Research Article

Decolourization of Reactive Red 120 Using Agro Waste-Derived Biochar

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Adsorption behavior of Reactive Red 120 from aqueous solutions onto rice husk-derived biochar was examined in batch mode of operation. To obtain the optimized conditions, various adsorption variables including temperature, initial dye concentration, biochar dosage, pH, and contact time were studied for effective remediation of the dye. The results showed that biochar uptake capacity varied linearly with biochar dosage and pH, but varied nonlinearly with temperature. The optimum value of pH, temperature, and a dosage of biochar was obtained as 2.0, 35°C, and 1 g/L, respectively, for reactive red 120 adsorption. TG analysis, FTIR, and SEM were used to investigate biochar characterization, and the results revealed that dye sorption onto biochar caused biochar variation. The possibility of reusing the biochar was examined from desorption studies, and they are conducted by studying different elutants and by altering the ratio of solid to liquid. From the results of experiments, the rice husk-derived biochar was reported to remediate reactive red 120 with the maximum removal efficiency of 75%.

1. Introduction

The usage of water has increased to a large extent due to the rapid growth of industrialization and population in the modern world. Several pollutants are released into rivers and streams in large quantities from industries, which result in degradation of water quality and also cause disturbance to the aquatic ecosystem [1]. Water pollution is increasing rapidly, and it is considered a major challenge in the modern world. Water pollution is majorly due to a large amount of sewage and wastage released from industries during the manufacturing and processing of raw materials. The used water for processing increased the number of harmful contaminants in the water, which was then discharged into the environment without sufficient treatment. Colorings are one of the key contaminants that contribute to excessive surface pollution. It is due to the usage of dyes in major industries. Dyes differ from one another and are generally categorized as synthetic dyes and natural dyes [2]. Chemical methods are used to manufacture synthetic dyes. The loss of water quality was primarily caused by dyes commonly discharged from industries. [3]. Modern-day procedures and technologies are insufficient to handle these enormous volumes of dye-bearing wastewater [4]. In India, sewage treatment capacity is less than the volume of wastewater generated in major cities [5]. Dye-containing effluent from industry is discharged directly into surrounding water sources without treatment. The overuse of dyes often results
in a large volume of dye waste. The dye-contaminated effluents are mostly carcinogenic and nonbiodegradable [6]. When dye-bearing effluent is discharged into freshwater, it has ill effects on public health.

Dyes can be harmful to one’s health, causing respiratory ailments, allergies, and even kidney and liver cancer [7]. As a result, it is required to remove these hazardous compounds from wastewater. To remove dyes from wastewater, several methods are available, including ion exchange, adsorption, oxidation, ozonation, and membrane filtration [8]. Besides this, there is the biological procedure known as bioremediation, which involves the treatment of dye with biological materials. In the biological technique of treatment, biomaterials taken from nature were transformed into biochar under specific parameters such as temperature for successful dye remediation [9]. Biochar is a carbon-rich compound that is produced in the oxygen absence by the thermal decomposition of organic molecules. This is known as pyrolysis. Its efficiency in treating dye-bearing wastewater is great due to its carbon-rich composition. Because it is environmentally beneficial, this approach has grown in popularity in industrial wastewater remediation [10]. Biochar has a variety of properties, including many pores, pore size, and functional groups. Because of these properties, biochar is an effective substance for the decolorization of hazardous contaminants in wastewater. Remazol dye, when combined with various reactive groups, produces azo-based chromophores [11]. Approximately 50% of Remazol dyes may be lost in washing water during textile dyeing [12]. It has been discovered that the standard activated sludge treatment technology can only remove 10% of the total Remazol dyes in wastewater [13]. As a result, new and practical methods are required for the successful treatment of wastewaters containing dye. The main objective of the present study is to examine the potential of the biochar produced from rice husk for the decolorization of reactive red 120 (RR120). Rice husk is available in huge quantities in India since it is one of the major contributing crops. So, utilization of this waste biomass for the dye removal will reduce the solid waste generation and a sustainable solution will be obtained for dye removal.

2. Materials and Methods

2.1. Dye and Chemicals. The reactive red 120 (RR120) dye was with an empirical formula of C_{44}H_{24}Cl_{2}N_{14}O_{20}S_{6}Na_{6}, the molecular weight was of 1469.98 g/mol, and wavelength of 509 nm was used in the current research. The structure of reactive red 120 (RR120) is shown in Figure 1. All the chemicals and the dye used in the present investigation were purchased from Sigma-Aldrich (India).

2.2. Agrowaste and Biochar Preparation. Rice Husk was used as a biosorbent for the removal of reactive red 120 from wastewater. The materials were collected from rice mills of local areas (Rajam, Andhra Pradesh, India). The collected raw material was washed many times with distilled water to remove the impurities present in it. After washing, they are allowed to dry under the natural light for 24 hours. After drying, the raw material was grinded into a fine powder with a mixer grinder. The powder is then sieved to obtain uniform particles of size 75 mm. After sieving, the required amount of material was taken in an empty crucible, and it is covered with aluminum foil. The crucible is then placed in an electrical muffle furnace and operated for 120 minutes at a temperature of 400°C. The sample is converted into biochar in the absence of oxygen. After completion of 2 hours, the furnace was allowed to cool down to normal condition and the crucible was taken out of the furnace [14].

2.3. Batch Experiments. Batch studies were carried out to obtain information about the effect of basic parameters for the adsorption of RR120 with rice husk-derived biochar. Desired weight (control: 1 g/L) of biochar was taken in a conical flask of 250 mL containing 100 mL RR120 solutions of known concentration (control: 5 mg/L). These conical flasks were placed in an orbital shaker for 6 hours in set to 200 rpm. At regular intervals, samples were removed from the orbital shaker and carefully transferred into vials, centrifuged for 25 min at 2600 rpm. After the completion of the centrifuge, supernatants were collected carefully without any disturbance. Using this supernatant, a spectrophotometer calibrated at a wavelength of 597 nm was used to determine the final concentration of the dye [15].

2.3.1. Influence of Biochar Dosage. An equilibrium dosage of biochar was obtained from these experiments. Dosage of biochar was altered as 0.5, 1, 2, 4, 6, 8, and 10 g/L. These experiments were carried out at constant pH (2.0), temperature (35°C), and initial concentration (15 ppm).

2.3.2. Influence of Equilibrium pH. The pH was altered between 2.0 and 5.0. These experiments were carried out at constant biochar dosage (1 g/L), initial concentration (15 ppm), and temperature (35°C).

2.3.3. Influence of Initial Concentration. Isotherm studies were performed to obtain the maximum uptake capacity of biochar. These experiments were performed by altering the initial dye concentrations as 5, 10, 15, 25, 50, and 100 ppm. The experiments were carried out at constant pH (2.0), temperature (35°C), and biochar dosage (1 g/L).

2.3.4. Influence of Temperature. Optimum temperature was determined from these experiments. The temperature values were varied from 30–45°C. The experiments were carried out at constant biochar dosage (1 g/L), initial concentration (15 ppm), and solution pH (2.0).

2.4. Biochar Characterization. Analytical methods were used to analyze the characteristics of the biochar. The thermal stabilities of rice husk-derived biochar were studied using a thermogravimetric analyzer. The surface characteristics of the biochar were examined by the scanning electron microscope as they are very important in the molecular adsorption of dye using the pores present on the surface.
Fourier transform infrared spectroscopy was used to obtain information about the functional groups present in the biochar as they are very important in the adsorption of dye molecules.

2.5. Desorption Studies. Desorption tests were conducted to assess the possibility of reusing biochar in successive adsorption and desorption. The potential of biochar was studied by using sodium hydroxide, ammonium hydroxide, hydrochloric acid, sodium carbonate, methanol, and EDTA as elutants. The solid-to-liquid (S/L) ratio was studied to analyze the optimum use of elutants. Regeneration studies were conducted to conclude the number of cycles that a sorbent can be effectively used for the adsorption of dye [16].

3. Results and Discussion

3.1. Biochar Characterization. The thermogravimetric analysis was performed to investigate the influence of temperature on the material’s thermal stability. The thermal stability of a material is essential in the creation of biochar [17]. The findings revealed that an increase in temperature reduced the weight of the biomaterials. At a temperature of 699°C, a total weight loss of around 67.83% was observed. The thermal decomposition of the rice husk was categorized into three zones. The first degradation occurred between 0 and 100°C and resulted in a total weight loss of 9.90% due to the presence of moisture content. The second active decomposition zone occurred between 100 and 350°C, with a total weight loss of 34.21% reported. According to the observations, the largest decomposition occurred in the second stage due to the partial degradation presence of cellulose, lignin, and hemicellulose content of the rice husk and total moisture content had been escaped [18]. The final disintegration stage occurred between 350 and 500°C, with a weight loss of 24.77%, and a subsequent increase in temperature resulting in mass sample content. As a result, a peak curve was achieved at a temperature of 438.8°C, which is nearer to the pyrolysis temperature of 400°C that was chosen for the biochar.

The surface of raw rice husk biochar before and after adsorption of reactive dye was studied using the scanning electron microscope, and they are shown in Figure 2. It was clear from the observations that the raw biochar had numerous pores and improved binding sites. These biochar properties may favor dye molecule adsorption on the surface of the biochar [19]. Figure 2 represents that the surface of the biochar was observed to be smooth after adsorption, indicating the adsorption of dye molecules over the surface of the biochar.

The FTIR spectra of the raw rice husk biochar and RR120 dye adsorbed biochar are illustrated in Table 1. The characteristics of the biochar were found to be complex based on Table 1. This complex nature increases the adsorption of the dye molecules among different functional groups [20]. The biochar is composed of primary alcohols, alkanes, and alkyl groups as observed from the results. It is also noted that, after dye molecule adsorption, there are significant shifts in the FTIR spectra, indicating that dyes and functional groups were bound together.

3.2. Effect of Biochar Dosage. The effect of rice husk-derived biochar dosage on reactive red 120 removal efficiency and uptake capacity was studied. The dosage of biochar was taken as 0.5, 1, 2, 4, 6, 8, and 10 g/L. These experiments were conducted at optimum conditions by keeping other variables constant (pH at 2.0, temperature at 35°C, and initial concentration of the dye at 15 ppm). Figure 3 represents the variation of uptake capacity and % removal efficiency of biochar with biochar dosage. Results showed that, with the rise in dosage of biochar from 0.5 to 10 g/L, the uptake capacity of RR120 by biochar falls from 11.78 to 1.04 mg/g. Higher values of uptake capacity were obtained at low biochar dosage due to the availability of fewer binding sites compared to a large amount of dye concentration. Because of this reason, the functional groups of biochar were used completely which resulted in higher uptake capacity [21]. The % removal efficiency of biochar declined gradually with an increase in dosage of biochar, as shown in Figure 3. The percentage removal efficiency of biochar towards RR120 enhanced gradually from 39.27% to 69.27% with a rise in the dosage of biochar. This enhancement in removal efficiency is due to an increase in the surface area of biochar and the availability of a large amount of exchangeable binding sites on the surface of biochar [22]. From the results obtained, the optimum value of dosage was taken as 1 g/L and is used in all batch trails.
3.3. Effect of Equilibrium pH. The value of pH is an important parameter in the adsorption process of dye as it affects the surface charge of the biochar. The effect of pH on reactive red 120 adsorption onto rice husk-derived biochar was investigated by altering the values of pH as 2.0, 2.5, 3, 3.5, 4, 4.5, and 5.0, respectively. These experiments were conducted under optimum conditions by keeping other variables constant (biochar dosage at 1 g/L, temperature at 35°C, and initial concentration of the dye at 15 ppm). Figure 4 shows the influence of pH on RR120 removal. During sorption, the pH of the equilibrium solution is very important in determining the sorbent’s sorption capacity [23]. From Figure 4, it is noticed that uptake capacity and % removal efficiency decline gradually with an increase in pH of the solution. The uptake capacity was noticed as 8.42 mg/g and 6.52 mg/g at pH 2.0 and pH 5.0, and the removal efficiency was noticed as 56.13% and 43.47% at pH 2.0 and pH 5.0. The highest value of dye sorption at low pH values was due to electrostatic interactions between anions of biochar and dye. At low values of pH, the functional groups of biochar were expected to have H+ ions and surface possess positive charge [24]. The dyes in the solution are negatively charged ions and react with the sorbent’s positively charged surface [25]. From the results obtained, the optimum value of pH was taken as 2.0 and is used in all batch trails.

Table 1: FTIR spectra of raw rice husk biochar and dye adsorbed biochar.

<table>
<thead>
<tr>
<th>Type of vibration</th>
<th>Wavenumber (cm−1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rice husk biochar</td>
</tr>
<tr>
<td>==C–H bend</td>
<td>792.73</td>
</tr>
<tr>
<td>C–O stretch</td>
<td>1071.09</td>
</tr>
<tr>
<td>C==C stretch and N–H bend</td>
<td>1507.30</td>
</tr>
<tr>
<td>C==C stretch</td>
<td>2110.44</td>
</tr>
<tr>
<td>C–H stretch</td>
<td>2921.04</td>
</tr>
<tr>
<td>O–H and N–H stretch</td>
<td>3309.26</td>
</tr>
<tr>
<td>==C–H bend</td>
<td>792.73</td>
</tr>
</tbody>
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Figure 2: Scanning electron micrographs of raw rice husk biochar (a) and dye RR120 dyeadsorbed biochar (b).

3.4. Effect of Temperature. The adsorption of RR120 on biochar was examined by varying temperatures as 30°C, 35°C, 40°C, and 45°C. These experiments were conducted under optimum conditions by keeping other variables’ constant (Biochar dosage at 1 g/L, pH at 2.0, and initial concentration of the dye at 15 ppm). From Figure 5, results indicated that the uptake capacity of biochar towards RR120 was increased from 7.72 mg/g at 30°C to 8.42 mg/g at 35°C and decreased to 3.41 mg/g at 45°C, respectively. As shown in Figure 5, it was observed that the removal efficiency of biochar increases and then decreases with temperature. The efficiency of rice husk-derived biochar towards RR120 increased from 51.49% at 30°C to 56.13% at 35°C and decreased to 22.72% at 45°C, respectively. From the results obtained, it is observed that an increase in temperature decreased the uptake capacity, and this may be due to a higher temperature, the rate of diffusion being very high, resulting in less removal efficiency. From the results obtained, the optimum value of temperature was taken as 35°C and is used in all batch trails.

Figure 3: Effect of biochar dosage on the sorption capacity and RR120 removal.

3.4. Effect of Temperature. The adsorption of RR120 on biochar was examined by varying temperatures as 30°C, 35°C, 40°C, and 45°C. These experiments were conducted under optimum conditions by keeping other variables’ constant (Biochar dosage at 1 g/L, pH at 2.0, and initial concentration of the dye at 15 ppm). From Figure 5, results indicated that the uptake capacity of biochar towards RR120 was increased from 7.72 mg/g at 30°C to 8.42 mg/g at 35°C and decreased to 3.41 mg/g at 45°C, respectively. As shown in Figure 5, it was observed that the removal efficiency of biochar increases and then decreases with temperature. The efficiency of rice husk-derived biochar towards RR120 increased from 51.49% at 30°C to 56.13% at 35°C and decreased to 22.72% at 45°C, respectively. From the results obtained, it is observed that an increase in temperature decreased the uptake capacity, and this may be due to a higher temperature, the rate of diffusion being very high, resulting in less removal efficiency. From the results obtained, the optimum value of temperature was taken as 35°C and is used in all batch trails [26].
3.5. Effect of Initial Concentration. These experiments were conducted by altering the concentration of the dye as 5, 10, 15, 25, 50, and 100 mg/L. These experiments were conducted at optimum conditions by keeping other variables constant (biochar dosage at 1 g/L, pH at 2.0, and temperature at 35°C). By increasing the initial concentration of dye, the biochar’s uptake potential increases, as shown in Figure 6. At a concentration of 5 mg/L and 100 mg/L, an uptake capacity of 2.80 mg/g and 75.68 mg/g was obtained. Higher concentration of the dye resulted in uptake capacity saturation which further results in no change in uptake capacity. By enhancing the concentration of biochar from 5 to 100 mg/L, the percentage removal efficiency of RR120 was increased from 56 to 75.68%, as represented in Figure 6. There was an increase in removal efficiency at elevated initial RR120 concentration, and it may be due to the availability of a sufficient amount of binding sites towards excess dye molecules [27]. From the results obtained, the optimum value of initial concentration was taken as 15 mg/L and is used in all batch trails.

3.6. Desorption Studies. Figure 7 shows the effect of different elutants’ desorption efficiency of biochar. The maximum desorption efficiency of 98% was attained for sodium hydroxide, as shown in Figure 7. This could be because of the presence of more OH- ions which favored the removal of dye molecules from the biochar, as reactive dyes are composed of more positive ions onto the biochar. It is important to perform solid-to-liquid (S/L) ratio experiments to optimize the volume of the elutants to be utilized in desorption investigations. The optimum value of the S/L ratio was taken as 5, as shown in Figure 7(b). Regeneration studies
were also conducted to examine biochar’s potential in successive adsorption and desorption. Figure 7(c) shows that, for three sequential sorption-elution cycles, a maximum desorption efficiency was attained as 97.5%. So, based on the desorption investigations, sodium hydroxide with an S/L ratio of 5 was used for three sequential sorption-elution cycles.

4. Conclusion

As a result of the current study, it is possible to conclude that biochar can give effective solutions for the remediation of reactive red 120 (RR120) from dye-bearing wastewater. It was discovered that the biochar has extremely high uptakes towards the dye. From the batch studies, the optimum values of sorbent dosage, pH, and temperature were determined to be 1 g/L, pH 2.0, and 35°C, respectively. The biochar derived from rice husk had a maximum sorption uptake of 53.8 mg/g for RR120. It can be concluded that rice husk biochar can be used as effective sorbents for the treatment of various Remazol dyes from aqueous and wastewater solutions. As a low-cost and environmentally friendly substance, biochar can replace costly activated carbon in the remediation of dye-bearing wastewaters.

Data Availability

The data used to support the findings of this study are included within the article.

Disclosure

This study was performed as a part of the employment of Samara University, Ethiopia.

Conflicts of Interest

The authors declare that they have no conflicts of interest regarding the publication of this paper.

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