

Preparation, Characterization, and Utilization of Banana Pseudo Stem as a Sustainable Adsorbent

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ABSTRACT

Water pollution has been a thoughtful issue in recent decades, negatively affecting human health and ecology. The rapid development of industries, such as textile and leather, has contributed to water pollution due to an unprecedented amount of toxic industrial wastewater without a feasible wastewater treatment. Due to huge water consumption in all textile processes along with high concentration of lost dye as a result of low levels of dye-fiber fixation, dye removals from textile wastewater are an environmental concern. An attempt was taken to use the banana pseudo stem (BPS) to use as a sustainable adsorbent in removing dyes from aqueous solution. This experiment was carried out on a laboratory scale. The surface of banana pseudo stem (BPS) was modified by HCl and NaOH to observe the change in adsorption capacity. The acid modified BPS shows higher adsorption capacity than base modified BPS and unmodified BPS respectively. The FTIR spectrum was recorded to determine the main functional groups present on the surface of the banana pseudo stem. The effect of different physico-chemical parameters such as adsorbent dosage, contact time, initial concentration of dye, pH, and temperature on the removal of dyes from the aqueous solution has been studied. The maximum removal of a textile dye Congo red (CR) was found with a BPS mass of 1g/100 mL, at 30°C, at a concentration of 1×10^{-5} M, at pH 2.70 and 60 minutes of contact time. From the results, it is possible to conclude that banana pseudo stem could be a good alternative to the available adsorbent for the removal of reactive dyes from wastewater.

Keywords: Adsorption, Banana pseudo stem, Congo red, Mechanism of adsorption, Water pollution.

INTRODUCTION

A growing number of people worldwide are experiencing freshwater shortages due to factors such as industrial development, climate change, and rapid population growth. These elements significantly affect the quality of the water. Even though water makes up more than 70% of the earth's surface, less than 1% of this massive reserve is fit for human consumption [1,2]. Every year, a massive amount of contaminated water is released into the environment. The major source of water pollution is the redemption of untreated industrial effluents, as well as municipal wastes containing a variety of hazardous substances, including dyes, heavy metals, pesticides, organic and inorganic waste materials [3,4]. Among these, the most significant sources of industrial pollutants are the increasingly common dyes, such as Congo red (CR), methylene blue (MB), methyl orange (MO), Disperse Violet 26, rhodamine B (RhB), methyl red, and crystal violet. These dyes come from a variety of industries, including the textile, cosmetic, leather, food, pharmaceutical, paint and varnish, and pulp and paper industries [5-18]. A recent estimate puts the yearly global production of dyes at over 70 lakh tons [19]. Since processing 1.0 kg of textiles requires more than 100 L of water, the textile sector alone is responsible for a significant amount of pollution [20]. Aquatic ecosystems' ability to perform photosynthetic processes is negatively impacted when untreated wastewater containing dyes is dumped directly into natural water bodies

[21]. The presence of metals [22] and aromatics causes mutagenic or teratogenic effects on fish species and aquatic organisms [23]. In addition, dyes in environment can have tolerable to detrimental impacts on human health, such as allergy, dermatitis, mutagenic, carcinogenic, and kidney disease [24]. According to recent findings, dyes based on chromium have a complicated structure and can be carcinogenic to humans [25]. As a result, the dumping of dye into the environment spoils the water quality indirectly affecting the aquatic life and human health. Consequently, there has been a substantial increase in the number of research articles published on "Dye Removal," indicating that research in this field is still ongoing.

Congo red is sodium salt of 3, 3'-([1, 1'-biphenyl]-4, 4'-diyl)bis(4-aminonaphthalene-1-sulfonic acid) which contains azo group. It is water-soluble and yields a red colloidal solution. Thus, it is used as an indicator and as a biological stain. Congo red was formerly used to dye cotton. But it has been superseded by dyes more resistant to light and washing. Dye removal techniques fall into three categories: chemical, physical, and biological [26]. There are benefits and drawbacks to every one of them. Biological treatment is often the least expensive option when compared to other physical and chemical treatments. Because many microorganisms, including bacteria, yeasts, algae, and fungi, can accumulate and degrade various pollutants, industrial effluents are often treated using biodegradation techniques like fungal decolorization, microbial degradation, adsorption by (living or dead) microbial biomass, and bioremediation systems [27, 28]. However, their application is often restricted because of technological constraints. Chemical processes can include irradiation [29], photocatalysis [30], electrochemical processes [31], coagulation [32], flocculation [33], flotation [34], filtration [35], precipitation-flocculation utilizing Fe(II)/Ca(OH)₂ [36], electro-flotation [37], electro-kinetic coagulation [38], and traditional oxidation by oxidizing agents (ozone) [39]. Even when these chemical procedures are used to remove the colors, concentrated sludge builds up and poses a disposal issue. Furthermore, there's a chance that overuse of chemicals will result in a linked environmental issue. Other recently developed methods known as "advanced oxidation processes," which depend on the production of extremely potent oxidizing agents [40] like hydroxyl radicals, have shown promise in the breakdown of contaminants. Although these techniques are effective at purifying tainted water, they are also exceedingly expensive and unsightly from a business perspective. Two major issues are the growing need for electrical energy and the use of chemical chemicals [41].

Many physical techniques are also frequently applied, such as membrane filtration procedures [42] (e.g., reverse osmosis [43], electrodialysis [44], and nano-filtration [45]). The principal disadvantage of membrane processes is their limited lifetime before membrane fouling occurs, which means that any assessment of their economic viability must take periodic replacement costs into account. Liquid-phase adsorption yields high-quality treated effluent with appropriate adsorption process design, making it one of the most common techniques for eliminating impurities from wastewater, according to a large body of literature data [46-48]. Considering that the sorbent is low-cost and does not need a supplementary pre-treatment phase prior to application, this method presents a strong choice for the cleanup of contaminated streams [49]. Adsorption is one of the most versatile and extensively utilized methods in wastewater treatment technologies due to its cost effectiveness, superior performance, ease of operation, better proficiencies and straightforward design [50-52]. Currently, dye-containing wastewater is treated using different type of adsorbents, such as biosorbents [53], carbon-based nano-adsorbents [54], MOFs [55], transition metal-based oxides [56], and polymer-based adsorbents [57]. All of this adsorbent preparation is not economically feasible as well as not free from restraint. Numerous researches have been carried out to invent more affordable, environmentally friendly, and effective adsorbents to remove contaminants. Agricultural waste is considered as a better replacement of adsorbents due to its great adsorption efficacy and low cost [58]. These compounds have unique chemical structures, and are widely available, renewable, and affordable, making them suitable for application in the environmentally safe, low-cost elimination of dyes from aqueous systems. Therefore, turning these common resources into effective adsorbents for the removal of pollutants from aqueous systems will be a practical solution to diminish water pollution. Recently, numerous low-cost adsorbents have been generated from biomaterials and used as potential adsorbents which are viable to lessen pollution in water. A number of inexpensive adsorbents derived from biomaterials have been developed as possible adsorbents in recent years [59, 60].

In the following paper, we attempt to turn agricultural waste into an affordable adsorbent. The part of the banana plant that mimics a trunk is called the pseudo stem which can be used as a precursor for making

adsorbent. This organic waste produces greenhouse gases into the atmosphere, which is problematic for the environment because the majority of it gets disposed of in landfills, rivers, and lakes, that is why it is necessary to recover it and utilize it as an adsorbent. The main waste generated is pseudo stem from bananas, which has the advantage of being cheap, renewable, and having surface chemical groups that facilitate adsorption, making it an effective adsorbent for removing contaminants. We implement this adsorbent to extract the azo dye Congo red from waste water.

MATERIALS AND METHODS

Preparation, Modification, and Characterization of BPS

Banana pseudo stem was collected from local area of Barishal, Bangladesh, cut into small pieces and washed with distilled water to get rid of the undesirable particles from the surface of the BPS as well as dust and dirt. The moisture of the BPS was removed by oven drying. Then they were taken in an electric grinder to reduce their size for experimental testing. A solution of acid i.e., HCl having a concentration of 0.01M was prepared with distilled water in a 250 mL volumetric flask. Then 10g of processed BPS was soaked in a small amount of HCl solution overnight and then the solution was filtered. The wet BPS was dried at 100 °C in an electric oven for 6 hours. The acid modified scales were taken in a mortar to prepare fine particles of BPS. By following the same procedure KOH modified BPS was prepared. With the help of IR Tracer-100 (Shimadzu) the FTIR spectra of unmodified BPS, acid, and base modified BPS were investigated for the characterization of the functional groups present on the surface of the BPS.

Preparation of CR Solution and Adsorption Study

A solution of Congo red having a concentration of 1×10^{-2} M was prepared with distilled water in a 250 mL volumetric flask and kept as the stock solution. From the stock solution, diluted solutions having different concentrations from 1×10^{-3} M to 1×10^{-5} M were prepared in 100 mL volumetric flasks. The absorbance of each solution was measured with a double beam UV visible Spectrophotometer (Lambda-365). Distilled water was used as a reference solution for all the measurements. The desired adsorption was carried out with a fixed amount of BPS in an orbital shaker (Model No-JSOS-300). The percentage of dye removal efficiency was determined by the following equation where, A_0 and A_t are the absorbance of CR solution at 0 minutes and any time, t respectively.

$$\% \text{ of adsorption} = \frac{A_0 - A_t}{A_0} \times 100 \quad \dots\dots\dots (1)$$

RESULTS AND DISCUSSION

The absorption maximum of Congo red was determined spectrophotometrically from its absorption spectrum. The major peak was observed at $\lambda_{max} = 498$ nm and the obtained molar extinction coefficient (ϵ) is 1.494×10^4 L mol⁻¹cm⁻¹. However, all the experimental analysis was carried out at this λ_{max} .

Effect of BPS Dosage

The availability and accessibility of adsorption sites on adsorbent are occupied by adsorbent dosage [61]. As BPS dosage increases keeping all the other parameters at a constant value, dye removal efficiency initially increases, reaches a maximum and finally decreases (Figure 1). The adsorption was increased and reached maxima with the increase of adsorbent dose to 1g of adsorbent. Then the percentage of adsorption was reduced with the rise of adsorbent dose. Basically, the number of activation sites is abundant with lower adsorbent concentration. However, due to the increase in adsorbent dosage, aggregation of particles may take place. Consequently, the dye removal efficiency decreases. So, 1g is the optimum amount of adsorbent for Congo red removal using banana pseudo stem. There is also a possibility of desorption after the equilibrium or maximum adsorption is established. At that stage of the adsorption process, the percentage of adsorption is not increased whatever the adsorbent dosage is. It might be a result of the overlapping of maximum adsorption sites due to overcrowding of adsorbent particles [62].

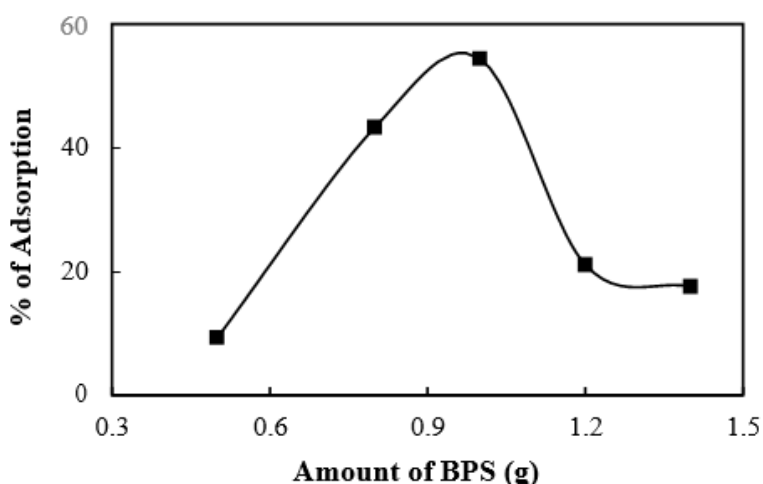


Figure 1: Percentage of adsorption at different amounts of BPS. $[[CR]_o=1 \times 10^{-5} \text{ M}$, $t = 60 \text{ minutes}$, $T = 25^\circ\text{C}$, $\text{pH} = 2.70]$

Effect of Contact Time

The contact time effect on the removal of Congo red dye using banana pseudo stem was operated at different contact times (0 to 60 minutes) using 100 mL solution with 1g of BPS (Figure 2). As time progresses, the surface coverage of the adsorbent is high. So, for 1g of adsorbent, the percentage of adsorption with time (from 0 to 60 minutes) increased from 1.28% to 54.38%. Usually, the efficiency of the adsorption is directly proportional to the contact time. The experimental result showed that the percentage of dye removal was increased because a large number of free surface sites of bio-sorbent were available to interact with the dye molecule [63].

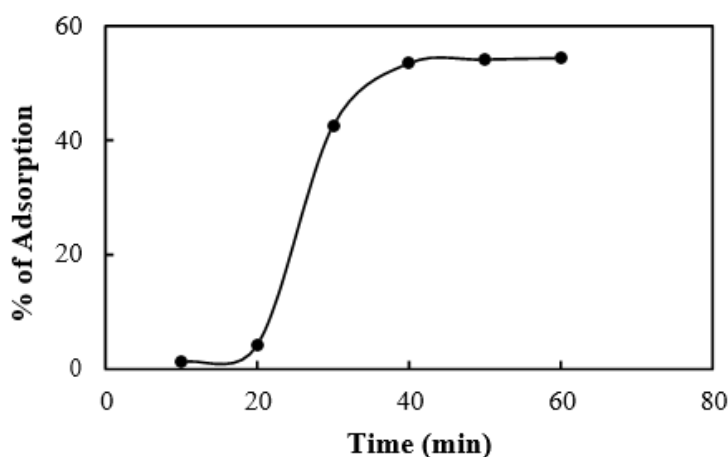


Figure 2: Percentage of adsorption at various time (min) intervals. [Amount of BPS = 1g, $[CR]_o=1 \times 10^{-5} \text{ M}$, $T = 25^\circ\text{C}$, $\text{pH} = 2.70]$

Effect of Concentration

The effect of initial concentration on the adsorption efficiency is shown in Figure 3. Initial concentration was varied from $1 \times 10^{-5} \text{ M}$ to $9 \times 10^{-5} \text{ M}$ keeping all other parameters at constant value. The dye removal efficiency decreases from 54.38% to 5.1% with the increase in dye concentration. The preliminary concentration of dye molecules provides a vital driving force to encounter all mass transfer resistance of the dye between the solid phase adsorbent and dye molecules [64]. Initially, the rise of dye concentration refers to a reduction in adsorption process, suggesting the adsorption of this dye is highly reliant on dye concentration. The adsorption of dye molecules takes place on the unoccupied active sites on the bio-sorbent surface. After a certain concentration, the bio-sorbent surface should be impregnated [65]. The further increase of dye molecules lowers the percentage of adsorption because there is a conflict between the dye molecules to adsorb on the surface.

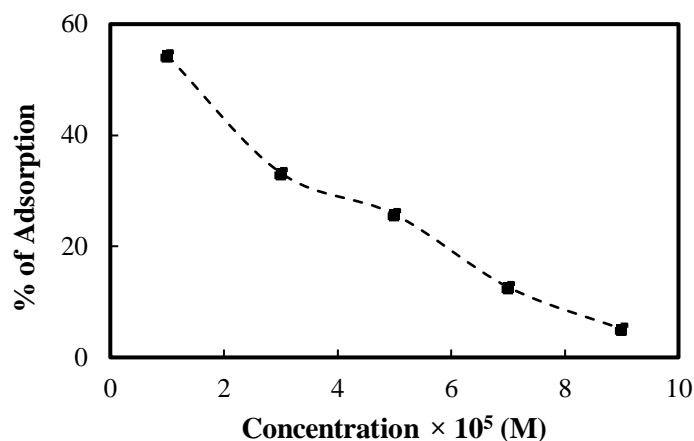


Figure 3: Percentage of adsorption at different concentration of CR. [Amount of BPS = 1g, t = 60 minutes, T = 25°C, pH = 2.70]

Effect of pH

The adsorption of dye molecules on the surface of the banana pseudo stem was investigated in the pH range 2-11. It exhibited lower adsorption efficiency at higher pH values. The decreasing pH value increases the adsorption efficiency. Finally, it became highest at pH 2.70. With the decrease in pH of the dye solution, the number of negative charges on surface sites reduces and the number of positively charged surface sites rises which favors the adsorption of dye anions due to electrostatic interaction [66].

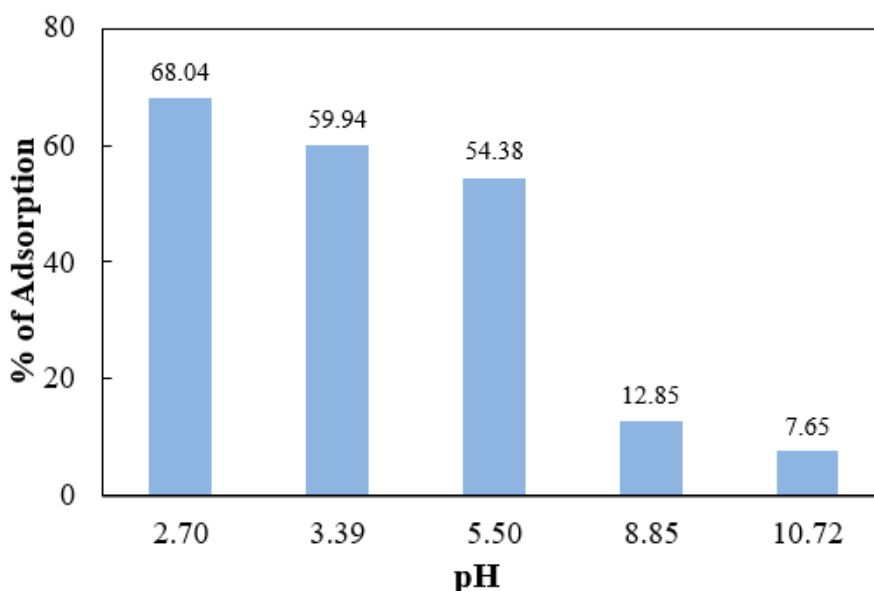


Figure 4: Percentage of adsorption at different pH of Congo red solution. [Amount of BPS = 1g, [CR]₀ = 1 × 10⁻⁵ M, t = 60 minutes, T = 25°C]

Effect of Temperature

Temperature is considered a crucial parameter that influences the adsorption process. The effect of adsorption of CR onto banana pseudo stem as a function of temperature is exhibited in Figure 5. It is obvious from the experimental results that the adsorption efficiency is diminished when the temperature is enhanced, which reveals the exothermic nature of the adsorption of CR dye on the surface of BPS. The utmost quantity of CR was adsorbed at 30°C on BPS. Then the rise in temperature directs to a lessening in dye removal efficiency. The reduction in the adsorption of CR at elevated temperatures was due to the disabling of the required forces between adsorbent active sites and adjacent CR molecules during adsorption process [67]. The lowering of adsorption after 30°C was occurred because of the reduction in surface activity at elevated temperatures. It reveals that the adsorption of CR molecule onto banana pseudo stem is physical adsorption [68]. Similar

phenomena were reported for the adsorption of anionic dyes on the surface of palm kernel fiber as a function of temperature [69]. Therefore, the desorption of CR molecules at elevated temperatures was due to the weakening of adsorptive forces between CR molecules and functional groups on the BPS surface.

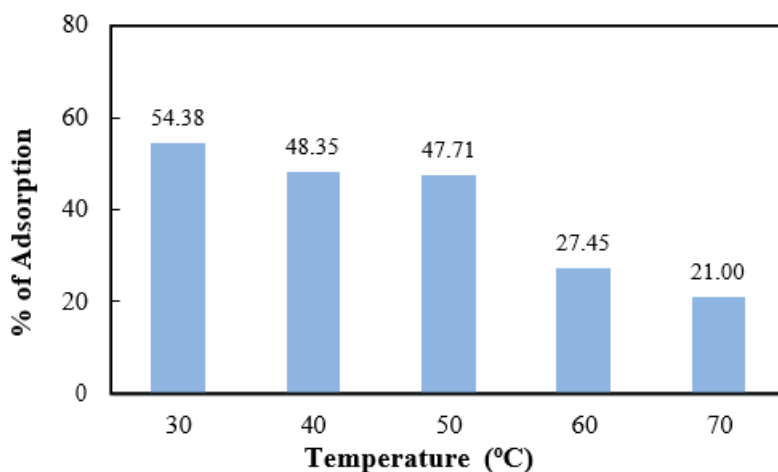


Figure 5: Percentage of adsorption vs. temperature (°C). [Amount of BPS = 1g, [CR]₀ = 1 × 10⁻⁵ M, t = 60 minutes, pH = 2.70]

Effect of Acid and Base Modified BPS

According to surface chemistry, surface modification is a chemical technique that involves the use of acid, alkali or salt to improve the functional groups of surfaces. In this research, the surface modification of banana pseudo stem was executed by using acid or base such as HCl or NaOH, which have a great influence on the adsorption capacity of the adsorbent. The effect of adsorption on the acid and base modified BPS is shown in Figure 6. After 60 minutes, the acid modified BPS appeared higher adsorption capacity (71.31%) than base modified BPS (8.12%) and unmodified BPS (54.38%). For surface modification by acid, the specific surface area and the pore volume concentration might be improved which leads to a higher adsorption capability. This may be due to the fact that the BPS adsorbent absorbs a negative charge on the surface that improves the adsorption of positively charged species. This phenomenon is also supported by the effect of pH on adsorption which is mentioned earlier.

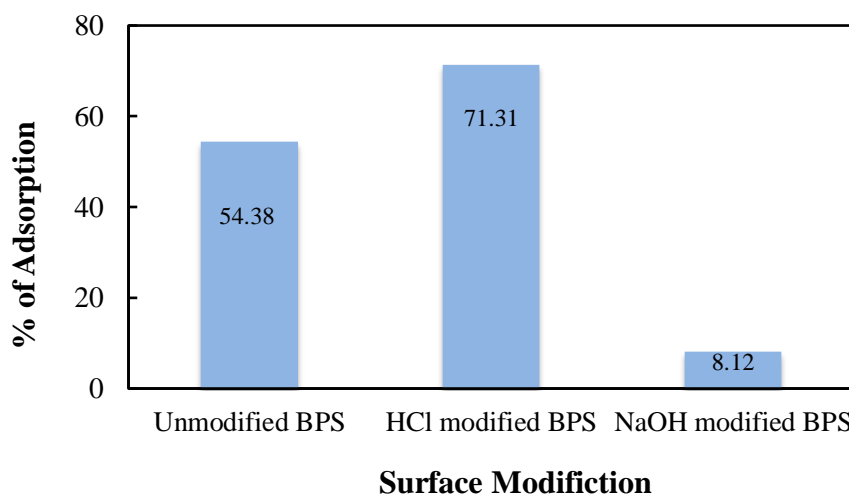


Figure 6: The adsorption efficiency of unmodified, acid, and base modified BPS adsorbent.

FTIR Study

The BPS may contain different functional groups that can influence the adsorption process. The bonds in the functional groups of BPS may vibrate at different frequencies which may help to identify the functional groups by measuring their energy of absorption. Fourier transform infrared (FTIR) spectra were used to characterize the main functional groups present on the surface of the banana pseudo stem (Figure 7). The FTIR spectra

were recorded in the wavelength range 4000-400 cm^{-1} . The data were collected at 2.0 cm^{-1} resolution. The broad absorption band observed at 3050- 3615 cm^{-1} indicates the O–H stretching vibration and at 2928 cm^{-1} corresponds to the C–H stretching vibrations of cellulose. The narrow band around 2357 cm^{-1} is related to the existence of (NH_2^+ and NH^+) amine groups. The sharp band at 1630 cm^{-1} corresponds to C=O stretching vibration in α , β -unsaturated group of lignin. The band around 1594 cm^{-1} indicates the C–C stretching aromatic skeletal vibrations of lignin groups. In addition, band at 1560 cm^{-1} indicates the existence of bending vibration of primary $-\text{NH}_2$ group. The narrow band observed at 1404 cm^{-1} recommends the existence of NH_3^+ amine salts. The absorbance around 1211 cm^{-1} is attributed to the C–O–C stretching vibrations of cellulose, hemicellulose, and lignin, revealing that the sample contains etheral character. A band around the region 774 cm^{-1} corresponds to the aromatic C-H out of plane bending vibration of lignin. The absorbance at 669 cm^{-1} is related to the existence of C–S thiol and sulfide groups [70].

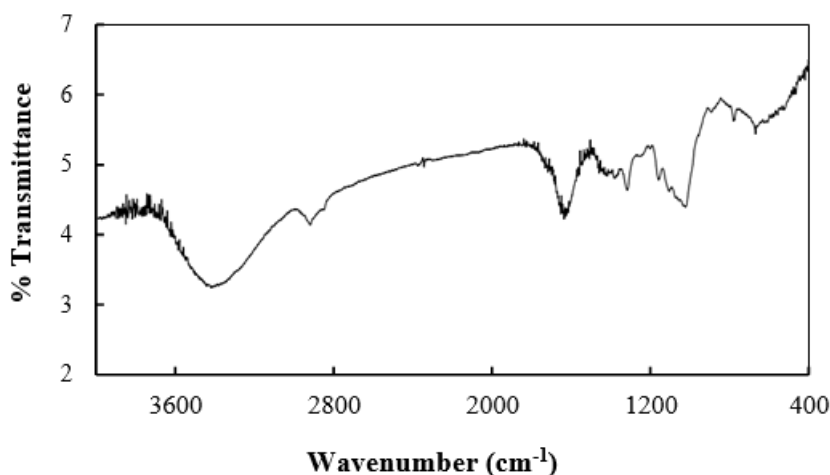


Figure 7: FTIR spectra of banana pseudo stem (BPS).

Mechanism of Adsorption on BPS

The adsorption is significantly influenced by the characteristics of adsorbent’s surface [71]. The BPS contains a variety of functional groups on its surface having acidic, basic and/or ionic characteristics. These groups have an impact on the adsorption of dyes through the formation of (a) strong hydrogen bonds, (b) electrostatic interactions, (c) $n-\pi$ interaction, (d) $\pi-\pi$ interaction etc. There might be an electrostatic interaction between the cationic center of the adsorbent and the negatively charged groups of the dye molecules or vice-versa. The $\pi-\pi$ interaction occurs between the π -electron clouds of the adsorbent and aromatic rings of the dye molecule [72]. The BPS surface is rich with acidic oxygen functional groups which are responsible for the formation of strong hydrogen bonding between the adsorbent and the dye molecule. The $n-\pi$ interaction between the adsorbent and the dye molecule can also exaggerate the adsorption processes.

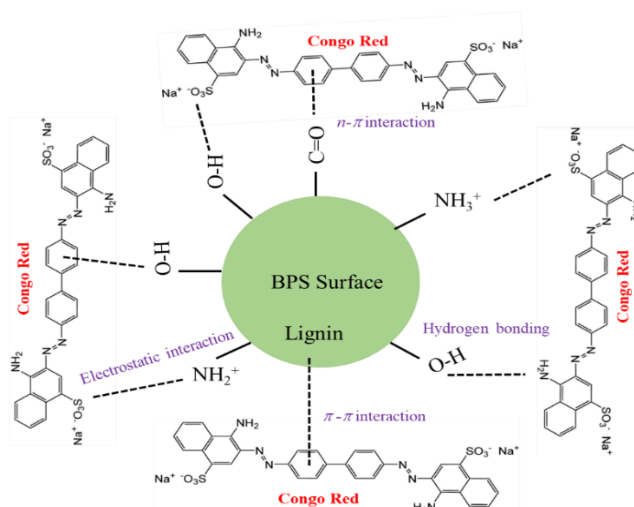


Figure 8: Proposed mechanism for the adsorption of Congo red on BPS.

CONCLUSION

The higher adsorption efficiency of banana pseudo stem makes it an alternative to commonly used adsorbents. Not only the cost-effectiveness but also the usage of banana pseudo stem as bio-adsorbents can remove the multitude of ecological complications created by its disposal. Moreover, it is a perfect low-cost precursor material for the manufacture of activated carbon using conventional activation techniques due to its extensive accessibility when compared to the commercially used adsorbents. In conclusion, the feasibility of CR removal from aqueous solution with banana pseudo stem as sorbent is confirmed. The experimental results showed that the maximum CR removal of 54.38% was achieved at optimum conditions, initial concentration of CR was 1×10^{-5} M, temperature of 30°C and the bio-sorbent dosage of 1 g using banana pseudo stem. The acid modified BPS showed higher adsorption capacity (71.31%) than the base modified BPS (8.12%) and unmodified BPS (54.38%). The main functional groups exist on the surface of the banana pseudo stem were investigated by the FTIR spectrum. All of the results are beneficial to the practical application of BPS into the treatment of dye. In summary, banana pseudo stem are alternative substitutes to activated carbon as bio-adsorbents, which are plentiful in the nature. Therefore, the viewpoint of BPS as adsorbent for removal of CR from aqueous dye solution is feasible.

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