

# Removal of Congo Red by Acrylic Acid-co-[2-[2- (Benzimidazole) Azo]-3-Methyl-4-Nitro Phenol] Composite from Aqueous Solution by Adsorption process

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## ABSTRACT

This study is concerned with the adsorption of Congo red from solution on acrylic acid-co-[2-[2- (benzimidazole) azo]-3-methyl-4-nitro phenol] composite (AA-co-L<sub>2</sub>H). The purpose of this study into the search for an active surface to be used to remove dyes from wastewater. Fourier transform infrared spectroscopy (FTIR) and SEM-EDX characterized the morphology and chemical structure of prepared samples. Ultraviolet-visible (UV-vis.) spectrophotometric technique has been used to produce quantitative adsorption at different conditions of time, temperature and concentration of dyes. The calculated data were in accordance with Langmuir equation and the adsorption isotherms are of L-curve. The results obtained show greater removal uptake of dye on composite. The calculated data were in accordance with Langmuir equation and the adsorption isotherms are of L-curve. The results obtained show greater removal uptake of dye on composite. The adsorption was a function of temperature (10, 20 and 30°C). The extent of adsorption of Congo red on the composite was found to increase with decreasing temperature (endothermic process). The basic thermodynamic functions have also been calculated.

**Keywords:** Health, Organic compounds, Removal, Water treatment.

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**Conflict of interest:** None

## INTRODUCTION

Wastewater from the textile finishing industry can have a strong impact on the aquatic environment because it is discharged in high quantity and may contain many biorecalcitrant contaminants.<sup>1</sup> Many dyes used in textile industry are particularly difficult to remove by conventional waste treatment methods since they are stable to light and oxidizing agents and are resistant to aerobic digestion.<sup>2</sup>

The removal of color from dye-bearing effluents is a major problem because of the difficulty in treating such wastewaters by conventional treatment methods.<sup>3</sup> Most dye-containing effluents from various industrial branches, mainly dye manufacturing, and textile finishing, are discharged into river streams.<sup>4</sup> The removal of dyes in an economical fashion remains an essential problem, although recently, a number of successful systems have been evolved using adsorption techniques.<sup>5</sup>

The aim of this work in to investigate the capability of AA-co-L<sub>2</sub>H composite for the prevention of toxicity by Congo red in different conditions of temperature and concentration.

## EXPERIMENTAL

### Chemicals and Materials

Acrylic acid was supplied by (Himedia, India). The activated N,N,N',N'-tetra methyl ethylene diamine (TEMED) was also supplied by (Himedia, India), The initiator, potassium persulfate (KPS) was supplied by Merck, Germany. The multifunctional crosslinker is N, N'-methylene bisacrylamide (NMBA) was purchase from (Fluka, Germany). Sodium chloride was obtained from (Fluka, Germany). Miconazole was purchase from (Sigma-Aldrich, Germany). Sodium Hydroxide and Hydrochloric acid were supplied from (Fluka, Germany). 5,6-Dimethyl-1H-benzimidazole, 2-Amino benzimidazole, 3-Methyl-4-nitro-phenol, and Sodium nitrite (NMBA) were purchase from (Fluka, Germany).

### Characterization

Shimadzu accomplished Fourier Transform Infrared Spectroscopy (FTIR) analysis. FTIR. 8400S instrument with KBr in the 400–4000cm<sup>-1</sup> region. The morphology of prepared materials was noted by scanning electron microscopy (JEOL, JSM-6701F, Japan) operated at an acceleration voltage of 8.0 kV.

### Preparation of AA-co-L<sub>2</sub>H

The co-polymer of AA-co-L<sub>2</sub>H composite was prepared by solving of 0.25 gm from L<sub>2</sub>H powder to 20 mL of distilled water with vigorous stirring at temperature range (50–60°C), then it cooled at room temperature to form the L<sub>2</sub>H solution. 0.05 mol of AA was added to 10 mL of L<sub>2</sub>H solution under constant stirring at 60°C for 10 min. Then the Cross-linked (N, N-Methylene-Bisacrylamide) and initiator (KPS) were added under the nitrogen gas stream for 2 hours. The prepared copolymer was several washed by deionized water and dried at 60 °C in the oven. The grinding and sieving of bulky co-polymer follow that for resulting co-polymer with a particle size of 150µm. The hydrogels' surface was used without further treatment.<sup>6,7</sup>

### Adsorption Isotherm

Solutions of Congo red (10 mL) of known concentrations (1–100 ppm) at 20°C were added to stoppered flasks containing 0.05g of a composite. The flasks were shaken in a water bath at a speed of 150 cycle/minutes till equilibrium is attained (180 min). This time is sufficient for the adsorption process to reach equilibrium. After the equilibrium time elapsed, the suspensions were either centrifuged at 4000 rpm for 10 min. or filtered using double filter papers. The clear supernatants were assayed for dye, after appropriate dilution, spectrophotometrically. Equilibrium concentrations were obtained by comparing the experimental data with the calibration curve.

The quantity of dye adsorbed was calculated according to the following equation<sup>8</sup>:

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

Where:

- x: the quantity adsorbed.
- m: weight of adsorbent (g).
- C<sub>o</sub>: initial concentration (mg/l).
- C<sub>e</sub>: equilibrium concentration (mg/l).
- V: volume of solution (l).

### Effect of Temperature

An experiment of adsorption was repeated in the same manner at temperatures of 10, 20, and 30 °C to estimate the thermodynamic functions.

## RESULTS AND DISCUSSION

### Characterization

Before and after the adsorption process, the composite, the infrared spectra in Figure 1, showed the appearance of a broad absorption band at the range 3187–3510 cm<sup>-1</sup> indicating that there was overlapping between the OH band and the NH band. The bands shown at the 2800–2943 cm<sup>-1</sup> represents the mass vibration of the CH<sub>2</sub>-CH<sub>3</sub> groups due to the presence of CH bonds in the aliphatic compounds. Also, the presence of bands at the wavenumber 1676-1740 cm<sup>-1</sup>, indicates the presence of carbonyl bonds (C=O) for carboxyl groups and the bands that

appear at the range of 1020–1430 cm<sup>-1</sup> due to the vibration of bonds C-N, C-O and C-C.<sup>9</sup>

The morphology is identified using SEM Figure 2 shows FE-SEM analysis of HPMC-co-AA tend to congregate together to form multilayer agglomerates. After adsorption, shows roughen surface and Miconazole uniformly distributed as bright dots on the surface of the hydrogel. These observations demonstrate the presence of both HPMC-co-AA and Miconazole.

### Adsorption of Congo Red

With the exception of the isotherm of Congo red on composite, the isotherms of dye comport with a type L-Giles Classification

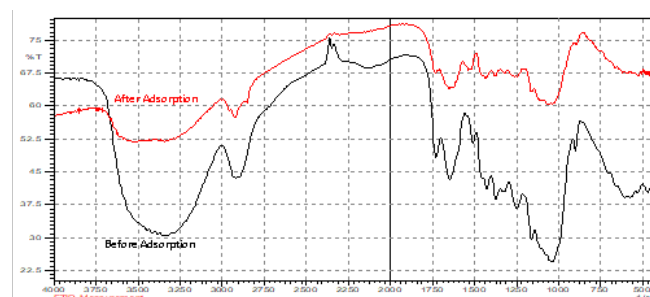


Figure 1: FTIR analysis of composite before and after adsorption of dye

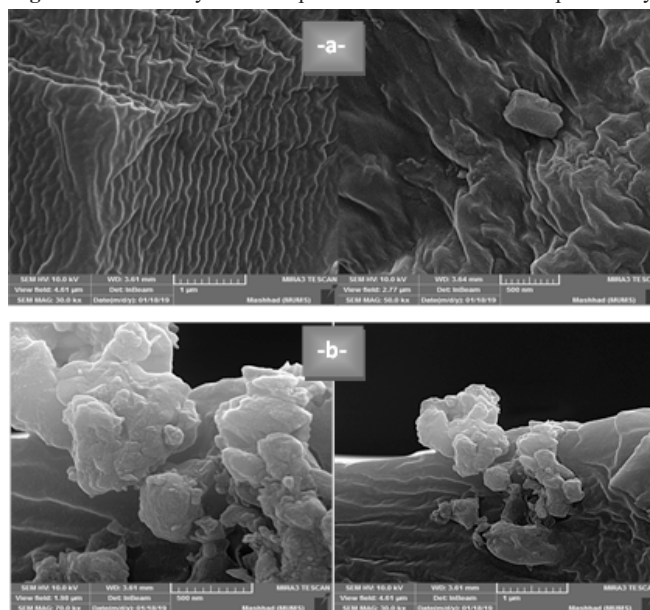


Figure 2: SEM images: (a) before adsorption (b) after adsorption

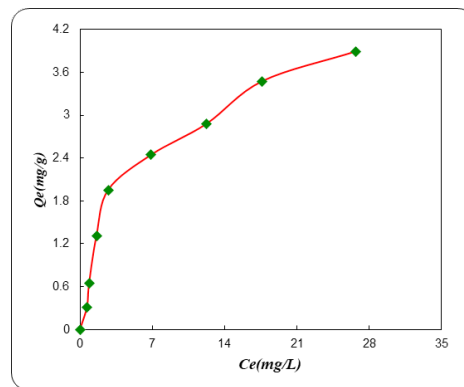


Figure 3: Adsorption isotherms of Congo red on AA-co-L<sub>2</sub>H at 20°C

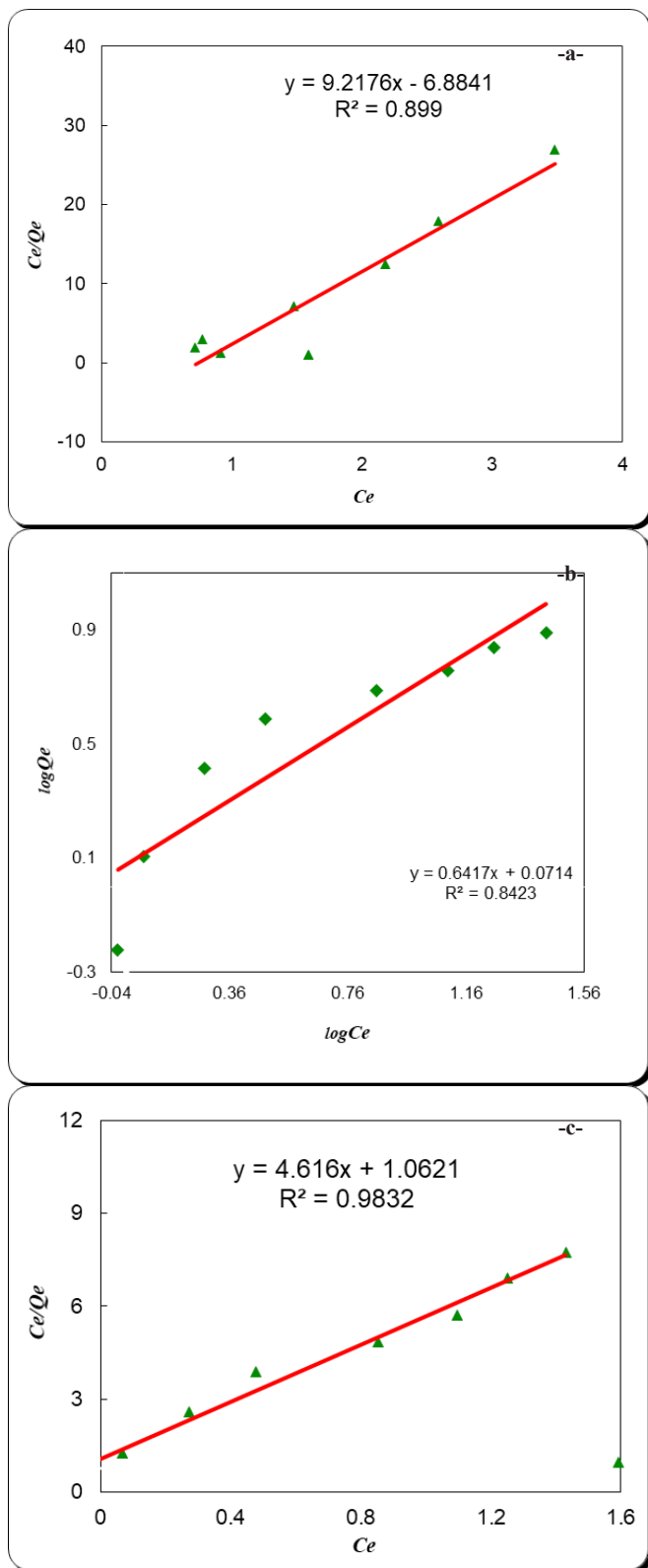


Figure 4: Adsorption model of: a- Langmuir, b- Freundlich and c- Temkin isotherm

Table 1: Amounts of dye uptake by AA-co-L<sub>2</sub>H at 20°C with proper calculations for the application of Langmuir, Freundlich, and Temkin equations

Langmuir equation			Freundlich equation			Timken equation		
$k_L$	$q_m$	$R^2$	$k_F$	$n$	$R^2$	$k_T$	$b$	$R^2$
1.338	0.108	0.8990	1.178	1.558	0.8420	1.258	4.616	0.9830

(Figure 3).<sup>9</sup> L-shaped adsorption isotherm indicates the adsorbed solute molecules are most likely being adsorbed in a flat geometry, which is based on the assumption of high adsorption affinity between the dye and the surface.<sup>10-12</sup>

The adsorption equilibrium data were analyzed using Langmuir, Freundlich, and Temkin isotherm expression. Table (1) summarizes the values of the correlation coefficients for each of these isotherm models. The Langmuir isotherm for the adsorption of Congo red on composite was found to be linear (Figure 4) with a good linear coefficient ( $r^2 = 0.8990$ ) showing that the data also fit the Langmuir relation. This result is in agreement with other publications.<sup>13-15</sup>

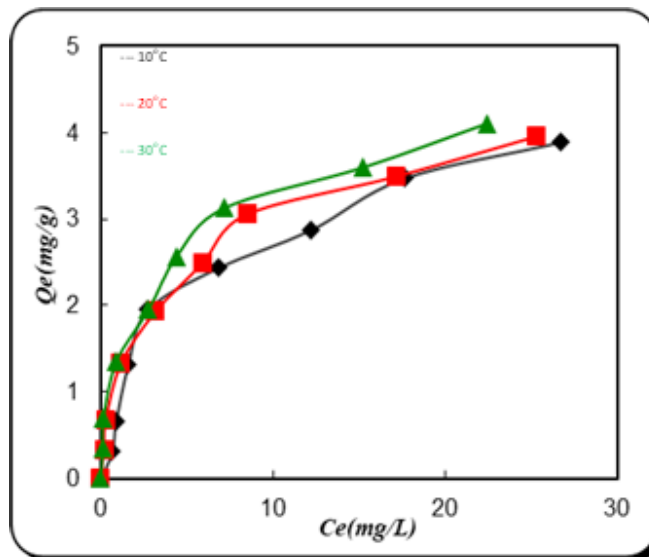


Figure 5: Adsorption isotherms of Congo red on AA-co-L<sub>2</sub>H at different temperatures (°C)

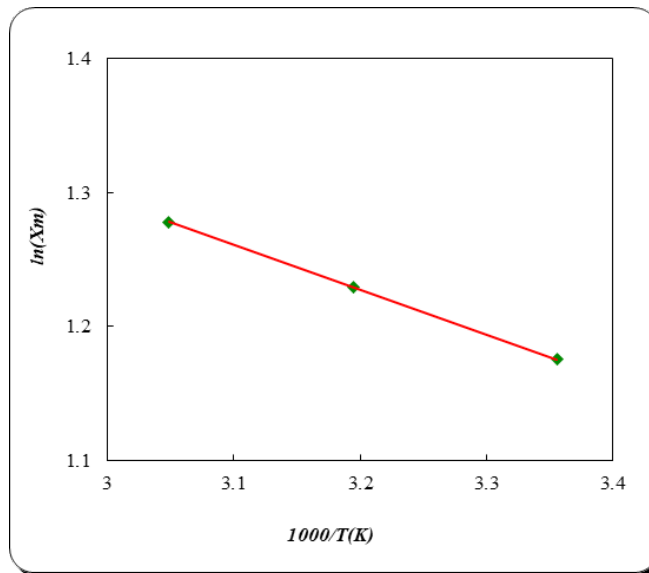


Figure 6: Plot of  $\ln X_m$  against reciprocal absolute temperature for adsorption of Congo red on the composite

**Table 2:** Effect of temperature on the maximum adsorbed quantity for adsorption of Congo red on the composite

$T^{\circ}C$	$T^{\circ}K$	$1000/T\ K^{-1}$	$C_e = 15.40$	
			$X_m$	$\ln X_m$
10	283	3.36	3.24	1.18
20	293	3.19	3.42	1.23
30	303	3.05	3.59	1.28

The effect of temperature on adsorption extent of dyes by adsorbents was investigated at 10, 20, and 30°C, and the results are shown in Figure 5.

The results showed a slight increase in the amount of Congo red adsorbed on composite with increasing temperature, indicating that the dye adsorption process is controlled by an endothermic process. The extent of adsorption of some dye was found to increase with the increase of temperature.<sup>16</sup>

The basic thermodynamic quantities of adsorption of dyes on the adsorbents were estimated by calculating  $X_m$  values at different temperatures (Table 2 and Figure 6). Thermodynamic parameters obtained are summarized in Table (3). The negative value of free energy (DG) indicates the non-spontaneous<sup>17-19</sup> of the adsorption process of dye, and the negative value of entropy (DS)<sup>20</sup> suggests the decrease of randomness at the solid-solution interface during the adsorption of dye on the adsorbent surface.<sup>21-22</sup>

## CONCLUSIONS

- Composite has been found to be economically viable for the removal of dye from aqueous solution.
- Due to the higher activity of composite surface in adsorption of the pollutants, they can be used for the elimination of pollutants from water or wastewater.
- The Langmuir, Freundlich and Temkin isotherms fit the experimental data well for the adsorbates studied.
- Adsorbate - adsorbent reactions exhibited high enthalpy values (endothermic).

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**Table 3:** Values of thermodynamic functions of the adsorption process of Congo red on the composite at 20°C

Equilibrium Constant (K)	$\Delta S$ ( $J.mol^{-1}. K^{-1}$ )	$\Delta G$ ( $kJ.mol^{-1}$ )	$HA$ ( $kJ.mol^{-1}$ )
2.779	-3.560	+21.272	+4.208

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