Removal and decolorization of dye bearing textile effluents by sulfinated furfural-acetone resin

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ABSTRACT

In this study, we aimed to investigate the removal and decolorization of dye bearing textile effluents by sulfinated furfural-acetone (SFA) resin. Various textile effluents were collected and treated with various mixtures of SFA resin, rice husk and animal charcoal. The resultant liquids were almost colorless with very low COD. The sludge can also be used for pigmentation as well as filler for plastic manufacturing. The produced polymers may have entity in environmental science. This sulfinated resin was characterized by FT-IR spectroscopy and scanning electron microscopy. The adsorption properties of this resin were investigated under different adsorption conditions with different initial dye concentrations, contact times, and pH values. The adsorption equilibrium data were analyzed with Langmuir and Freundlich models. The adsorption behaviors of various textile effluents onto the SFA- resin were better described by the Freundlich model.

Keywords: Sulfinated resins; Adsorption; Textile effluents

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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 chemical classes of dyes ideal more recurrently in the industrial field are the azo-based chromophores mutual with different types of reactive groups. [3] 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 coloring pigments. [4] In addition, some dyes as well as their metabolites are either toxic or mutagenic and carcinogenic. [5] Many dyes are also toxic to some specific organisms, which causes the straight annihilation of marine communicates. [4] According to the convention of Ministry of Environment and Forestry of Turkey, the perimeter of these materials in wastewater should be lower than 10 mg/L because dyes are considered ''precarious and destructive materials''. [6] The conventional methods for the removal of dyes from wastewater include coagulation and flocculation, oxidation or ozonation, membrane separation, and adsorption. [7–11] 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, [12,13] and the exclusion of various dye categories has been discussed. [14–17] 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. [18] Pereira and coworkers [20,21] 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 colors. [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. [22] 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. [23, 24] In recent years, research importance in the

2693

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 SFA resin. A literature survey did not yield any research on the use of SFA-resin as a sorbent. Furfural-acetone resins are the oldest industrial polymers that are still used because of some of their superior properties and their low manufacturing cost. In addition, the reactive carbonyl groups of furfural-acetone resin can be modified easily by various modification agents containing -SO_3H and -COOH, -NH_2 groups. Materials that have these functional groups exhibit high adsorption properties. Consequently, we attempted to incorporate the -SO_3H 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, SFA-resins may be a new way to remove some dye molecules from textile effluents because of their low cost and local availability.

MATERIALS AND METHODS

Materials and all the necessary reagents like Fural (F), Acetone (A), 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 (UV–vis (Dunmon, UK)) spectrophotometer.

2.1. Preparation of the sulfinated furfural-acetone (SFA) resin as sorbent
Step 1: Preparation of the furfural-acetone (FA) resin
The polycondensation reaction of furfural and acetone was carried out according to a known procedure [25] with a 3:1 molar ratio of furfural to acetone. 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. Acetone (37 g), Furfural (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 furfural amount according to the hydroxylamine hydrochloride method, [26] and the reaction was carried out until a constant free furfural value was reached. At the end of the reaction, the resol type furfural-acetone (FA) resin was purified in vacuum in a rotary evaporator system. The product was characterized by FTIR spectroscopy.

Step 2: Sulfonation of the furfural-aceone resin
The sulfinated resol furfural-aceone (SFA) resin was synthesized by the sulfonation reaction of FA-resin, which was prepared in step 1, with sodium hydrogen sulfite (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 FA-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 chemical analysis and was found to be 1 wt %. [27] Finally, SFA-resin was used as a sorbent for the removal of the basic dyes from aqueous solutions after curing at 168 °C for 1 h.

2.2. Characterization of SFA-resin
The FTIR spectrum of FA-resin exhibited the characteristic absorption peaks. In this spectrum, 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$_2$).

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$_3$H 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. 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$_3$H groups and the methylol groups of resol resins. These changes observed in the spectrum indicated the incorporation of SO$_3$H groups into the resin structure after sulfonation.

Scheme – 01
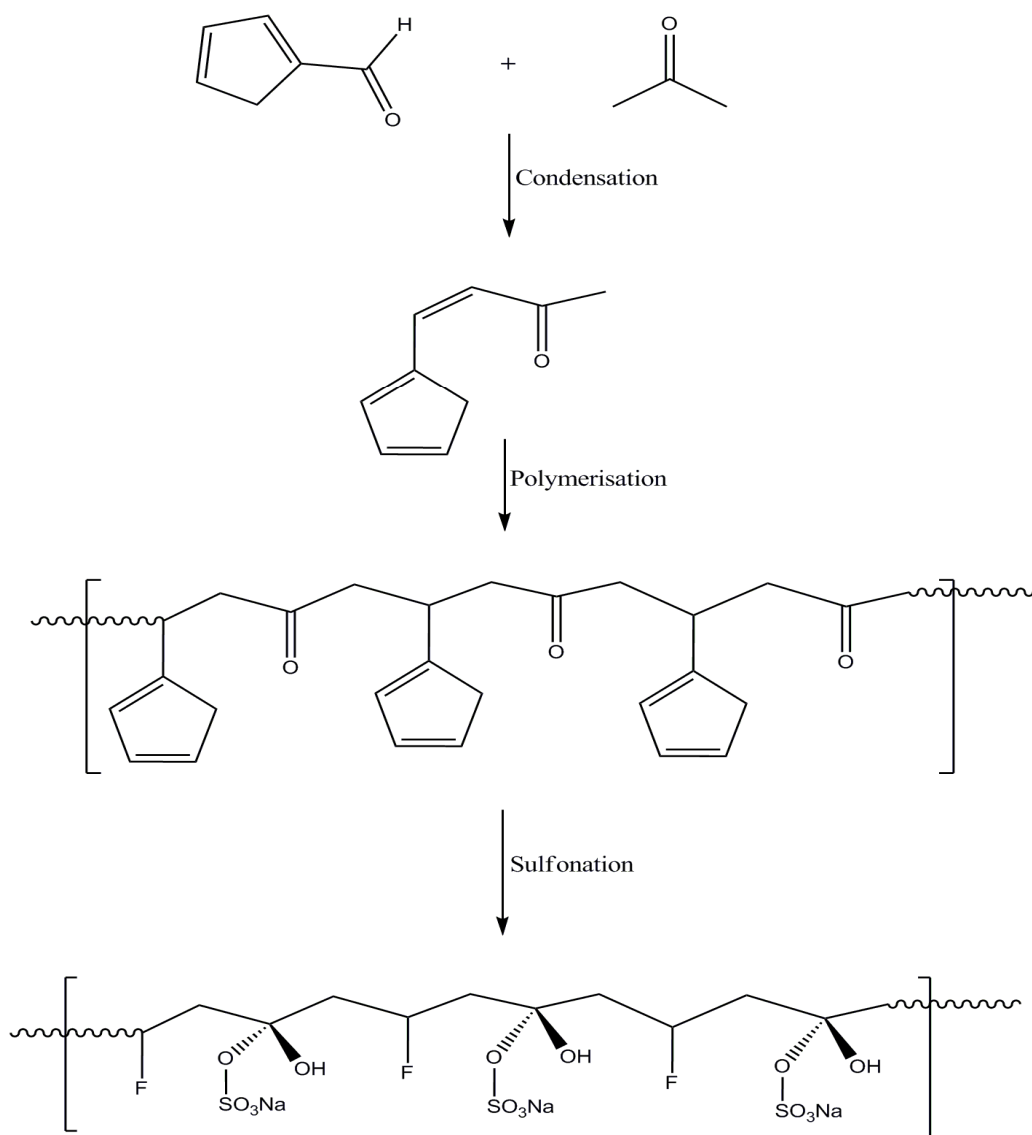
2.3. Dye adsorption experiments

Adsorption experiments were carried out in 100 ml beaker flasks containing 50 ml of synthetic dye influents at 25 °C. SFA-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 analyzed colorimetrically with a spectrometer by the measurement 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.
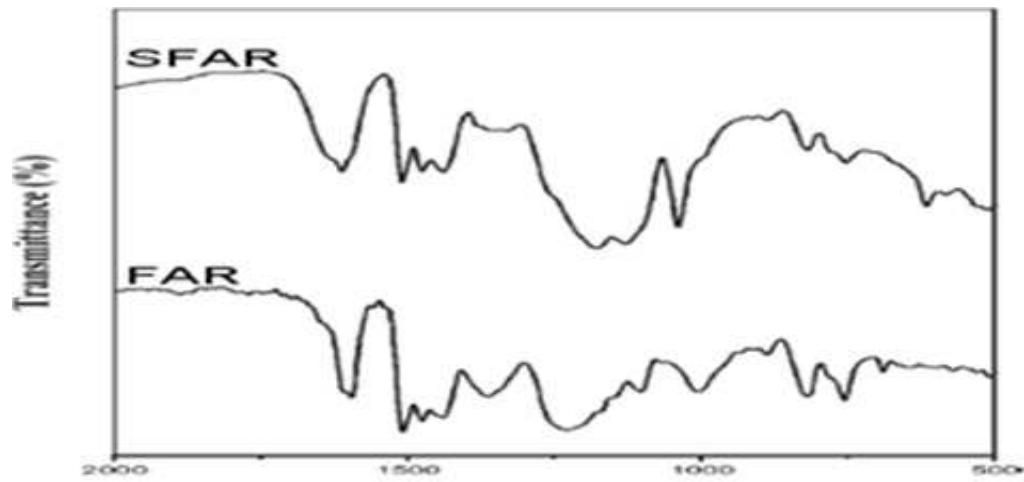
Figure - 01

Solid Lump   *Fine Powder*   *Dyes Adsorbed*

Figure – 02

Dyes effluents   *Before*

After treatments

Figure – 03

2696

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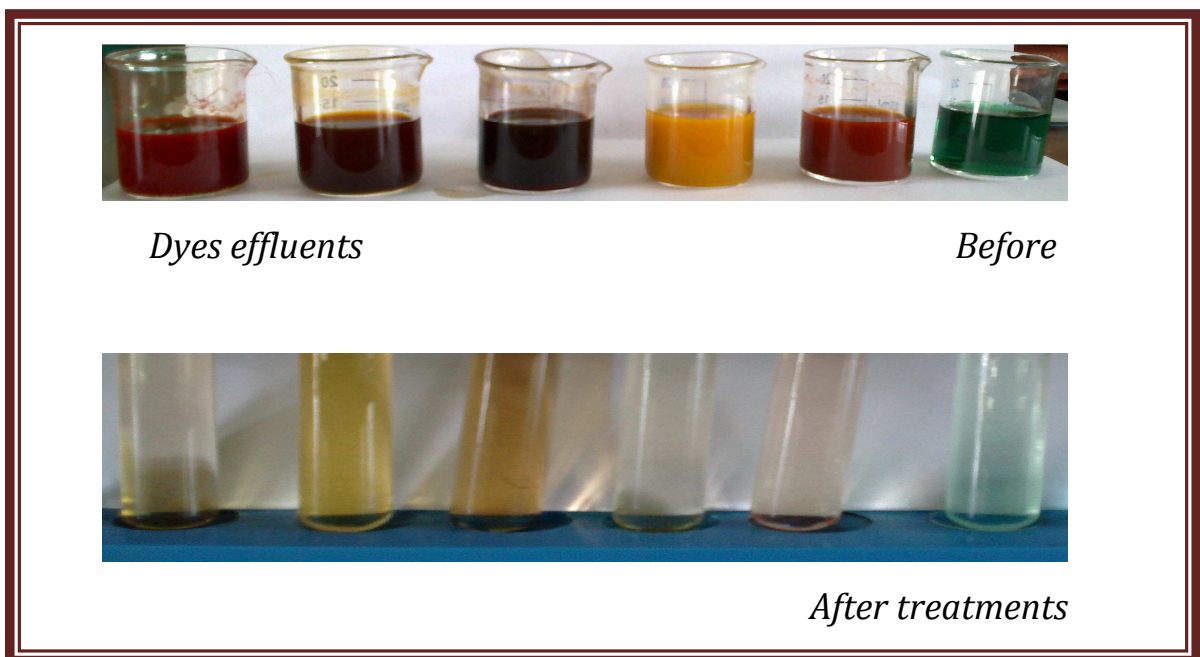## RESULTS AND DISCUSSION

FTIR analysis of SFA-resin after dye adsorption shows the FTIR spectra of SFA-resin before and after dye adsorption. As expected, the adsorption peaks that were easily seen at 621 and 1126 cm^{-1}, which were attributed to the symmetric stretching vibration of SO_3H groups and to the stretching vibration of the sulfonate anion, in the spectrum of SFA-resin before adsorption disappeared after dye adsorption. In addition, because of the interference between the peaks attributed to methylol groups (1328–1383 cm^{-1}) and to a newly formed band at 1330–1420 cm^{-1} (SO_2 group), the intensity of the peaks in this region increased significantly.

2.4. Scanning electron microscopy analysis of SFA-resine
The scanning electron micrograph of the SFA-resin sorbent was taken at a magnification of 2500. The scanning electron micrograph of the SFA-resin sorbent showed its smooth and nonporous surface.

2.5. UV–vis spectroscopy analysis of SFA-resine
At the end of 6 h of adsorption, the adsorption capacities of the SFA-resine were determined as about 110 mg/g for all of the basic dyes efulents. Because the SFA-resine surface demonstrated a nonporous structure, we can say that the incorporation of SO_3H groups into the structure provided sorbent characteristics to the resin.
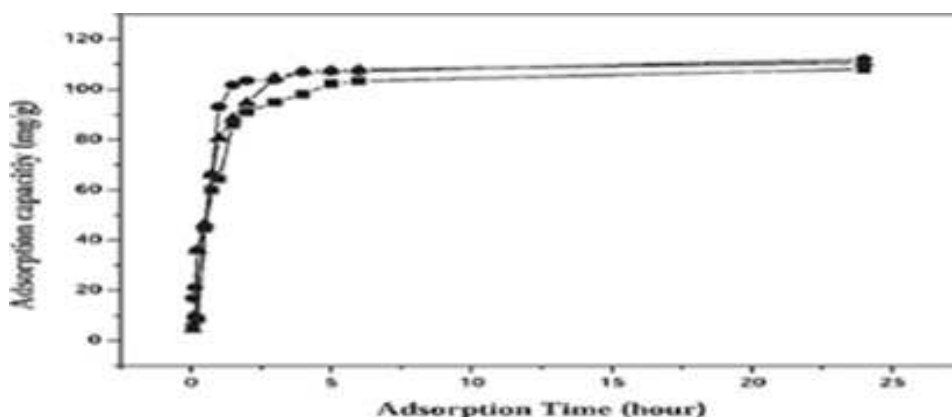

Figure -04

2.6. Adsorption behavior of the cationic dyes
The sulphinated resol-type FA-resin had many ionizable 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.

2.7. 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. 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.

2.8. Effect of the initial dye concentration
The adsorption isotherms were determined in beaker flasks containing synthetic dyes effluent at 25 ºC 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 [Co's (mg/L)] of solution were 50, 100, 200, 300, 400 and 500 mg/L, respectively. The amounts adsorbed by the resin particles [qe's (mg/g)] were calculated by the mass balance relation:

$$q_e = \frac{(C_0 - C_e) \times V}{W}$$

Where Co and Ce 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 sulphinated resol type FA-resin (g). Several models

2697

have been published in the literature to describe adsorption isotherms. The Langmuir and Freundlich models are the most frequently used models. [28, 29] 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 (R20 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:

$$\text{Log } q_e = \log K_f + 1/\text{n} \log C_e$$

where K_f and n are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. When log qe 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, K_f, which is calculated from the intercept of the plots, and n and R2, are given in Table I. R_2's indicate whether the Freundlich isotherm is applicable for a system or not. The R2 values were 0.9865, 0.9889, and 0.9882 for ST, NBA, and BCB, respectively. n values between 1 and 10 indicate beneficial adsorption. [30-34] 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.

CONCLUSION

In this work, FA-resin was prepared and sulfinated with sodium hydrogen sulfite. Then, this sulfinated FA-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 analyzed with the Freundlich and Langmuir models.

Our results show the following:
• After the incorporation of SO_3H groups to the resin structure, the adsorption capacity of the resol resin increased noticeably. The adsorption capacities for textile enfluents 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 resol resin may be used as an alternative sorbent for the removal of some dye molecules from wastewaters.

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