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Adsorptive removal of reactive dye from dyed effluent with modified natural absorbents

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Abstract

In this study, Oryza sativa straw (RS), Eucalyptus globulus sawdust (SD), and Cocos nucifera (CC) coir were chemically modified with sulfuric acid to develop a biodegradable cationic adsorbent. The Feasibility of the modified cellulosic materials as adsorbent for the removal of reactive dye and improvement of water quality parameters was investigated. FTIR analysis was conducted to find out the changes that occurred in the surface of the materials for the modifications and the treated effluent was assessed with UV-VIS spectroscopy to detect the changes in color concentration and water quality indicators (BOD, COD, TDS, TSS, pH, etc.). FTIR analysis of the surface of the treated material showed the existence of different functional groups (C-H, O-H, and C=C) which enhanced, disappeared or shifted after modification with sulfuric acid and treatment. According to the study's findings, modified CC led to 75.86% elimination of dye from the wastewater, making it the most efficient method for decolorizing effluent. A 1.0 gm adsorbent dosage of modified RS used at room temperature resulted in the largest BOD reduction, which was 67.5%. With 1 gm of adsorbent dosage, modified SD showed the greatest COD reduction, which was 62.125%. And after utilizing modified RS, TDS showed the least reduction (just about 17.3% reduction). Modified CC was responsible for the highest amount of TSS and pH reduction with a 1.0 gm dose (38.24% and 22.85%). This study indicated that a higher dosage of adsorbents resulted in more adsorption capacity of water contaminants, which can be attributed to the fact that a greater surface area was available for adsorption. However, after a certain period of time, adsorbents exhibited a decline in adsorption of water contaminants.

Keywords: Natural Adsorbent, Adsorption, Wastewater treatment, Dyeing effluent, Water Pollution.

1. Introduction

The textile industry is the most rapidly expanding and vital industry in Bangladesh. Bangladesh has a large chain of textile industries which includes 4000+ dyeing and printing industries[1]. These industries generate a lot of wastewaters each day that is damaging to our ecosystem since it contains various dyes and other toxic substances[2]. The amount of dye in the wastewater has consequently increased due to increased dye consumption as there is more production than ever in the textile manufacturing sector. Consequently, a wide range of contaminants that are harmful to both aquatic and land bodies may be present in untreated wastewater [3]. Textile dyes have been developed to be extremely resilient to the impacts of the natural environment along with chemical and photolytic action. Dyes are responsible for a lot of various cardiovascular, dermatologic, and haematological problems [4]. To get rid of these problems, a lot of techniques have been developed to treat wastewater.

In the past, different technologies were applied to remove unwanted compounds from textile wastewater. Among them most widely used technologies are coagulation, flocculation, biological membrane filtration, adsorption, and advance oxidation methods. When it comes to the amount of energy and chemicals used, photooxidation, microbiological degradation, chemical oxidation, ozonation, and coagulation are among the most expensive processes [5]. Adsorption method has, however, proven to be the most promising technology due to its efficacy, usefulness, and simplicity [6].

At the industrial level, activated carbon is the favoured traditional adsorbent to remove pollutants. The removal of contaminants from drinking water sources, such as groundwater, rivers, lakes, and reservoirs, as well as the adsorption of contaminants from wastewater streams, are also common uses for activated carbon[5], [7]. But due to the high cost and high energy needed to produce activated carbon, its use is not nearly as widespread as it could be[8]. Given that affordability is a key factor in the majority of developing nations, attempts have been made to investigate the potential use of a range of affordable alternatives that are abundant, easily accessible, biodegradable, and manufactured from waste [9]. In a recent study, an adsorbent was developed using wood sawdust-based amorphous carbon thin film using long-chain palmitic fatty acid and it was successful in removing contaminants from the oil and petroleum industry[7]. In another study, the potential of using sawdust as a low-cost adsorbent was conducted and it removed around 37% of total suspended solid and only 9% of chemical oxygen demand[10]. In another study, rice straw was chemically modified by means of phosphorylation, and then it was further modified with sodium ion in order to yield potentially biodegradable cationic sorbent and it was successful in removing 98% of the dye from the wastewater[11]. In another study, three different adsorbents were tested to find out their potential in removing Methylene Blue dye from water where coconut fibre showed the most capacity to remove dye from the wastewater[12]. Attempts are being made to produce less expensive adsorbents: and in this regard, several agricultural materials have been tested to check their potential to remove dyes and auxiliaries from the wastewater[13].

In this study, sawdust, rice straw, and coconut coir modification were conducted with sulfuric acid to increase their absorbency. Sulfuric acid treatment is a common method used to modify the surface properties of various materials, including natural fibres. When these cellulosic materials are treated with sulfuric acid, all the impurities such as lignin, wax, and other impurities get removed and the fibrous structure slightly breaks down, leading to enhanced adsorption properties. Moreover, modification of the surface of cellulosic fibre with cellulosic fibre can introduce different functional group onto the surface of the fibres, such as carboxyl and hydroxyl group which has natural absorbance property.

In this paper, the feasibility of using modified cellulosic materials as a medium to remove dyes as well as reduce other environmental characteristics of wastewater was analyzed.

2. Materials

2.1 Preparation of the adsorbents

RS was collected from a local farm in Tangail, Bangladesh, SD was collected from a local sawmill for timber and woods from Tangail, Bangladesh and CC was collected from the local market of Dhaka. They were cut and crushed into smaller pieces to increase the surface area of the adsorbents. 5% sulfuric acid solution was mixed with adsorbents in three different beakers and stirred for a few minutes so that all the adsorbents are fully immersed. Then the beakers were stored at 22^0C temperature, ensuring that all the adsorbents were under the solution. After 4 hours of incubation time, the adsorbents were rinsed with water to remove any residual acid. The process of rinsing was repeated multiple times to make sure all of the sulfuric acid was removed. Once, rinsed, the adsorbents were taken on a tray and dried with a help of a desiccator shown in **Fig 1A.**

2.2 Collection of wastewaters

Wastewater was collected from Dyes and Chemical lab from BUTEX after a sample batch was run to dye the cotton fabric with reactive dye. Wastewater was then stored in airtight bottle into a refrigerator at 5^0C.

3. Methodology

3.1 Characterization of the adsorbent

Fourier Transform Infrared spectrometer was used to determine the changes of functional groups on the surface of RS, CC, and SD adsorbents before and after modification with sulfuric acid as well as after treatments.

3.2 Applying adsorbents on wastewater

Modified materials (sawdust, rice straw, or coconut coir) were added to the effluent carefully at 0.5 gm and 1.0 gm on 20 mL of the effluent. Mixtures were stirred gently using a glass rod to ensure proper contact between the modified materials and the effluent. This allowed the pollutants in the effluent to come into contact with the adsorbent surface of the materials. After that, the mixture of modified materials and effluent sits for 20 hours for adsorption to occur. And the parameters were checked with 5 hours intervals and data for environmental parameters such as BOD, COD, TDS, TSS and pH were collected.

3.3 Decolorization of wastewater

The effects of contact time and the amount of modified dose on the decolorization of the textile wastewater using a modified adsorbents (SD, RS and CC) were investigated. The wavelength of maximum absorbance and the equilibrium time of the wastewater was determined on a UV-VIS spectrophotometer. The colour removal efficiency is calculated using:

$$\%R = \frac{\text{Co} - \text{Ce}}{\text{Co}} \times 100$$

Where, $\text{Co} = \frac{\text{Ao}}{\text{K}}$ and $\text{Ce} = \frac{\text{Ae}}{\text{K}}$

Thus, $\%\text{R} = \frac{\text{Ao}-\text{Ae}}{\text{Ao}} \times 100$

Where Ao is the absorbance of the wastewater before adsorption and Ae is the absorbance at equilibrium (after adsorption), Co is the concentration of the wastewater before adsorption and Ce is the concentration at equilibrium (after adsorption).

3.4 Characterization of effluent

The effluent was collected from the Dyes and Chemical Laboratory, Bangladesh University of Textile, Dhaka, Bangladesh. The characterization of the treated effluent has been conducted at Masco group ETP laboratory with the following reference methods of American Public Health Association (APHA) [14] and compared with the standard values.

Table 1: Treated effluent characterization

Parameters	Test methods
BOD	APHA 5210.B
COD	APHA 5220.B
TDS	APHA 2540.C
TSS	APHA 2540.D

4. Result and discussion

4.1 Surface functional group

The FTIR spectra in **Fig-1B** highlights the changes in the functional groups of the modified and treated absorbents compared with raw absorbents. The spectra for all raw absorbents (fig 2c, 2d, 2e) were similar to cellulose, containing a broad band at 3650–3445 cm^{-1} which indicates to the intra- and inter-molecular hydrogen stretching of hydroxyl groups (-OH)[7]. After the treatment, the -OH brand became broadened and intensified, which indicates the absorption of the dye effluent (fig 2b) in the absorbents. The peaks at 1110 cm^{-1} indicates C-O-C twist bending vibration for lignin in raw absorbents (fig 2c, 2d, 2e) and the transmittance values were lower in modified absorbents which indicate the reduction in the amount of lignin in modified with sulfuric acid. Moreover, 1060 cm^{-1} and 1035 cm^{-1} indicate the C-O stretching of cellulose and hemicelluloses in the raw absorbents. Finally, it can be said that different infrared spectra have been shifted, reduced or disappeared when treated with 5% sulfuric acid and new peaks have introduced, broadened or intensified due to the absorption of the reactive dye (Abdulsalam, Giwa, and Adelowo 2020).

4.2 Colour removal

Fig 1C illustrates the impacts of adsorbent dose on the percentage of colour removal and the relationship between the percentage of colour removal and the number of adsorbents. From the **Fig 1C(a),** it can be seen that effluent treated with CC was less coloured than the other two treated material. It was corroborated by the UV-VIS test that in the **Fig 1C(b)** and **Fig 1C(c)** as CC removed more than 70% dye from the concentration while RS was least effective as it reduced around 50% dye concentration.

4.3 Water quality parameters

The efficacy of colour removal was shown to rise as adsorbent mass increased as indicated by **Fig 2**, with 1.0 gm doses of all three adsorbents having better colour removal rates than 0.5 gm doses. With higher adsorbent dosages, there are more adsorption sites available, which results in larger pore surface areas.

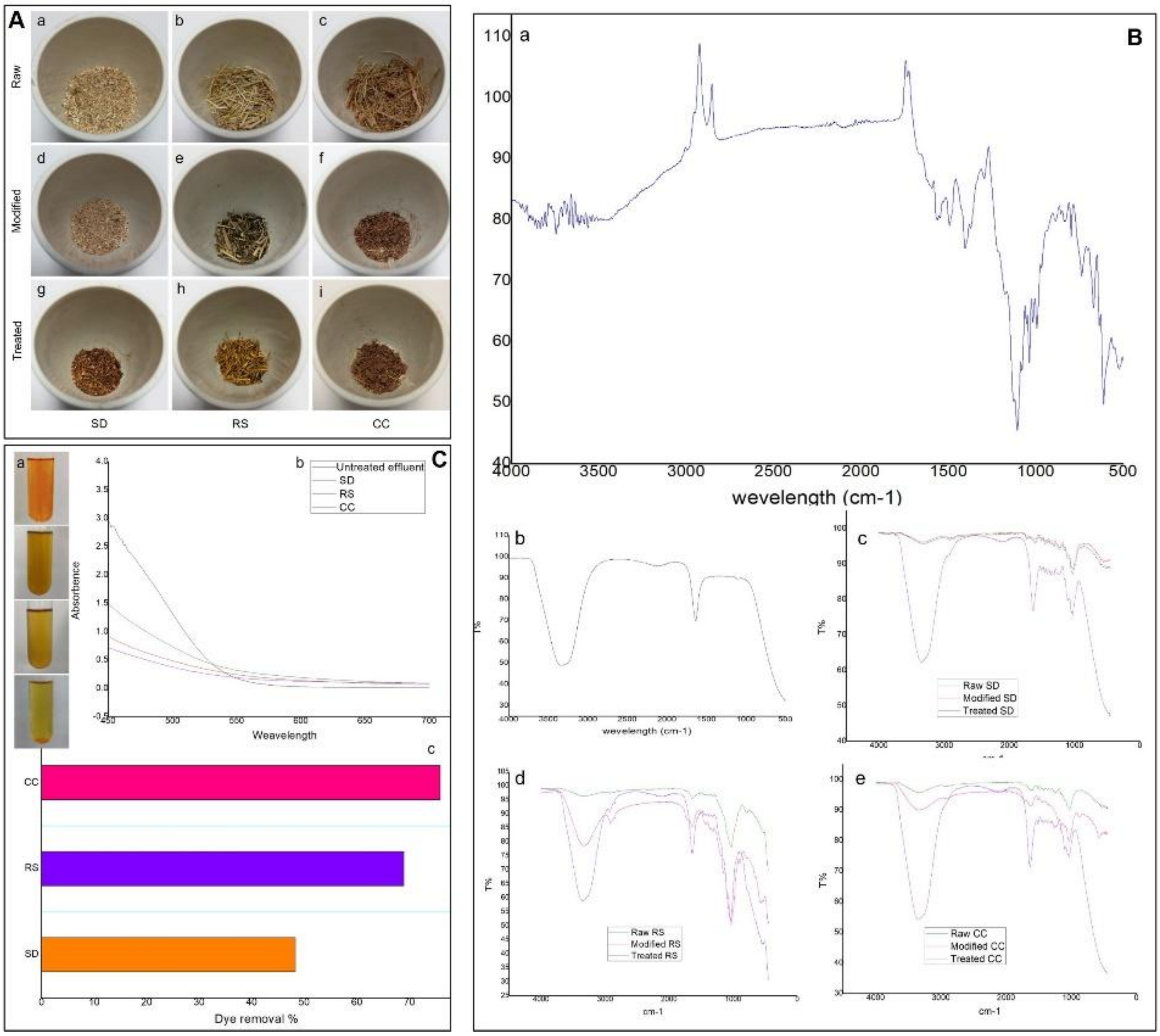

Fig 1: A. Raw, modified and treated materials (SD- Saw Dust, RS- Rice straw and CC- Coconut Coir); B. FTIR spectra of (a) Raw reactive dye, (b) dyed effluent (c), Sawdust (SD) (d) Rice straw (RS) and (e) Coconut coir (CC). C. (a) Wastewater samples before and after treatment, (b) absorbance spectra of untreated and treated effluent, (c) Percentage of dye removal.

From **Fig 2a**, it can be seen the reduction of BOD increased with the dose for all of the adsorbents. Among the three adsorbents, modified RS showed the greatest reduction for BOD as it reduced BOD from 225 ppm to 73 ppm and 100 ppm for both 0.5 gm and 1.0 gm of adsorbent dosages respectively. Modified SD, on the other hand, reduced COD the most, by 56.25% and 62.125%, respectively, with a 0.5 gm and 1.0 gm adsorbent dose which can be seen from **Fig 2c** and **Fig 2d**. When it came to removing TDS from the effluent, from **Fig 2**e and **Fig 2f**, we can these modified adsorbents performed the least well. Only 17.3% of TDS was removed from the effluent using 1.0 g of RS adsorbent which was the highest among all three adsorbents with doses of 0.5 gm and 1.0 gm. TSS was reduced to the highest amount of CC for both 0.5 gm and 1.0 gm. TSS of the untreated sample wastewater was 285 ppm which was reduced to 213 ppm, 221 ppm, and 209 ppm for 0.5 gm of SD, RS, and CC respectively and it was reduced to 190 ppm, 185 ppm, and 176 ppm for modified SD, RS and CC respectively. For pH, CC was most effective in reducing pH from the wastewater for both 0.5

gm and 1.0 gm doses as it had a reduction of 19% and 22% respectively. Both SD and RS showed the trend of reducing pH with the increase of dose from 0.5 gm to 1.0 gm. SD was least effective in removing pH as it lowered pH from 10.5 to 8.7 and 8.4 for 0.5 gm and 1.0 gm respectively. From the curves of **Fig 2**, we can see the effects of contact time on the water quality indicator from the wastewater by modified RS, SD, and CD were examined. From **Fig 2**, it can be seen that the longer contact time led to a greater uptake of the dye and a reduction in water quality parameters. Contact time did not, however, lower the water quality parameters after a certain amount of time. From **Fig 2**, it can be seen that three modified adsorbents showed the highest amount of adsorption till 10 hours. After 10 hours of contact time, adsorbents were slower in reducing water quality parameters.

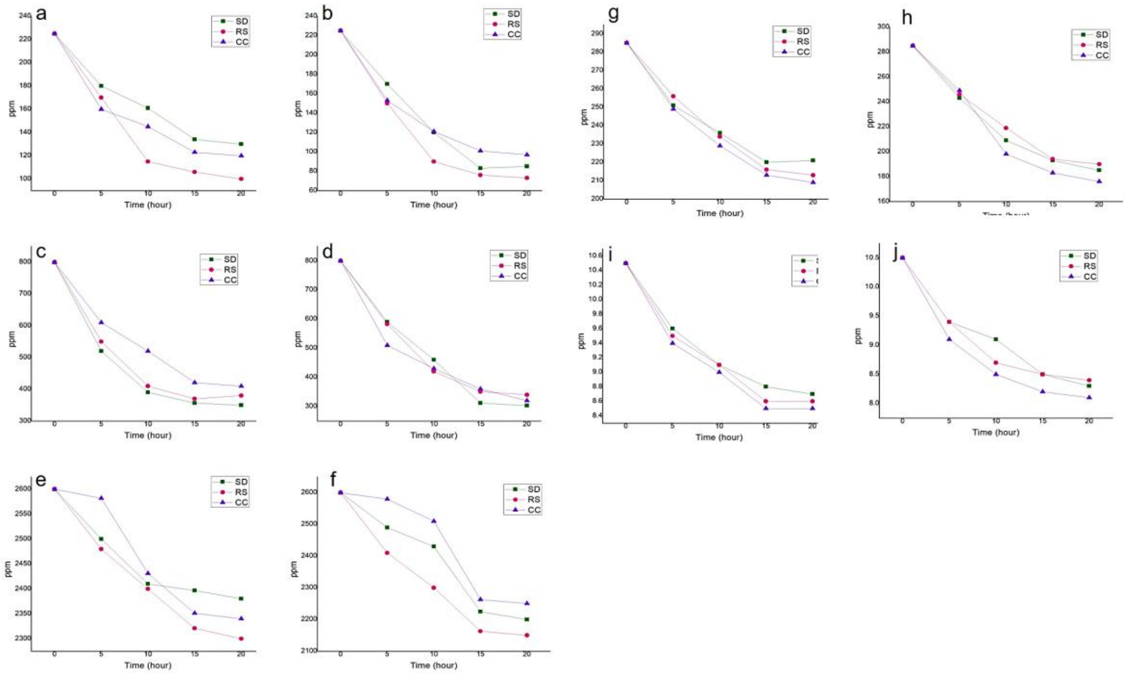

Fig 2: BOD reduction from wastewater with (a) 0.5 g dose of adsorbents, and (b) 1.0 g of adsorbents; COD reduction of wastewater with (c) 0.5 g dose of adsorbents, and (d) 1.0 g of adsorbents; TDS reduction of wastewater with (e) 0.5 g dose of adsorbents

5. Conclusion

The study's findings showed that modified CC was the most effective adsorbent for decolorizing reactive dye effluent, while SD was most efficient in reducing COD from wastewater, and RS performed best for BOD reduction. The reduction of all BOD, COD, and TDS in wastewater was seen to rise with the addition of more adsorbent. However, it stopped decreasing the wastewater's BOD, COD, and TDS after a certain amount of time. All things considered, these improved adsorbents shown excellent capacities to remove dye particles and other contaminants that can be used commercially.

However, several gaps in the research such as, microstructural analysis, cost analysis of producing and scaling these modified adsorbents, regeneration and reuse of the adsorbents and broader applicability across varying industrial scenarios warrant further investigation for the broader applicability across varying industrial scenarios.

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