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Sorption Study of Acid Blue in Aqueous Solution by Synthetic Poly Urea-Formaldehyde

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ABSTRACT

Poly urea-formaldehyde was synthesized simply and rapidly from urea and formaldehyde by condensation polymerization and studied for the sorption of trace acid blue from aqueous solution. The optimum pH value for sorption of the acid blue was 4. Experimental results showed that the sorption capacity of poly urea-formaldehyde for acid blue was determined. The synthetic polymer can be reused for 5 cycles of sorption-desorption without any significant change in sorption capacity. The equilibrium adsorption data of acid blue on poly urea-formaldehyde were analyzed by Langmuir models. Based on equilibrium adsorption data the Langmuir constants were determined about 19 $L.mg^{-1}$ at pH 4 and 20°C.

Keyword: Polymer urea-formaldehyde; Acid blue; Isotherm study; Sorption; Textile dye; Contaminant.

1. INTRODUCTION

As a result of industrial development, many chemical substances generate pollution in air, water, and soil. In the textile industry, dyes usually exist in its wastewaters, which have different toxicities, mobilities and bioavailabilities. There are thousands commercially, synthetic dyes in the leather tanning and textile industries [1]. Most of them are difficult to be decolorized due to their synthetic origin and complex structure. They are specifically designed to resist fading upon exposure to water, light, sweat and oxidizing agents [2, 3]. Acid and basic blue is one of important dyes in this industry [4]. In recent years, due to the extensive use of these compounds in industrial processes a large quantity of dyes containing wastes that lead to serious problems and hazardous risks for human health are discharged into the environment.

Therefore a number of methods exist for removal of these pollutants from liquid waste [5-17]. The purpose of the present study is to indicate the feasibility of using poly urea-formaldehyde as a solid-phase extractant for

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removal of trace acid blue in aqueous samples. The acid blue adsorption behavior on synthesized urea-formaldehyde as a function of initial pH solution, initial acid blue concentration and so on, were also studied.

2. EXPERIMENTAL

2.1. Reagents and solutions

CH_3COOH, CH_3COONa, NaH_2PO_4, Na_2HPO_4, HCl, H_2SO_4, HNO_3, NaOH, urea, formaldehyde, were products of Merck (Darmstadt, Germany).

All the solutions were prepared in deionized water using analytical grade reagents. The stock solution (1000 mg.L^{-1}) of acid blue, were prepared by dissolving appropriate amounts of this dye, in deionized water. Acetic acid-acetate and phosphate buffer were used to adjust the pH of the solutions, wherever suitable. The equilibrium concentrations of each solution were measured by UV-spectrophotometer (Shimadzu UV-2101PC) at the wavelength of 575 nm.

2.2. Synthesis of poly urea-formaldehyde as polymeric sorbent

Urea-formaldehyde was synthesized by reacting formaldehyde (HCHO) with urea (CON_2H_4). In the 20 mL reaction biker, pH of 6 mL of 37% formaldehyde was adjusted to 8 with 20% sodium hydroxide solution. 3 g urea was added to the mixture and kept in the water bath at 70°C for 25 min with intermittent stirring. Then it was acidified with hydrochloric acid 1 M to pH 2-3. Thereafter, it was kept at room temperature for 24 h, and then the precipitated polymer washed for three to four times with warm water to remove unreacted urea and formaldehyde and dried by applying vacuum in a vacuum desiccator. Poly urea-formaldehyde synthesized was of white color resinous material. The reaction scheme is shown in Figure 1.

2.3. Batch method

A sample solution (100 mL) containing (0.5 µg.mL^{-1}) of acid blue was taken in a glass stoppered bottle, after adjusting its pH to the optimum value. The 0.5 g of poly urea-formaldehyde was added to the bottle and the mixture was shaken for optimum time. The polymer was filtered and remained acid blue was determined by UV-Vis spectrophotometer.

2.4. Isotherm studies

Isotherm studies were carried out by adding a fixed amount of poly urea-formaldehyde (0.5 g) to a series of beakers filled with 50 mL diluted solutions of acid blue (10-50 µg.mL^{-1}). The beakers were then sealed and placed in a water bath shaker and

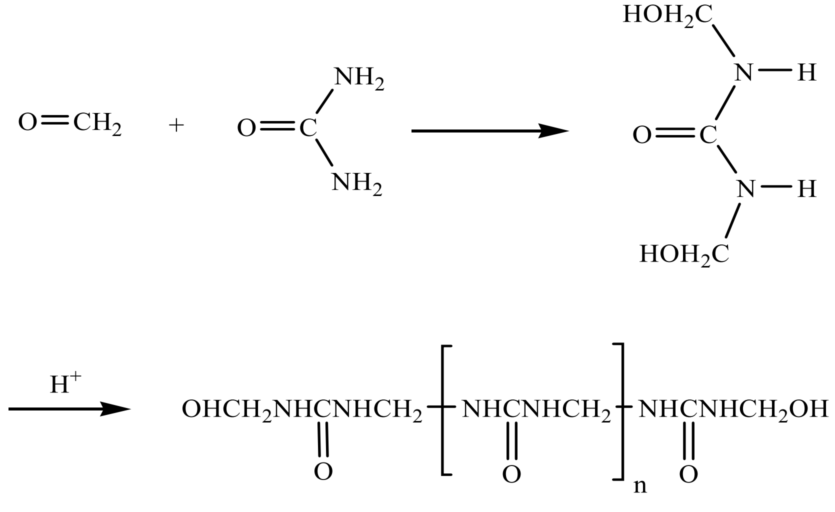

Figure 1: *The methodology of synthesize of poly urea-formaldehyde.*

shaken at 250 rpm with a required adsorbent time (4 h) at 20°C and optimum pH. The pH adjustments have been done using 0.01 M acetate buffer. The beakers were then removed from the shaker, and the final concentration of acid blue in the solution was measured by UV-Vis spectrophotometer. The amount of acid blue at equilibrium q_e (mg/g) on poly urea-formaldehyde was calculated from the following equation:

$$q_e = (C_0 - C_e)\, V/W \qquad (1)$$

where C_0 and C_e (mg/L) are the liquid phase concentrations of acid blue at initial and equilibrium, respectively, V (L) the volume of the solution and W (g) is the mass of adsorbent used.

3. RESULTS AND DISCUSSION

3.1. Acid blue sorption as a function of pH

The degree acid blue sorption at different pH values was determined by batch equilibration technique. A set of solutions (volume of each 100 mL) containing 0.2 µg.mL^{-1} of acid blue was taken. Their pH values were adjusted in range 3-9 with 0.01 M acetate and phosphate buffer solutions. The 0.2 g of poly urea-formaldehyde was added to each solution and the mixture was shaken for 4 h. The optimum pH values for quantitative uptake of metal ions were ascertained by measuring the acid blue content in supernatant liquid. The optimum pH range for the sorption of the acid blue is shown in Figure 2. The maximum sorption was obtained at pH 4.

3.2. Total sorption capacity

The 50 mL solution containing 10-50 µg.mL^{-1} of acid blue and 0.3 g of poly urea-formaldehyde beads were stirred for 5 h at optimum pH. The sorption capacity of the poly urea-formaldehyde for the acid blue was ascertained from the difference between the acid blue concentrations in solution before and after the sorption. The saturated adsorption capacity of the polymer was shown in Figure 3. This figure indicates the effect of initial concentration of the acid blue in the solution on capacity sorption of acid blue by poly urea-formaldehyde. The capacity goes up with increasing initial concentration of the acid blue in the solution.

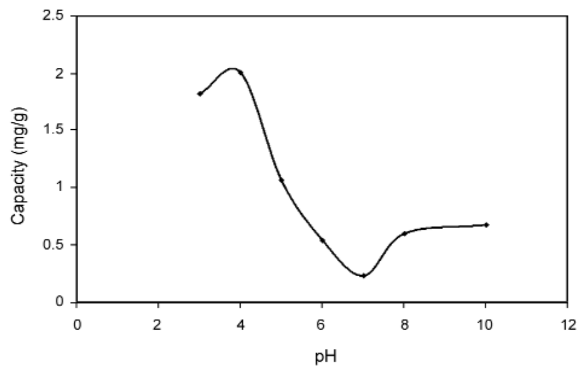

Figure 2: *Effect of pH sorption of acid blue onto poly urea-formaldehyde.*

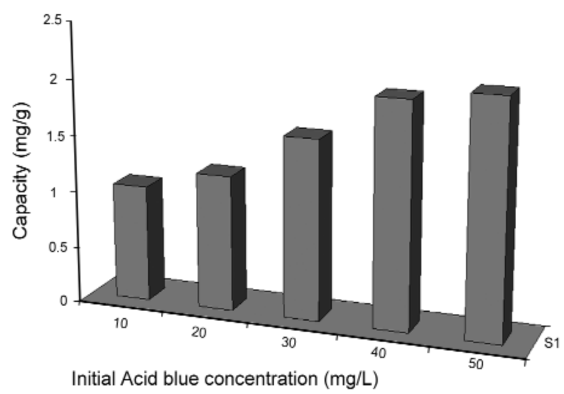

Figure 3: *Effect of initial concentration of the acid blue in the solution on capacity sorption of acid blue onto poly urea-formaldehyde.*

3.3. Stability and reusability of the resin

The acid blue was sorbed (1 mg.g^{-1}) and desorbed on 0.5 g of the poly urea-formaldehyde for several times. It was found the sorption capacity of poly urea-formaldehyde after 5 cycles of its equilibration with acid blue, changes less than 5%. Therefore, repeated use of the poly urea-formaldehyde is feasible. The poly urea-formaldehyde after loading it with samples can be readily regenerated with methanol. The sorption capacity of the poly urea-formaldehyde stored for more than 6 month under ambient conditions has been found to be practically unchanged.

3.4. Adsorption isotherms

The Langmuir model is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of sorption is constant and there is no migration of adsorbate compound in the surface plane. The Langmuir isotherm is given by [18]:

$$C_e/q_e = (1/q_{max}.K_L) + (C_e/q_{max}) \quad (2)$$

where qmax is the maximum adsorption capacity corresponding to complete monolayer coverage on the surface ($mg.g^{-1}$) and K_L is the Langmuir constant ($L.mg^{-1}$). The constants can be calculated from the intercepts and the slopes of the linear plots of C_e/q_e versus C_e (Figure 4). The data fitted well in the Langmuir equation as shown by the regression coefficient values ($R^2 = 0.9966$). The K_L and q_{max} values determined from the slopes and intercepts of the straight-line plot are 19.06 $L.mg^{-1}$ and 2.07 $mg.g^{-1}$, respectively. Good fitting of experimental data by Langmuir isotherm indicates the homogeneous nature of acid blue-binding sites on poly urea-formaldehyde. The essential characteristics of a Langmuir isotherm can also be expressed in terms of a dimensionless constant separation factor RL, given by the following equation [19]:

$$R_L = 1 / (1+K_L.C_0) \quad (3)$$

where C_0 is the initial acid blue concentration (mg/L) and K_L is the energy of interaction at the surface. For a favorable adsorption, the separation factor R_L lies between 0 and 1. Thus, R_L value of 1.05×10^{-3} calculated at optimum pH lie between 0 and 1.0 indicating a highly favorable adsorption.

3.5. Optimization of sorption time of metal ions

Poly urea-formaldehyde (0.2 g) was shaken with 100 mL of solution containing 10 $\mu g.mL^{-1}$ of acid blue at different time (5-180 min) under optimum pH. After filtration concentration of acid blue in supernatant was determined with UV/Vis using recommended batch method. The sorption as a function of contact time for acid blue is shown in Figure 5. Less than 15 min shaking was required for 70% sorption. The profile of acid blue uptake on this sorbent reflects good accessibility of the sites in the polymer. The sorbent was saturated at 60 min.

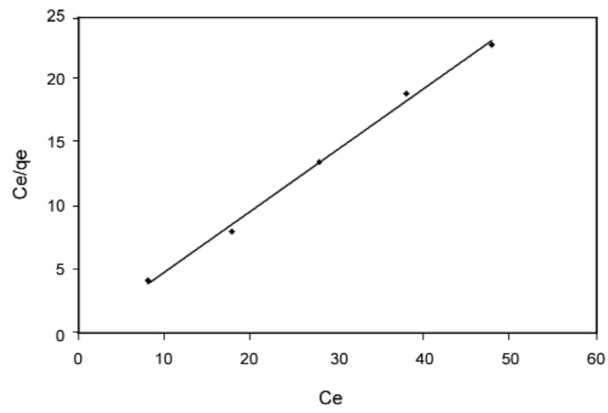

Figure 4: *Langmuir isotherm for acid blue adsorption onto poly urea-formaldehyde at 20°C.*

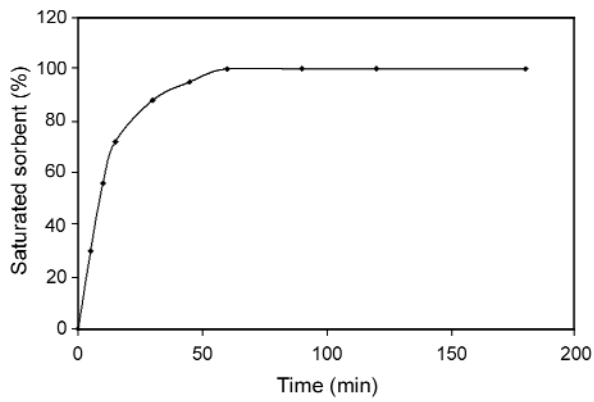

Figure 5: *Effect of contact time on sorption of acid blue onto poly urea-formaldehyde*

4. CONCLUSIONS

Poly urea-formaldehyde was synthesized with urea and formaldehyde by condensation polymerization. The synthesis of the polymer is simple and economical. The polymer has a good potential for the sorption trace amount of acid blue from large sample volumes. The polymeric sorbent also present the advantage of reasonable adsorption capacity, good reusability and high chemical stability. Based on the Langmuir isotherm analysis, the monolayer adsorption capacity was determined to be 2.07 (mg/g) at 20°C.

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