

Decolorize dye effluents of textile industries by sulfonated urea-formaldehyde resin

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- **Novelty and Highlights:**

- 1 – Synthesis of cheapest modified porous urea-formaldehyde resin.
- 2 – Removal and decolourization of textile effluents by environmental friendly method.
- 3 – The resultant liquids were almost colourless with very low COD.
- 4 – Adsorption properties were investigated under different conditions.

- **Graphical Abstract:**

Comparative absorption capacity of modified urea-formaldehyde resin shows excellent absorption and degradation of dyes molecules from effluents.



Decolorize dye effluents of textile industries by sulfonated urea-formaldehyde resin

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Abstract:

Synthetic dyes have a complex aromatic molecular structure. Effluent of dye industries contains a number of contaminants, such as acid or caustic dissolved and suspended solids, toxic compounds, and colouring pigments. In the present article, sulfonated urea-formaldehyde resin was used to decolorize dye effluent obtained from textile industries. Sulfonated urea-formaldehyde resin is used because of their low cost and local availability. Textile effluents were collected and treated with various mixtures of sulfonated urea-formaldehyde resin, rice husk and animal charcoal. The resultant liquids were almost colourless with very low chemical oxygen demands. Adsorption properties were investigated under different conditions.

Keywords: Sulfonated resins; adsorption; textile effluents

Introduction

Now a day, synthetic dyes are extensively used in many fields of technology, for example, the textile, leather, paper, rubber, plastics, cosmetics, pharmaceutical, and food industries [1]. Most of the synthetic dyes have a complex aromatic molecular structure and demonstrate substantial structural diversity [2]. The widespread use of dyes often poses severe pollution tribulations because of the effluent of industries contain a number of contaminants, such as acid or caustic dissolved and suspended solids, toxic compounds, and colouring pigments [3]. Many dyes are also toxic to some specific organisms, which causes the straight annihilation of marine communicates [3]. The conventional methods for the removal of dyes from wastewater include coagulation and flocculation, oxidation, membrane separation, and adsorption [4–5]. Activated carbons have the benefit of exhibiting high adsorption ability for organic pollutants such as dyes. The adsorption of different dyes from aqueous mediums onto activated carbons has already been investigated [6], and the exclusion of various dye categories has been discussed [7]. According to these studies, the adsorption capacities of different dyes onto activated carbon changes from 50 to 90%, depending on the properties of the activated carbon, the initial dye concentration, and the type of dye [8]. Pereira and co-workers [9] reported that the percentage of dye deletion with activated carbon for different types of dyes changed in the range 5–80%. However, a relatively high price; high operating costs, and problems with regeneration prevent its large-scale application. Therefore, there is a growing need to find low-cost, renewable, locally available materials as

sorbents for the removal of dye colours [2]. Some low-cost materials have also been directly used as sorbents, such as chitosan, zeolites, clay, fly ash, coal, natural oxides, and industrial wastes, for dye adsorption [10]. There are also many articles about removal of basic dyes with different types of sorbent. These studies have shown that the utmost dye uptake capacities of different types of sorbents change in a large scale from 50 to 200 mg/g [11]. In recent years, research importance in the production of better substitute sorbents to replace conventional sorbents has intensified because of their low cost and local availability. The aim of this study is to investigate the possibility of the dye adsorption of sulfonated urea-formaldehyde (SUF) resin. A literature survey did not yield any research on the use of SUF resin as a sorbent. In addition, the reactive carbonyl groups of SUF resin can be modified easily by various modification agents containing $-\text{SO}_3\text{H}$ and $-\text{COOH}$, $-\text{NH}_2$ groups. Materials that have these functional groups exhibit high adsorption properties. Consequently, we attempted to incorporate the $-\text{SO}_3\text{H}$ group into the resin by a sulfonation reaction. Then, this resin was used as a sorbent for the adsorption of basic dyes from textile effluents for the first time. Finally, SUF-resins may be a new way to remove some dye molecules from textile effluents because of their low cost and local availability.

Experimental

Materials and all the necessary reagents like Formaldehyde (F), Urea (U), and other necessary chemicals were all purchased from local companies. The rest of the materials were synthesis or analytical grade. Fourier transform infrared (FTIR (Randolph, MA, USA)) spectra of the

samples were recorded on a Digilab Excalibur-FTS 3000 MX instrument in the range 400–4000 cm^{-1} . To prepare the sample pellets, the samples were diluted with IR grade Merck KBr (sample/KBr 5 1: 200 w/w). A Jeol JSM-5600 scanning electron microscope (Tokyo, Japan; acceleration voltage = 5 kV) was used to examine the surface morphology of the resins. The micrographs were taken at a magnification of 2500. Spectrophotometric measurements were also carried out with a Jenway 6105 ultraviolet-visible (Dunmon, UK) spectrophotometer.

Preparation of the sulfonated urea-formaldehyde (SUF) resin as sorbent

Step 1: Preparation of the urea formaldehyde (UF) resin

The polycondensation reaction of urea and formaldehyde was carried out according to a known procedure [12] with a 3:1 molar ratio of urea to formaldehyde. The reaction system was a 500-mL four-necked glass reaction kettle equipped with a mechanical stirrer, a reflux system, a temperature control system, and a heating mantle. Urea (37 g), Formaldehyde (52 g), and NaOH (0.42 g) as a catalyst were added to the reaction kettle at room temperature and stirred mechanically and the temperature was increased to 68°C and kept constant. The reaction was followed by the determination of the free formaldehyde amount according to the hydroxylamine hydrochloride method, [13] and the reaction was carried out until a constant free formaldehyde value was reached. At the end of the reaction, the resin type urea-formaldehyde (UF) resin was purified in vacuum in a rotary evaporator system. The product was characterized by FTIR spectroscopy (figure 1).

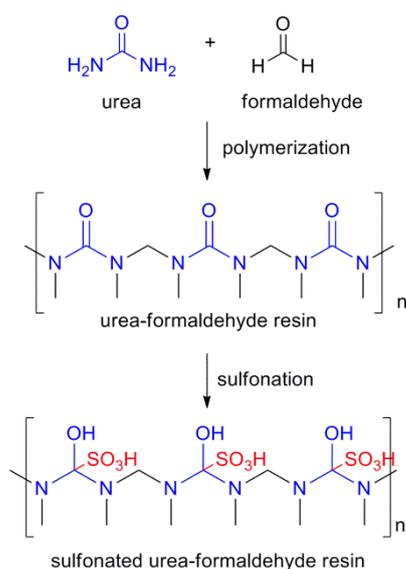


Figure 1 Synthesis of SUF resin

Step 2: Sulfonation of the urea-formaldehyde resin

The sulfonated urea-formaldehyde (SUF) resin was synthesized by the sulfonation reaction of UF-resin (figure 1), which was prepared in step 1, with sodium hydrogen sulphite (NaHSO_3). The sulfonation reaction was carried out in a 500-mL four-necked glass reaction kettle equipped with a mechanical stirrer, a reflux system, a temperature control system, and a heating mantle. At first, 84 g of UF resin was added to the reaction kettle at room temperature, and the temperature was raised to 56 °C. NaHSO_3 (25 g) dissolved in 60 mL of distilled water was added to the solution with a burette where the adding velocity was 1.8 mL/min. Then, the temperature of the solution was kept at 65 °C for 80 min. The resin prepared according to this procedure had a solid content of approximately 59–60%. The number of sulfonate groups per unit of the polymeric chain was determined by wet oxidation of pulp followed by estimation of sulphate by precipitation of barium sulphate (Canadian Pulp and Paper Association Standard G28 1970) and was found to be 1 wt. % [14]. Finally, SUF resin was used as a sorbent for the removal of the dyes from effluents solutions after curing at 168 °C for 1 h.

Characterization of SUF-resin

The FTIR spectrum of UF-resin exhibited the characteristic absorption peaks. In this spectrum (figure 2), absorption peaks 1012–1019 cm^{-1} (deformation vibration of OH due to the methylol groups and CO stretching), 1109 cm^{-1} (CO stretching), 1232 cm^{-1} (CO stretching and dimethylene carbonil bridges), 1367 cm^{-1} (deformation vibration of OH due to the methylol groups), 1439 cm^{-1} (asymmetric bending vibration of CH_2).

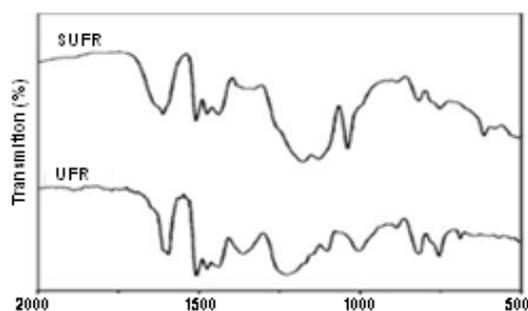


Figure 2 FTIR spectrum of SUF-resin

The spectrum of SFA-resin showed additional peaks, which was different from the spectrum of FA-resin. These new absorption peaks were observed at about 621, 1038, 1126, and 1182 cm^{-1} . The absorption peaks at 621, 1038, and 1126 cm^{-1} resulted from the symmetric stretching vibration of SO_3H groups and the stretching vibration of the sulfonate anion, respectively. In addition, sulfonic

group vibration bands were observed at 1182 cm^{-1} , as reported previously [15]. Moreover, after sulfonation, a significant decrease in the intensity of methylol groups (1360 cm^{-1}) supported the occurrence of a sulfonation reaction between the SO_3H groups and the methylol groups of resins. These changes observed in the spectrum indicated the incorporation of SO_3H groups into the resin structure after sulfonation. In addition, because of the interference between the peaks attributed to methylol groups ($1328\text{--}1383\text{ cm}^{-1}$) and to a newly formed band at $1330\text{--}1420\text{ cm}^{-1}$ (SO_2 group), the intensity of the peaks in this region increased significantly.

Dye adsorption experiments

Adsorption experiments were carried out in 100 ml beaker flasks containing 50 ml of synthetic dye influents at $25\text{ }^\circ\text{C}$. SUF-resin (0.25 g) was added to the textile dyes influents with concentrations of 500 mg/L for the determination of adsorption capacity. At different time intervals of 5, 10, 15, 30, 45, 60, 90, 120, 180, 240, 300, and 360 min and 24 h at pH 6, the dye concentration in the influents was analysed by colorimetric with a spectrometer by the measurement of change in intensity of absorbance at the maximum absorption wavelength. In the equilibrium adsorption isotherm experiments, a fixed amount of sorbent (0.25 g) was contacted with 50 ml of dyes influents with different concentrations (50–500 mg/L). The amount of residual dye in aqueous solution was determined with a UV–visible spectrophotometer after 24 h. All of the experiments were carried out in triplicate.

COD Measurement

Chemical oxygen demand (COD) of treated dye effluents gets significantly reduced after adsorption on different combination of adsorbents. COD of the effluents after adsorption shows significant decrease from 1285 mg/l to 704 mg/l (resin), 768 mg/l (resin + wood scrape), 228 mg/l (resin + charcoal) and 210 mg/l (resin + wood scrape + charcoal).

Results and discussion

Scanning electron microscopy analysis of SUF-resin

The scanning electron micrograph is widely used to study the morphological features and surface characteristics of the adsorbents. SEM of the SUF-resin sorbent after and before adsorption was taken at a magnification of 2500 (Figure 3 and 4 respectively). The surface of SUF resin becomes smooth due to adsorption of dye molecules from effluents. This also shows the importance of surface availability for the adsorption of dye on it.

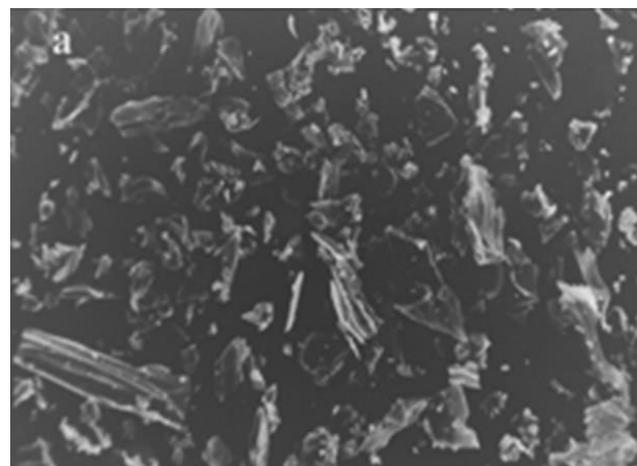


Figure 3. SEM image of SUF resin before adsorption

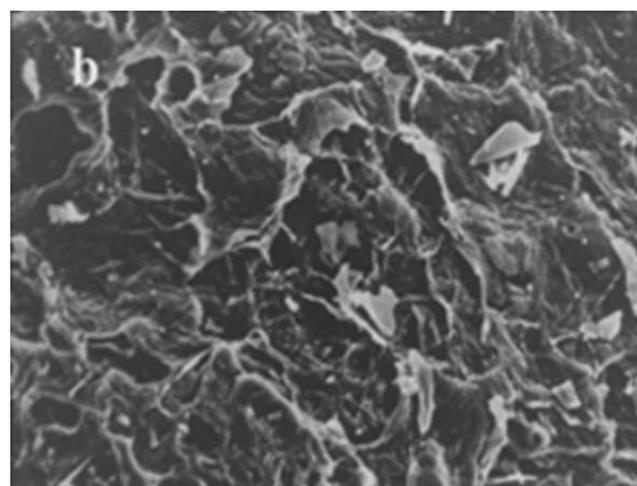


Figure 4. SEM image of SUF resin after adsorption

UV–vis spectroscopy analysis of SUF-resin

At the end of 6 h of adsorption, the adsorption capacities of the SUF-resin were determined as about 110 mg/g for all of the basic dyes effluents. Because the SUF-resin surface demonstrated a nonporous structure, we can say that the incorporation of SO_3H groups into the structure provided sorbent characteristics to the resin.

Adsorption behaviour of the cationic dyes

The sulphonated UF-resin had many ionisable groups, such as SO_3H groups. At pH 6, the SO_3H groups were in their ionized form, and electrostatic interaction could occur between the SO_3H groups of the resins and the cationic groups of the basic dye molecules consequently, the dye adsorption ability became better (figure 5).

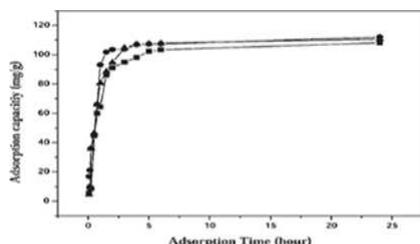


Figure 5. Adsorption of the cationic dyes

Effect of the contact time and pH

The residual dye concentrations in solution were determined at different times from initial solutions of 500 mg/L and a sorbent dosage of 0.2 g/L. According to the adsorption studies, which were carried out at different pH values, the optimal pH value was determined as 6, and all experiments were carried out in triplicate at this pH value. This result was compatible with other results given previously in the literature [16,17]. Furthermore, it has also been reported that the pH values of the basic dye effluent from the dyeing processes are below 7.39. The adsorption capacities for dyes effluent were increased with the increase of the adsorption time. After the equilibrium adsorption time of 6 h, the adsorption capacities for different dyes influents were measured. As a result, the dye uptake capacities of this sorbent for these basic dyes were compatible and comparable with that other sorbents that have been given in the literature.

Effect of the initial dye concentration

The adsorption isotherms were determined in beaker flasks containing synthetic dyes effluent at 25 °C and pH 6. A fixed amount of 0.25 g of sorbent was contacted with 50 mL of dyes effluent with different concentrations. The initial concentrations of solution were 50, 100, 200, 300, 400 and 500 mg/L, respectively. The amounts adsorbed by the resin particles [mg/g] were calculated by the mass balance relation:

$$q_e = (C_o - C_e) \times \frac{V}{W}$$

Where C_o and C_e are the initial solution concentration (mg/L) and equilibrium concentration (mg/L), respectively; V is the volume of the solution; and W is the weight of the dry sulphonated resol type FA-resin (g). Several models have been published in the literature to describe adsorption isotherms. The Langmuir and Freundlich models are the most frequently used models [18,19]. In this study, the Langmuir and Freundlich models were used to describe the relationship between the amount of dye adsorbed and its equilibrium concentration in solution. However, when the Langmuir isotherm model was applied to these systems, the regression coefficient

(R^2 s) values were found to be 0.4917, 0.3617 and 0.5389 for different dyes influents. Therefore these results are not suitable for describes the adsorption of these basic dyes. The logarithmic form of the Freundlich model is given by the following equation:

$$\log(x/m) = \log K_f + \frac{1}{n} \log C_e$$

Where, K_f and n are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. When $\log(x/m)$ was plotted against $\log C_e$, a straight line was obtained with slope $1/n$, which showed that the adsorption followed a Freundlich isotherm well. The parameters of the Freundlich isotherm (figure 6), K_f , which is calculated from the intercept of the plots, and n and R^2 , are given in Table I. R^2 's indicate whether the Freundlich isotherm is applicable for a system or not. The R^2 values were 0.9865, 0.9889, and 0.9882 for ST, NBA, and BCB, respectively, n values between 1 and 10 indicate beneficial adsorption [20, 21]. For the adsorption of textile effluent over the surface of SFA-resin, where value of n is always greater than 1, but above the critical beneficial adsorption the value of $n = 1$.

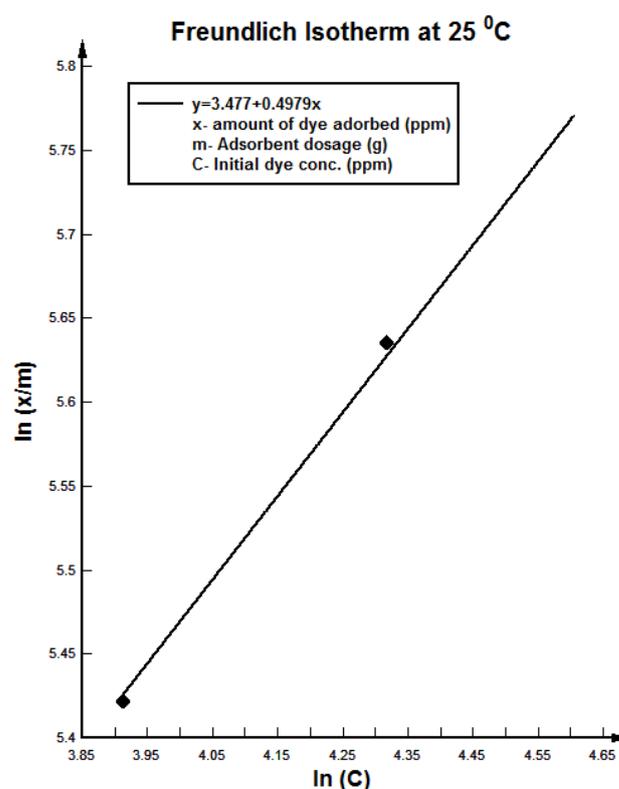


Figure 6. Freundlich Isotherm



Conclusions

In this work, UF-resin was prepared and sulfonated with sodium hydrogen sulphite. Then, this sulfonated UF-resin was used as a sorbent in adsorption studies for the textile effluent. The adsorption properties were investigated under different adsorption conditions with different initial dye concentrations, contact times, and pH values. The adsorption equilibrium data were analysed with the Freundlich and Langmuir models. After the incorporation of SO₃H groups to the resin structure, the adsorption capacity of the resin increased noticeably. The adsorption capacities for textile effluents increased with the increase of the adsorption time until a plateau value was reached. After the equilibrium adsorption time of 6 h, the adsorption capacities for the textile influents were reached about maximum values of mg/g. At the end of this study, we can say that the sulfonated resin may be used as an alternative sorbent for the removal of some dye molecules from wastewaters.

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