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REMOVAL OF INK DYE FROM WASTEWATER USING ADSORPTION BY NANOCELLULOSE BASED HYDROGELS

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Abstract: *Adsorption's high efficiency, low operating cost, and versatility have made it a popular and successful approach for removing contaminants from wastewater. Various synthetic and natural adsorbents have been created for this purpose and used to remove a variety of contaminants, including printing inks. Growing environmental concerns have spurred interest in creating more environmentally friendly and biodegradable materials. Hydrogels are produced using a variety of recently developed or identified monomers and cross-links, as well as pre-made biocompatible polymers and cutting-edge synthesis techniques. Hydrogels can be made more intelligent by altering their morphology, crosslinking, chemical structure, or manufacturing methods. Hydrogels must be collected, regenerated, and reused in order to be deemed life cycle sustainable. This is an economic system in which natural ecological feedback or technological means transform waste into resources.*
In this work, dye adsorption experiments were carried out using wastewater from printing. Hydrogels based on nanocellulose were employed as adsorbents. Firstly, nanocellulose was produced. Nanocellulose was used to create hydrogels, while $ZnCl_2$ *was used as a cross-linker. The batch technique was used for the adsorption trials. ATR-FTIR, or attenuated total reflection/Fourier transform infrared spectroscopy, was used to examine the chemical structures of the hydrogels. The different parameters were found, including pH, contact time, and removal quantity. Thus, with the aid of produced hydrogel, red coloured dye used commercially in flexography inks effectively cleansed the wastewater.*

Key words: nanocellulose, hydrogel, dye adsorption

1. INTRODUCTION

The food, cosmetic, textile, pharmaceutical, and materials industries all employ pigments extensively. Synthetic pigments have been widely employed to address the industrial need for pigments because of their flexibility in changing chemical characteristics or colour, high manufacturing yield, and low cost of production (Bernard et al., 2024). The wastewater that results from using these pigments in printing ink is strongly coloured, signifying pollution. Such printing facilities are not allowed to directly release wastewater because of the harmful effects it has on both the environment and human health.
Various methods, including chemical, physical, and biological ones, are used to remove colorants, dyes, and pigments from wastewater. Coagulation-flocculation, filtration, adsorption, oxidation, ozonation, electrolysis, and bioremediation are some of these techniques. Every approach has a unique mix of benefits and drawbacks that change based on the particular sector in which it is used (Piaskowski et al., 2018, Liu et al., 2019; Nishat et al., 2023; Shaikh et al., 2021; Rashid et al., 2021; Khan et al., 2023; Ercan et al., 2015; Pavithra et al., 2019).
The use of adsorption as a popular and effective method of removing impurities from wastewater has grown significantly. Numerous benefits come with this approach, including great efficacy, minimal operating costs, and flexibility. As a result, scientists have created and employed a variety of synthetic and natural adsorbents to efficiently extract different contaminants, such as pigments, from wastewater. Environmentally friendly adsorbent production and application have grown in importance in recent years. Of these, the hydrogel derived from nanocellulose is a notable adsorbent since it is non-toxic, simple to manufacture, and reasonably priced (Kumar et al., 2021; Patra et al., 2024; Jagadeesh et al., 2023; Agarwala et al., 2023; Dutta et al., 2021; Osman et al., 2023).
In this study, a straightforward technique was used to create nanocellulose hydrogel in a way that was both economical and environmentally benign. The application of the nanocellulose hydrogel to eliminate coloured dye was the main focus of the investigation. The produced hydrogel was extensively analyzed by the use of methods like TGA and FTIR spectroscopy. In order to understand how several parameters, including pH, contact time, and pigment content, affected the adsorption process, the removal efficiency was calculated.

2. METHODS

2.1 Synthesis of cellulose

Alkaline and bleaching methods were used to separate hemicelluloses and lignin from the raw material in order to extract cellulose from wood sawdust. In summary, hemicellulosic components were removed from wood sawdust by boiling it in water for 20 minutes at 100°C. After that, an alkaline treatment using 1.0 M NaOH solution was applied to 50 g/L of leftover sawdust, and it was left for two hours at 80°C while being mechanically stirred. The remaining alkaline sample was rinsed with hot water and then bleached for one hour at 100°C and pH 4.5 using 2.5% w/v sodium chlorite at a material-to-liquid ratio of 1:20. In the end, the bleached cellulose was washed three times in boiling water to remove any leftover or unreacted chemicals, and it was then dried in an oven (Sriruangrungkamol et al., 2021).

2.2 Synthesis of cellulose nanocrystals (CNC)

The as-purified cellulose was treated with sulfuric acid for acid hydrolysis while an ultrasonic method was implemented. 60% (w/w) sulfuric acid was added to 10 g of pure cellulose to hydrolyze it and produce a suspension (10 mL/g cellulose). This suspension was sonicated for 60 minutes at 60°C to facilitate hydrolysis. Once hydrolysis was completed, the suspension was rapidly diluted five times with cold distilled water to stop the process. The suspension was then transferred into centrifuge bottles, spun at 12,000 rpm for 10 minutes, and the crystals were separated by decanting. The solid aggregates in the suspension became disordered due to sonication (Sriruangrungkamol et al., 2021).

2.3 Preparation of nanocellulose hydrogel

The following ingredients were added in droplets to create nanocellulose hydrogels. The surface of the CNC water dispersions along the walls of the cylindrical Teflon mould is treated with a 20% w/w $ZnCl_2$ water solution. In the subsequent procedures, 1% mass concentration CNC water dispersions were employed. The ultimate zinc ion concentration in each mixture used in this investigation was kept at 0.1 mol/L. After that, the mixture was allowed for a full day without being stirred to enable the creation of nanocellulose hydrogels. In order to eliminate unattached Zn2+, the resultant hydrogel was lastly washed with distilled water (Lu et al., 2020; Ai et al., 2023).

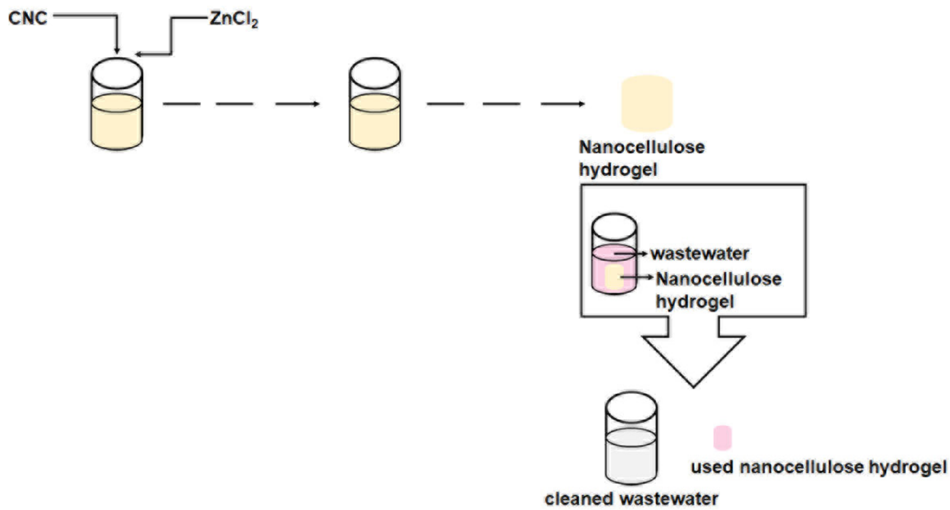

Figure 1: Preparation route of the hydrogel

2.4 Adsorption Studies

Using the produced nanocellulose hydrogel, adsorption experiments of the dye were conducted in batch mode with a shaker. The studies used precise amounts of adsorbent and 25 mL of pigment solution at different concentrations, all conducted at room temperature. The adsorption process was tuned for a number of factors, including pH, pigment content, and contact time. Solutions of diluted HCl and NaOH were used to alter pH. Whatman No. 44 filter paper was used to filter the adsorbent and solution, and a UV-Vis spectrophotometer operating at 511 nm was used to measure the filtrate's absorbance.

3. RESULTS AND DISCUSSIONS

3.1 Characterization of the prepared hydrogel

ATR-FTIR analysis was used to characterize the structural properties of the prepared hydrogel. Figure 2 displays the produced hydrogel's FTIR spectrum. The produced hydrogel's FTIR spectrum showed several noteworthy characteristics. The -OH band is represented by the large peak seen at about 3344 cm^{-1}. Furthermore, the stretching vibrations at 2908-2896 cm^{-1} are peaks that correspond to the $-CH_2-$ groups. The carboxylic acid groups' carbonyl groups are vibrating, which is the cause of the strong peak at 1700 cm^{-1}. O-H bending is responsible for the vibration peak at 1428 cm^{-1}. The produced hydrogel's ATR-FT-IR spectra showed absorption bands corresponding to O-H bending, C-O stretching, CO-O-CO stretching, and C-H bending were detected at 1315 cm^{-1}, 1161 cm^{-1}, 1030 cm^{-1}, and 985 cm^{-1} wave numbers, respectively (Figure 2). The spectral data of the prepared hydrogel were in agreement with the spectral data in the literature (Lu et al., 2020; Ai et al., 2023).

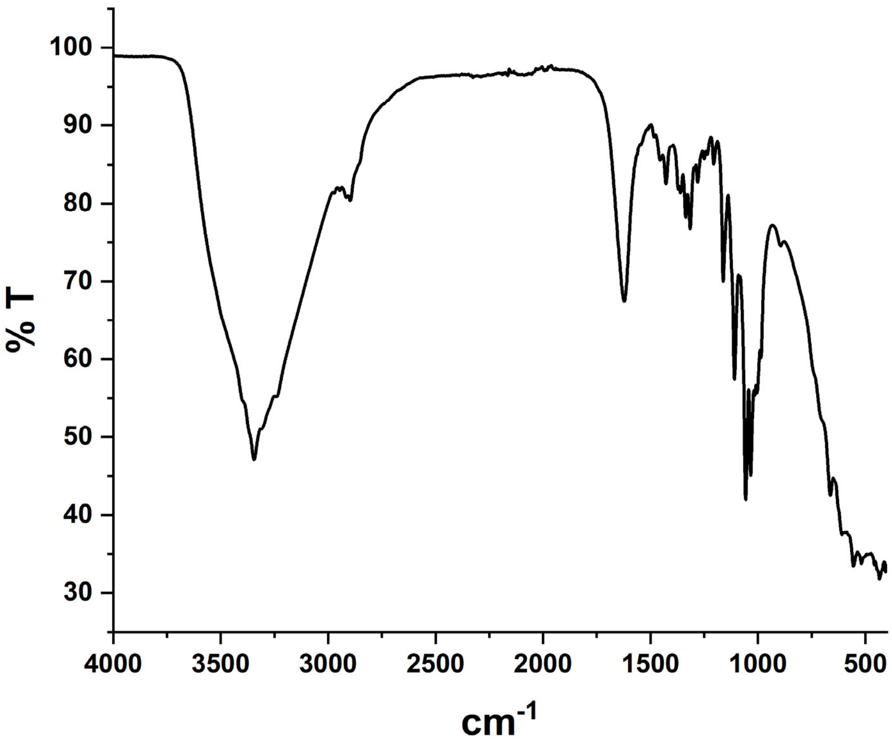

Figure 2: FTIR spectrum of the prepared hydrogel

Using TGA in a nitrogen environment, the produced hydrogel's thermal degradation behaviour was examined. In Figure 3, the TGA curve is displayed. The produced hydrogel's maximal heat degradation happened in two stages between 95 and 593ºC, and the breakdown of the hydrogel's absorbed water was responsible for 85% of its weight loss. The produced hydrogel's TGA spectrum revealed mass loss between 30 and 150ºC. Mass losses of water absorbed on the material happen in this temperature range (Sriruangrungkamol et al., 2021). The literature and these findings are in agreement. The temperature at which a 5% mass loss happens during decomposition is 80ºC, and a 10% mass loss occurs at 105ºC.

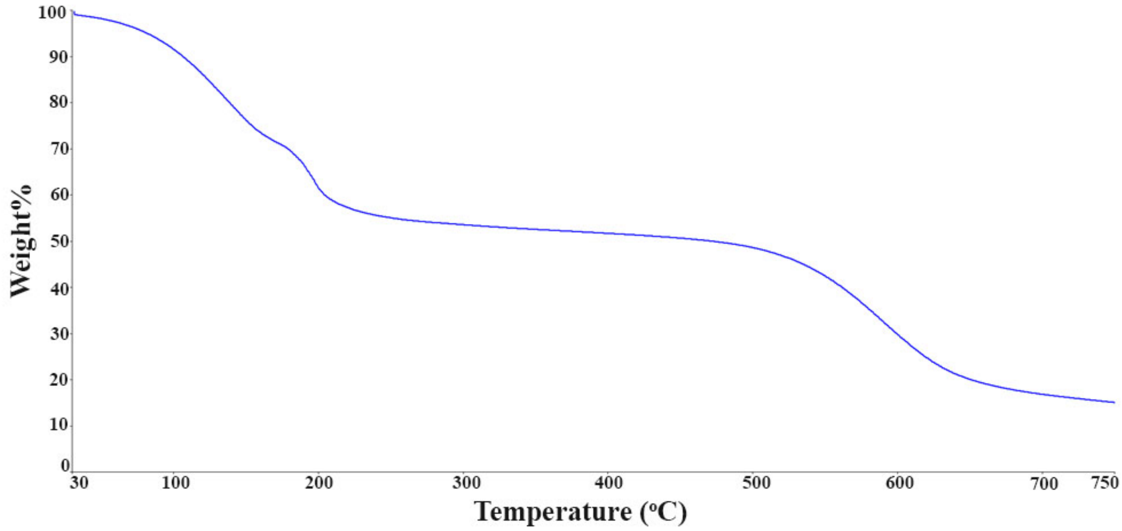

Figure 3: TGA curve of the prepared hydrogel

3.2 Effect of pH

The adsorption capacity of the hydrogel can be influenced by the pH of the solution. The impact of pH on the adsorption behaviour was examined within the range of pH 2-10. The results indicated that the maximum adsorption occurred at pH 2 (as shown in Figure 4), thus pH 2 was determined as the optimal condition. Figure 5 displays the colours of the dye solutions at different pH levels before and after adsorption, respectively.

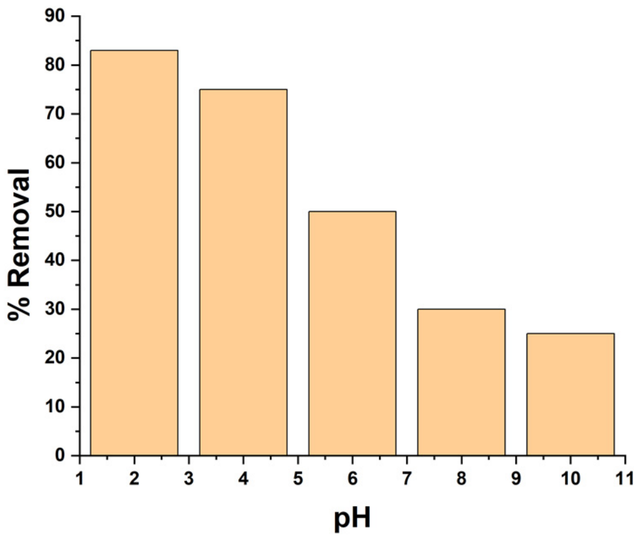

Figure 4: The influence pH on removal efficiency

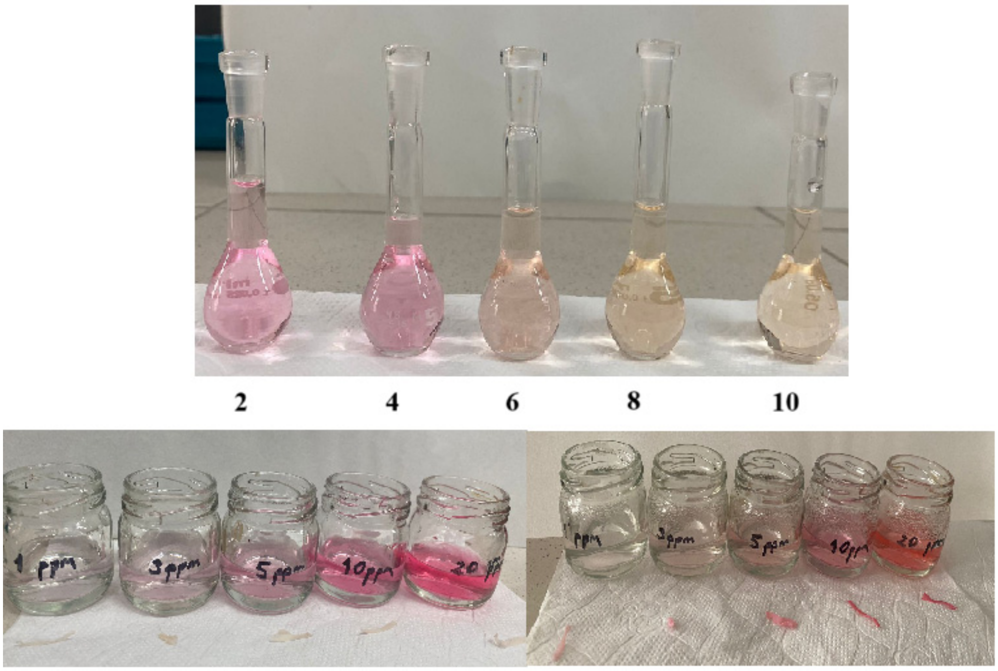

Figure 5: Colour Chancing of solutions before and after adsorption

3.3 Effect of contact time

During the adsorption process, it is essential to stir or shake the adsorbent and adsorbate for a specific duration until the adsorption equilibrium is reached. As the adsorption progress, the adsorbate molecules adhere to the active surface of the adsorbent, eventually reaching a point where further adsorption ceases to occur. The prepared adsorbent and dye solutions were agitated for varying durations, ranging from 1 to 75 minutes, at pH 2. The results are presented in Figure 6. It was observed that maximum colour removal was achieved within a very short time, and the optimum contact time was determined as 30 minutes.

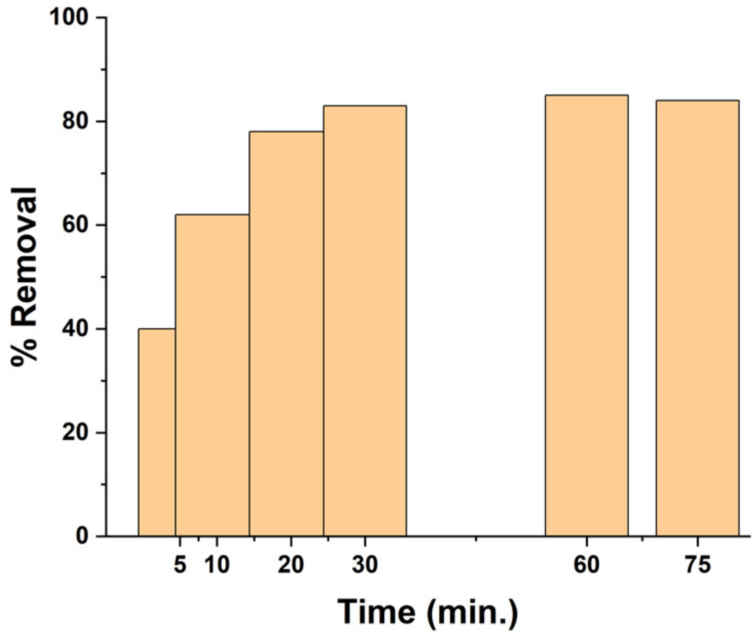

Figure 6: The effect of contact time

3.4 Effect of initial pigment concentration on adsorption

In order to evaluate the removal efficiency of the hydrogel for coloured dye, a series of adsorption experiments were conducted using coloured dye solutions with concentrations ranging from 5 to 20 mg/L. The experiments were performed at pH 2 and for a duration of 30 minutes and the removal efficiency of various concentrations of coloured dye was depicted in Figure 7.

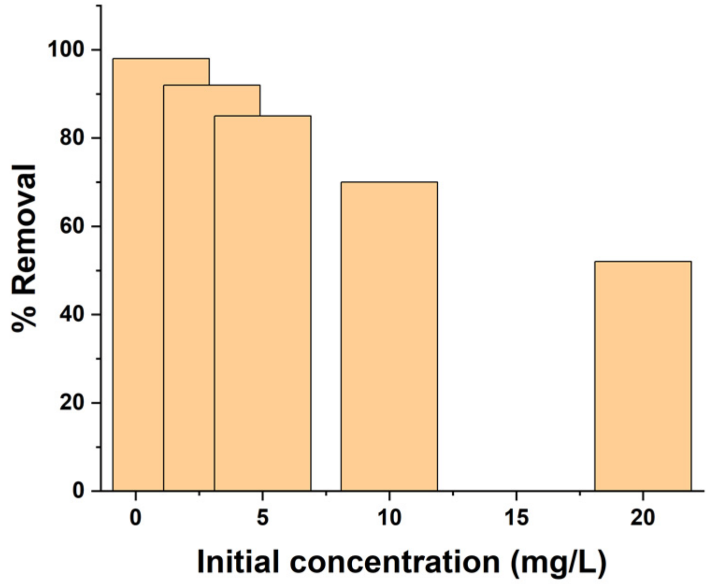

Figure 7: The effect of dye concentration on the removal efficiency

4. CONCLUSIONS

This study focused on the preparation of an environmentally friendly bio-based hydrogel used for the removal of coloured dye pigment from aqueous media. Adsorption experiments were carried out in a batch process. The adsorbent was characterized using attenuated total reflectance/Fourier transform infrared spectroscopy (ATR-FTIR) and thermogravimetric analysis (TGA). Various parameters including pH, contact time, and dye concentration were evaluated. The optimum contact time was determined to be 30 minutes, while the optimum pH was found to be 2. The results showed that the prepared adsorbent effectively removed red-coloured dye, which is commonly used in offset inks, from wastewater.

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