Minimization of dyestuff pollutions using native, alkali-treated or bleached cellulose of rice straw as adsorbent

I Abd El-Thalouth¹, H M El-Hennawi¹, a, S S Abd El-Salam² & E Adel²

¹Dyeing, Printing and Textile Auxiliaries Department, Textile Research Division, National Research Centre, Cairo, Egypt
²Faculty of Applied Arts, Helwan University, Cairo, Egypt

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Cellulose rice straw pulp has been prepared via alkali scouring and scouring+ bleaching and then used along with the raw material as dye adsorbents for some selected reactive dyes. Factors affecting dyestuff adsorption such as technique applied (mechanical shaking and ultrasonic), time, temperature, amount of substrate and concentration of the dyestuff have been thoroughly investigated. It is found that % colour removal depends on (i) nature of reactive dye used, (ii) degree of purity of adsorbent i.e. either native, alkali-treated or bleached cellulose, and (iii) technique applied during dye adsorption.

Keywords: Colour removal, Dyeing, Reactive dye, Rice straw, Ultrasonic technique

1 Introduction

Protecting the environment from pollution and contamination by various types of discharge is now in focus all over the world¹. Although sizing agents represent ~ 70% of pollutant in textile industry but still dyestuffs strike the eyes distinctly because of the coloration of streams².

Dyes are resistant to fading on exposure to light, water and many chemicals and therefore difficult to decolourise once released into the aquatic environment³. Some biological and physical/chemical methods have been employed for dye wastewater treatment⁴⁻¹¹. In all these methods, the sorption has been found to be economical and effective dye wastewater treatment¹². Agricultural wastes are considered to be low value products for dye sorption. Because of low utilization ratio, most of these biomaterials are arbitrarily discarded or set on fire. In recent years, some crude agricultural wastes have been utilized as sorbent, which includes coconut husk, palm-fruit bunch, wheat straw, orange peel, neem leaf and peanut hull¹³⁻²¹.

Rice straw is a lignocellulosic agricultural by-product containing cellulose (37.4%), hemi-cellulose (44.9%), lignin (4.9%) and silicon ash (13.1%)²². It is one of the abundant lignocelluloses waste materials in the world and one of the most common problems in Egypt, since the farmers oblige to burn it. The gases and fumes of its burning causes black cloud, leading to pollution of the environment²³, ²⁴.

In National Research Centre, Cairo, studies have been carried out to prepare some dye adsorbents for colour removal. Chemical modifications of some agricultural wastes, starches, Egyptian raw materials e.g. bentonite and kaolinite are used as dye adsorbents²⁵. In continuation of above, in this study, native raw rice straw, alkali-treated (scoured) and scoured/bleached rice straw pulp have been chosen as dye adsorbents for some selected reactive dyestuffs. Also, factors affecting dye adsorption such as shaking time, temperature, pH of aliquot, concentration of the dyestuff and amount of the adsorbent have been investigated.

2 Materials and Methods

2.1 Materials

Native rice straw supplied by Racta Company For Paper Manufacture, Alexandria, was used. Following two different reactive dyes, mostly used in the Egyptian Textile Industry were selected for the study:

- Sunzol Brilliant Violet 5 R (C.I. Reactive Violet 5) which is mono azo dye and its reactive center is vinyl sulphone. Its chemical structure is given in Scheme 1.
- Sunzole Blue 19 (C.I. Reactive Blue 19) which is anthraquinone reactive dye and its reactive
center is vinyl sulfone. Its chemical structure is given in Scheme 1.

Scheme 1—Structures of (A) Reactive Violet 5 and (B) Reactive Blue 19

Sodium hydroxide and Sodium hypochlorite both of laboratory grade chemicals were also used.

2.2 Methods

In the present work, native rice straw, alkali-treated (scoured) and scoured/bleached rice straw pulp were used as dye adsorbents. Here, these samples are referred as native, alkali-treated and bleached rice straw respectively.

2.2.1 Preparation of Alkali-treated Sample

Rice straw was cut to strips (2 cm length) and treated with 4% sodium hydroxide solution, maintaining liquor ratio at 5:1 for 2 h in a stationary autoclave at 120°C. The sample was left to cool, washed thoroughly with running water till free from alkali, and finally air dried at ambient conditions.

2.2.2 Preparation of Bleached Sample

The alkali-treated sample was subjected to sodium hypochlorite (NaOCl) bleaching (4g/L active chlorine) for 2h at room temperature, keeping liquor ratio at 10:1, followed by washing thoroughly with running water and finally air drying.

2.2.3 Procedure of Dye Adsorption

Different amounts of various substrates (native, alkali-treated and bleached rice straw) were added separately to aqueous solutions of the selected dyes (0.01g/L) dissolved in 1000 mL of distilled water. The suspension was treated using either mechanical shaking or ultrasonic technique for different time periods (5, 15, 30, 45 and 60 min) and temperatures (30, 40, 50 and 60°C). At the end, aliquot was centrifuged at 5000 rpm for 30 min and the dye concentration in the clear solution was evaluated colourimetrically at the maximum wavelength for every dyestuff. The absorbance was measured using a double-beam spectrophotometer (Thermo Electron Corporation Unican 300, England). The per cent dye absorption was calculated using the following equation:

\[
% \text{ of colour removal} = \frac{\text{CA of original sample} - \text{CA of treated sample}}{\text{CA of original sample}} \times 100
\]

where CA is the colour absorbance.

3 Results and Discussion

3.1 Dye Adsorption using Native Rice Straw

Native rice straw was mechanically grinded to fine powder and its different amounts (1.25, 2.5, 5 and 10g) were added separately to 100mL of dye solution prepared at a concentration of 0.01g/L.

The suspension was subjected to mechanical shaking or ultrasonic treatment. After treatment, aliquot was taken, centrifuged at 5000 rpm and the dye adsorption was measured before and after treatment from which the % colour removal (adsorbed) was calculated. The results obtained are given in Fig. 1.

It is clear from Fig. 1 that the % colour removal on using rice straw depends on both the techniques applied and nature of the reactive dye used. Generally, the rate of dye adsorption increases by increasing the amount of the substrate to a maximum and then level off or slightly decreases. However, the amount of raw rice straw at which a maximum adsorption occur depends on the technique adopted and on the nature of the reactive dye used.

In case of mechanical shaking the maximum dye adsorption is obtained at 2.5g for Reactive Blue 19 and at 5g for Reactive Violet 5. While in case of ultrasonic treatment the maximum dye adsorption is arrived at a concentration of 5g for the two reactive dyes used. The magnitude of dye adsorption in case of ultrasonic is relatively higher than in
mechanical shaking, irrespective of the nature of the reactive dye used.

3.2 Dye Adsorption using Alkali-treated Rice Straw

The prepared alkali-treated sample was grinded to a fine powder with different amounts (5, 10, 15 and 20g) and utilized as reactive dye adsorbent according to the afore-mentioned procedure indicated in the experimental section. The results are given in Fig. 1

It is clear from Fig. 1 that in all cases, i.e. on using either mechanical shaking or ultrasonic technique for both reactive dyes used, there is a remarkable improvement in the dye adsorption on using bleached rice straw. The maximum colour removal reaches to 61.1% and 70% on using mechanical shaking for Reactive Blue 19 and Reactive Violet 5 respectively. In case of ultrasonic, it increases to 78.8% and 77.3% on using Reactive Blue 19 and Reactive Violet 5 respectively.

The improvement in colour adsorption on using bleached rice straw is expected as it has high affinity towards reactive dyestuffs. The presence of the impurities in the raw and/or the alkali-treated samples decreases the adsorption of the colour by the substrate.

It is worthy to mention that for every substrate different concentrations were applied. The presented figures represent the most convenient data which shows the optimum adsorption condition for every substrate.

3.4 Effect of Dye Concentration

The effect of dye concentration on the colour removal of Reactive Violet 5 and Reactive Blue 19 on using the optimum concentration (raw 5g; alkali-treated 10g and bleached 15g for 45 and 30 min for mechanical and ultrasonic respectively) of native rice straw, alkali- treated and bleached rice straw via mechanical shaking or ultrasonic respectively.

It is clear from the Fig. 2 that as the concentration of the dye increases from 0.01 g/L to 0.5 g/L, the magnitude of adsorption increases regularly, but the
% colour removal decreases. This phenomenon holds true regardless of (i) the nature or the reactive dye used, (ii) the nature of the substrate and (iii) the technique applied (mechanical stirring or ultrasonic). For example, in case of Reactive Blue 19 on using native rice straw via mechanical stirring, the % colour removal decreases regularly from 53.3% to 14.9% by increasing the dye concentration from 0.01 g/L to 0.5 g/L.

It is observed that in all the cases as the concentration of the dye increases, the % colour removal decreases, however the magnitude of % colour removal depends on (i) nature of the reactive dye used, (ii) the degree of purity of adsorbent (native, alkali-treated or bleached), and (iii) the technique applied during dye adsorption (mechanical shaking or ultrasonic). The decrease in % colour removal by increasing the dye concentration may be due to the increase in the dye aggregation by increasing the dye concentration. Beside, as the dye concentration increases the mobility of the dye molecule and the substrate decreases. It can be concluded that the optimum dye concentration to use rice straw (before or after purification) as adsorbent for reactive dye is found to be 0.01 g/L water.

3.5 Effect of Treatment Time
To investigate the effect of treatment time on colour removal for raw rice straw using both Reactive Violet 5 and Reactive Blue 19, different samples containing 5g of grinded rice straw/100mL of the colour solution were subjected to either mechanical...
shaking or ultrasonic for different intervals of time (5-60 min). The absorbance of treatment dye solution after separation has been evaluated spectrophotometrically. The results are given in Fig. 3.

It is clear from Fig. 3 that the % colour removal increases by increasing the time of treatment to reach its maximum and then levels off or slightly decreases. This phenomenon holds true regardless of the nature of the colour used and the technique adopted (mechanical stirring or ultrasonic).

The maximum % colour removal is obtained after 45 min in case of mechanical shaking for both the two colours under investigation, while in case of ultrasonic the magnitudes of the % colour removal is higher (57.8% and 63.8%) in case of both colours Reactive Violet 5 and Reactive Blue 19 respectively, however in case of reactive blue it is obtained at 30 min.

It is clear that the ultrasonic is more active than mechanical shaking as the ultrasonic waves can reduce the particle size and increase mass transfer\(^2\). This result is confirmed with the Okitsu \textit{et al.}\(^2\) observation that the ultrasonic technique is effective in the decolorization and decomposition of azo dyes.

It is clear from Fig. 3 that for samples subjected to mechanical stirring the maximum dye adsorption is obtained at 45 min. for both the colours. It is found to be 52.6% and 55% for Reactive Violet 5 and Reactive Blue 19 respectively. While on using ultrasonic the maximum dye adsorption is obtained at 45 min on using Reactive Violet 5 and at 30 min on using Reactive Blue 19.

In addition, Fig. 3 show that at any specific time the % colour removal for bleached rice straw is higher than their corresponding samples of the untreated or alkali-treated rice straw (Fig. 3). This is expected since removal of the impurities open the structure of cellulose and increases the rate of its dye adsorption.

Irrespective of the technique applied, highest % colour removal is obtained on using Reactive Violet 5 compared to that obtained for Reactive Blue 19. This may be due to the difference between the two reactive dyes on their chemical structure, molecular weight, number and position of sulphonic groups as well as the presence of neighboring groups.

It is also clear from the data that ultrasonic treatment highly increases the rate of dye adsorption of bleached rice straw. The magnitude of the adsorbed dye, expressed as % colour removal, is higher and the time to reach to the maximum adsorption is shorter in case of ultrasonic as compared to that in case of mechanical stirring. For example, in case of Reactive Violet 5 the maximum dye adsorption is 70% at 45 min and 77.3% at 30 min for the samples subjected to both mechanical shaking and ultrasonic respectively.

3.6 Effect of Temperature

To investigate the effect of temperature on the rate of adsorption of the afore mentioned two reactive dyes, grinded alkali-treated rice straw samples were suspended with 100mL of each of the reactive dye subjected to either mechanical shaking or ultrasonic for 45 min at 30, 40, 50 and 60°C (Fig. 4). At the end, the alkali-treated rice straw was separated as usual and the adsorbed dye was evaluated spectrophotometrically.
It is observed that the increment of temperature from 30°C to 60°C is accompanied with a decrement in the % dye adsorption. This may be due to one or both of the following factors: (i) as the temperature increases the rate of hydrolysis for reactive dye increases and hence the number of the reactive dye molecules adsorbed and chemically bounded to cellulose decreases, and (ii) as the temperature increases the mobility of the dye molecules increases. As a result, the number of the dye molecules trapped or physically attached between the cellulose chains may decrease. This leads to a decrease in dye adsorption by the substrate.

4 Conclusion

The % colour removal increases by increasing the time of treatment and/or the amount of substrate. The opposite holds true by increasing the dye concentration. In all cases, magnitude of dye adsorption in case of ultrasonic is relatively higher than mechanical shaking. The magnitude of the adsorbed colour in case of using native rice straw is relatively higher than that obtained on using the alkali-treated sample, bleached rice straw acquires the highest affinity for dye adsorption.

References