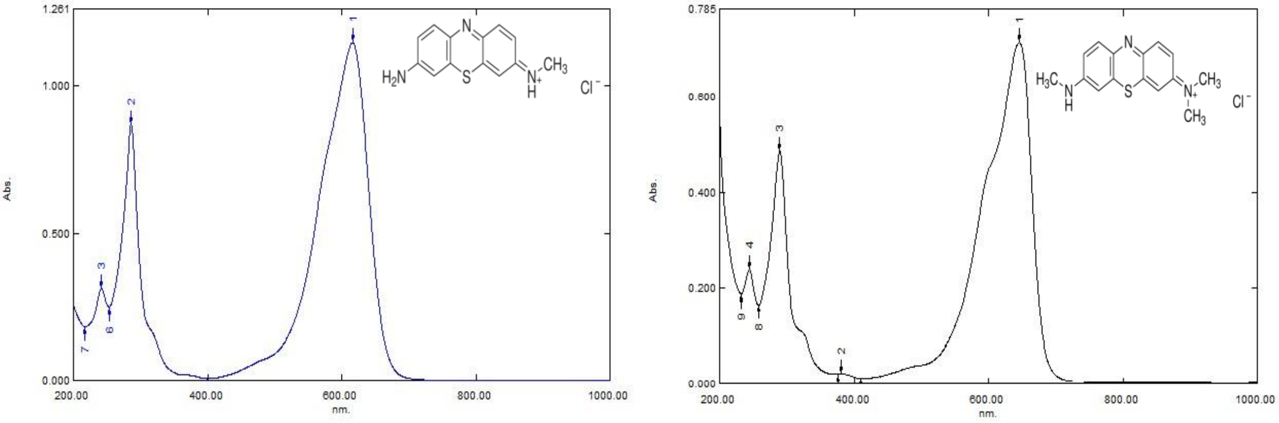
sodium chloride was supplied by Fluka. The dyes were purchased from Sigma-Aldrich Company (Germany). Acrylamide (AAm) supplied by from Merck (Darmstadt, Germany) and the anionic comonomer, crotonic acid (CA) supplied by from Aldrich Chemical The initiator, ammonium persulfate (APS) and the activator N, N, N', N'-tetramethylethylenediamine (TEMED) supplied from Merck(Darmstadt, Germany) and were used as the redox initiator pair. The multifunctional crosslinker is N,N'-methylenebisacrylamide (MBA) were purchased from Merck (Darmstad, Germany).

2.3- PREPARATION OF CROSSLINKED POLY(AAM-CO-CA) HYDROGELS:

5 g of AAm was dissolved in 5 mL distilled water and then 100mg CA were added to the aqueous solutions of AAm. and then the solution was added into in a three necked 250ml round bottom flask. which was equipped with a stirring apparatus and a reflux condenser. When the mixture is heated up to 45 ℃ under nitrogen protection, and 1.25 mL of 1% concentration of MBA was added to the aqueous solutions. Then 1 mL of APS (5 g/100 mL water) was added this solution as initiator, and finally, 1.25 mL of TEMED (1 mL/100 mL water) was added onto solution. polymerization process after 60 min. The reaction was stopped after 2 h. The prepared poly(AAm-co-CA) was poured into a Petri dish and was then dried in the oven of 50 ℃ for 24 h. the gels were soaked in distilled water for one day to remove any possible residual monomers and dried in vacuum at 80 ◦C for 5 h to form crosslinked poly(AAm-co-CA) hydrogels with constant weights.

2.4- METHODOLOGY:

The poly(AAm-co-CA) after prepared was washed with excessive amounts of distilled water, dried at 70^{o}C for three days. The hydrogels we ground and sieved to a particle size of 15 mm. wavelength of maximum absorbency (λ_{max}) were recorded for azure B and C dissolved in aqueous media and found 647nm and 615nm responsible Figure (1).



-a-

-b-

This value was utilized for estimation of quantity of dyes adsorbed. Solutions of different concentrations were prepared by serial dilution at wavelength of maximum and plotted against concentration values. The calibration curve in the concentration range that falls in the region of applicability of Beer-Lambert's law was employed.

2.4.1- ADSORPTION ISOTHERM

Solutions of dye (10 ml) of known concentrations (1-20ppm) were added to stoppered flasks containing 0.05g of polymer. The flasks were shaken in a thermostatically controlled Incubater at a speed of 150 cycle/min. till equilibrium is attained (240 min). This time is sufficient for the adsorption process to reach equilibrium. After the equilibrium time elapsed, the suspensions were either centrifuged at 3000 rpm for 10 min. The clear supernatants were assayed for dyes, after appropriate dilution, spectrophotometrically. Equilibrium concentrations were obtained by comparing the experimental data with the calibration curve.

The quantity of dyes adsorbed was calculated according to the following equation (Voyutsky 1978):-

$$Q_e \text{ or } \frac{x}{m} = \frac{V(C_o - C_e)}{m} \qquad (1)$$

Where:

x : the quantity adsorbed.
m : weight of adsorbent (g).
C_o : initial concentration (mg/L).
C_e : equilibrium concentration (mg/ L).
V : volume of solution (L).

2.4.2- EFFECT OF TEMPERATURE

Adsorption experiment was repeated in the same manner at temperatures of 15, 20, 25 and 30 ^{o}C to estimate the basic thermodynamic functions.

2.4.3- EFFECT OF IONIC STRENGTH

The effect of the addition (0.01-0.3g) of sodium chloride to solutions containing fixed concentration of adsorbate equilibrated with 0.05 g of adsorbent were investigated under the same experimental conditions described before.

3- RESULTS AND DISCUSSION

The adsorption of dyes from aqueous solution on poly(AAm-co-CA) has been studied (20˚C) and at other three temperatures (15. 25 and 30˚C). The general shapes of dyes adsorption isotherms are shown in Figure (2), where the quantities adsorbed on hydrogels are plotted as a function of equilibrium concentration at the constant temperature.

The results showed an increase in adsorptive capacities of the poly(AAm-co-CA) as the concentration of dyes increased. The hydrogels was found of reasonable surface activity in adsorption from solution of some dyes (Yongsheng *et al.* 2010). The adsorption capacities of poly(AAm-co-CA) increased with increasing of the dye concentration and the adsorption capacity of azure C for dyes was higher than that of azure B.

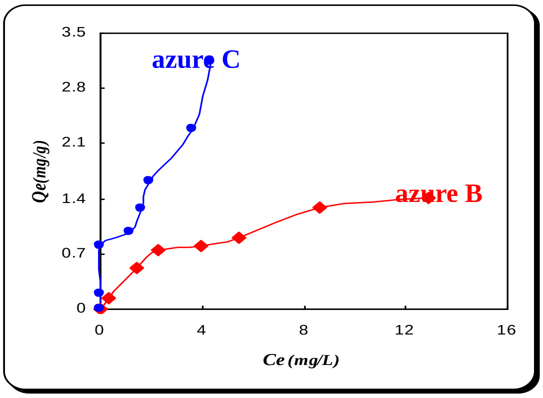


Figure (2) Adsorption isotherms of dyes on the poly(AAm-co-CA) at constant temperature (20^{o}C)

The shapes of dyes adsorption isotherms were found to coincide with the S-type isotherm reported by Giles et al. (1960).

The adsorption equilibrium data were analyzed using Langmuir and Freundlich isotherm expression. The adsorption of dyes on hydrogels, follow isotherms which are best represented by applying the Freundlich equation (Dursun & Kalayci 2005).

$$\frac{x}{m} = kC_e^{1/n} \tag{2}$$

Where $\frac{x}{m}$ is the quantity adsorbed in mg/g. C_e is the equilibrium concentration in mg/L, n and k are constants for the given adsorbent and solute. The applicability of Freundlich isotherm is indicated by using the linear from of Freundlich equation.

$$log\,\frac{x}{m} = log\,k + \frac{1}{n}\,log\,C_e \tag{3}$$

The Langmuir isotherm can be expressed as follows (Liu *et al.* 2004):

$$Q_e = \frac{q_m.K_L.C_e}{(1+K_L.C_e)}$$

Where

Q_e: amount adsorbed per unit weight of adsorbent at equilibrium (mg/g).
C_e: equilibrium concentration of adsorbate in solution after adsorption (mg/L).
q_m (mg/g) and K_L (L/mg) are the Langmuir isotherm constants.

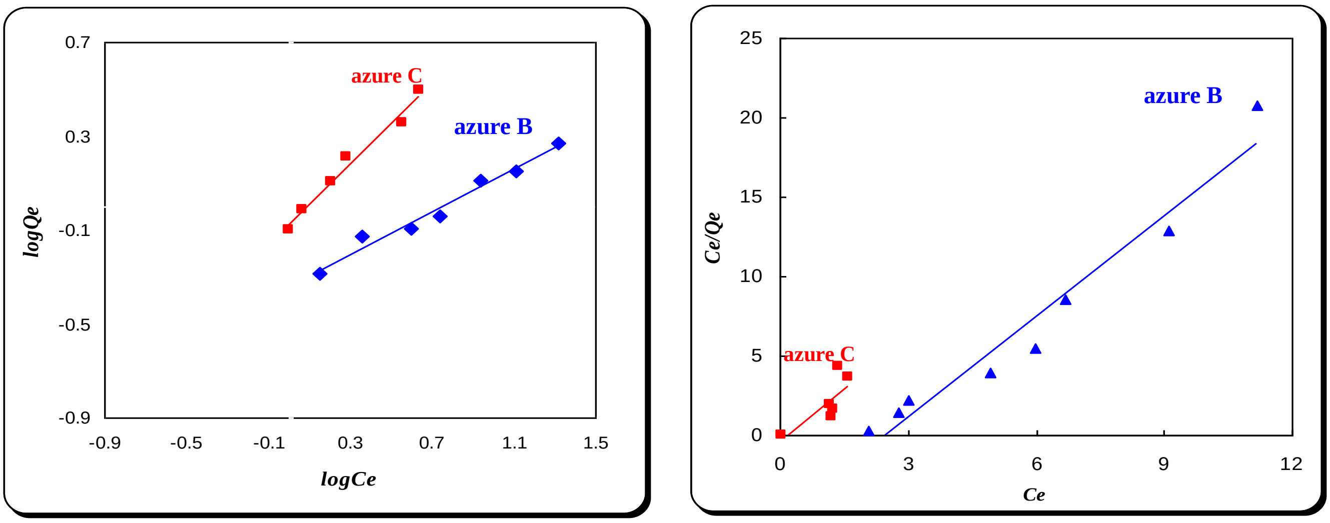
The Langmuir isotherm constants are evaluated through linearization of Eq.(4).

$$\frac{C_e}{Q_e} = \frac{1}{q_m K_L} + (\frac{1}{q_m}).C_e \tag{4}$$

Table (1) summarizes the values of the correlation coefficients for each of these isotherm models. Freundlich isotherm fits the data very well (Tables (1) and Figure (3)). The low values of correlation coefficients show that the Langmuir isotherm is less fitted to the adsorption of dyes compared to the Freundlich isotherm.

Table (1) Freundlich and Langmuir isotherm constants for dyes uptake by hydrogels

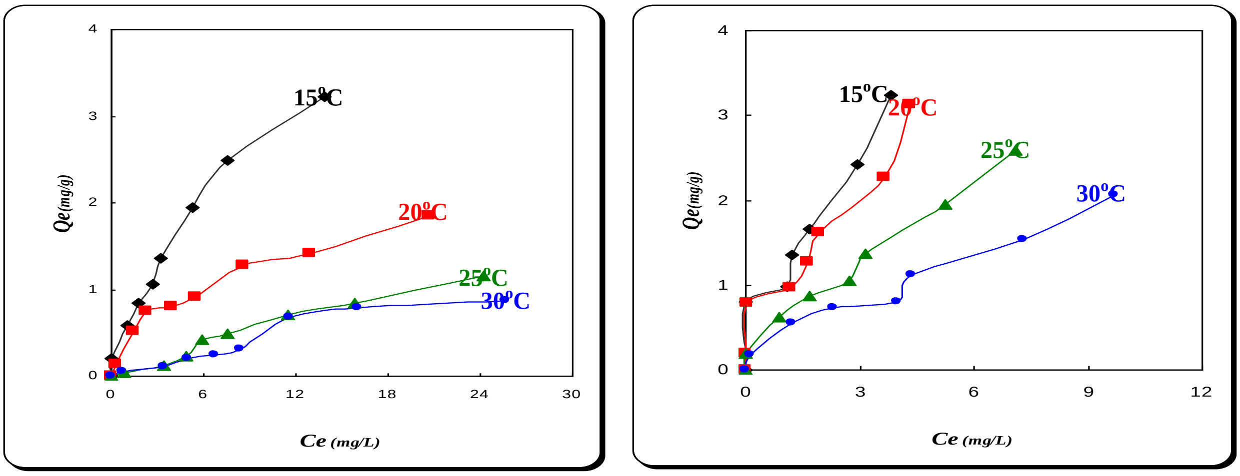
Dye	Langmuir equation			Freundlich equation		
	K_L	q_o	R^2	K_F	n	R^2
Azure B	1.000	0.474	0.8445	0.689	3.021	0.9673
Azure C	-	-	0.6042	0.839	1.163	0.9788



-a- -b-

Figure (3): Linearized models isotherms of dyes onto ploymer at 20°C: a- Freundlich b- Langmuir

The general shapes of dyes adsorption isotherms at four different temperatures are given in Figure (4).



(a) *(b)*

Figure (4) Adsorption isotherms of dyes on hydrogels at different temperatures: a- azure B b- azure C

The adsorption extent of dyes on poly(AAm-co-CA) was decreased with increasing temperature, indicating exothermic process. This could be interpreted as a result of weaking of attractive forces between the dyes molecules and the hydrogels surface with increasing temperature (Kamal 2014 & Xinpeng *et al.* 2014).

The reduction of adsorbate-adsorbent interaction with increasing temperature is reinforced by the temperature dependence of the solubility of dyes molecules. The better molecules are solvated at higher temperatures, the smaller their tendency to adsorb onto the poly(AAm-co-CA) hydrogels surface (Gerasimov 1974).The basic thermodynamic quantities of adsorption of dyes on the hydrogels were estimated through calculating $\mathbf{X_m}$ values at different temperatures. The heat of adsorption (ΔH) may be obtained from Van't Hoff equation: $\ln X_m = \frac{-\Delta H}{RT} + cons\tan t$, the change in free energy (ΔG) could be determined from equation (ΔG = –RTlnK) and the change in entropy (ΔS) was calculated from Gibbs equation The change in entropy (ΔS) may be obtained from Gibbs equation : ($\Delta G = \Delta H - T.\Delta S$). Table (2) and Figure (5) demonstrate these calculations.

Table (2) Effect of temperature on the maximum adsorbed quantity for adsorption of dyes on the poly(AAm-co-CA) hydrogels polymer

T(k)	**10^3/T(k^{-1})**	**azure B**		**azure C**	
		Ce= 5.2		**Ce= 3.8**	
		X_m(mg/g)	**ln(X_m)**	**X_m(mg/g)**	**ln(X_m)**
288	3.472	1.95	0.668	0.881	-0.127
293	3.413	0.90	-0.105	0.712	-0.339
298	3.356	0.35	-1.050	0.623	-0.473
303	3.300	0.20	-1.609		

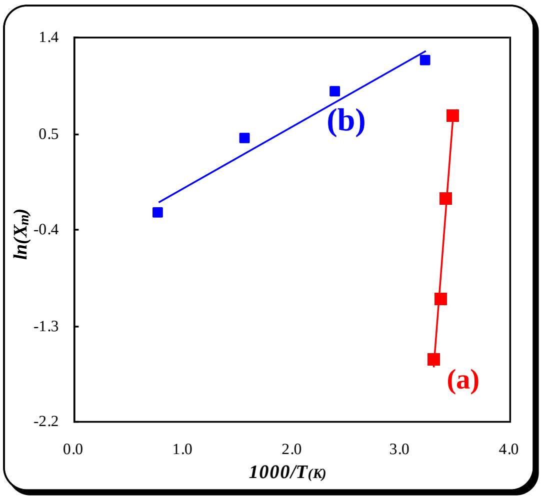


Figure (5): Plot of ln X_m against reciprocal absolute temperature on hydrogels: a- azure B b- azure C

Table (3) shows the basic thermodynamic values of adsorption of dyes on poly(AAm-co-CA). An adsorption of van der Waals type is suggested to take place as indicated by these values.

Table (3): Values of thermodynamic functions of adsorption process of dyes on the poly(AAm-co-CA) hydrogels at 20 °C

Dye	ΔH kJ .mol^{-1}	ΔG kJ.mol^{-1}	ΔS J.mol^{-1}.K^{-1}	Equilibrium Constant (K)
azure B	-112.921	-4.992	-374.752	7.500
azure C	-68.216	-7.027	-212.463	4.263

The adsorption of dyes on poly(AAm-co-CA) is exothermic and spontaneous as indicated by the negative values of enthalpy (ΔH) and free energy change (ΔG). The adsorption of dyes on hydrogels is exothermic in conjunction with a decrease in entropy. This result could be viewed through the fact, that the entropy change (ΔS) of the ordered constrained adsorbed layer is always less than that of dissolved solutes.

Figure (6) shows the effect of ionic strength on the adsorption uptake of the dyes on poly(AAm-co-CA) surface. The adsorption extent has increased on surfaces in the presence of electrolyte. This result is in agreement with that of Kamal (2014).

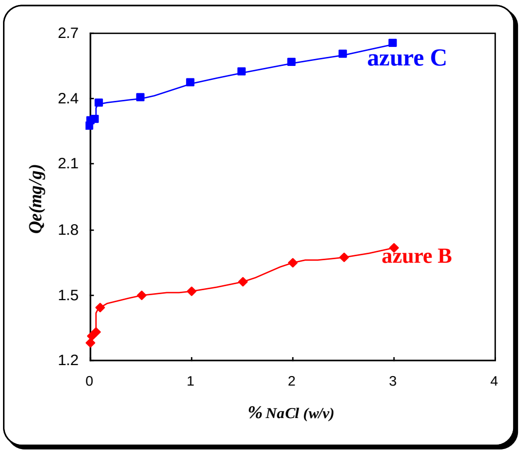


Figure (6) Adsorption isotherms of dyes on hydrogels polymer in the presence of different concentrations of sodium chloride at 20°C

An overall increase in dyes uptake with increasing electrolyte concentration (and hence the ionic strength) is shown in Figures (6). This behavior may be due to the reduction in adsorbate solubility as a result of higher interaction of electrolyte ions with the aqueous solvent. The solubility of ionic salts in aqueous media is normally higher than that of organic dyes molecules. Therefore, a competition between them to interact with the solvent molecules leads to an increase in the attraction between the hydrogels surface and the dye molecules (Xinpeng *et al.* 2014).

CONCLUSIONS:

1-Poly(AAm-co-CA) hydrogels surface adsorbent can be used for the removal azure A and B from solution.

2-Due to higher activity of Poly(AAm-co-CA) surface in adsorption of the dyes, it may be used as adsorbent in wastewater treatment for the removal of these dyes.

3- The adsorption capacity of Poly(AAm-co-CA) was higher for azure C than azure B.

4-The adsorption isotherms of dyes on Poly(AAm-co-CA) obeyed Freundlich isotherm.

5- Dye- Poly(AAm-co-CA) reactions exhibited low enthalpy values (exothermic).

6- There was a positive correlation between the amounts of dyes adsorbed and the ionic strength of solution.

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