Highly Efficient Removal of Rhodamine B Dye Using Nanocomposites Made from Cotton Seed Oil-Based Polyurethane and Silylated Nanocellulose

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Abstract
Biobased polyurethane nanocellulose nanocomposites were synthesized from cottonseed oil as the source for the biopolyol. The prepared composites were used to study the adsorption of Rhodamine B dye from water. Low functional polyol was derived from cottonseed oil using one-pot synthesis method. Nanocellulose was derived from pineapple leaves and then it was surface-functionalized via silylation. In-situ polymerization technique was used to incorporate the silylated nanocellulose into the polyurethane matrix. The prepared polyol from cottonseed oil was found to have an OH functionality of 2 which was confirmed by Fourier transform infrared spectroscopy (FT-IR) and Nuclear magnetic resonance (NMR) spectroscopy. Low functionality of polyol is the key factor in achieving flexible porous polyurethane. The silylated nanocellulose, polyurethane, and composites were characterized by FT-IR, X-ray diffraction analysis (XRD), and Scanning electron microscopy (SEM). The adsorption parameters were optimized using the Taguchi methodology and the adsorption efficiency was determined by carrying out adsorption at optimized parameters (5 wt% loading of silylated nanocellulose, pH 9, and temperature of 30 °C) for 8 h. Studies showed that the prepared composite has a high adsorption efficiency of 597 mg/g of silylated nanocellulose towards Rh-B.

Keywords Adsorption · Cottonseed oil · Nanocellulose · Polyurethane · Rhodamine B

Introduction
Water pollution is a critical issue of concern across the globe due to anthropogenic activities [1–3]. It is essential to remove the harmful water pollutants before the effluents from industries are discharged into the water bodies [4]. Recycling and reuse of water have gained momentum in recent years. A wide range of water treatment methods is available for industries, such as ion exchange, reverse osmosis, electrolysis, coagulation, flotation, evaporation, precipitation, crystallization, ultrafiltration, and adsorption [5]. Out of the available methods, adsorption is a convenient water treatment method as it involves simple setup, ease of operation, comparatively fast and inexpensive [6]. A significant amount of research work had been done on the removal of various water pollutants from wastewater using nano adsorbents from both synthetic and bio-derived sources. Though nano-based adsorbents have shown excellent adsorption capacity for the removal of heavy metals, dyes, pesticides, antibiotics, and other water contaminants present in wastewater, their recyclability, reusability, and recovery of these nano adsorbents after the adsorption are

Abbreviations
FT-IR  Fourier transform–infrared spectroscopy
NMR  Nuclear magnetic resonance
XRD  X-ray diffraction analysis
SEM  Scanning electron microscopy
FESEM  Field emission scanning electron microscopy
Rh-B  Rhodamine B
APTES  3-Aminopropyltriethoxysilane
MDI  Methylene diphenyl diisocyanate
DABCO  1,4-Diazabicyclo [2] Octane
PEG-6000  Polyethylene glycol
CSO  Cottonseed oil
FECS3  Formiated epoxy cottonseed polyol
still major challenges [7]. Polymer-based nanocomposites (PNCs) as adsorbents have a lot of advantages over nanomaterials in powder forms, such as higher stability, design flexibility, ease of handling, and ease of recovery. In PNC-based adsorbents, the polymer matrix acts as ideal support and facilitates the adsorption of targeted water pollutants by the nanoparticles which are embedded in the polymer matrix [8].

Amongst the diverse studies using nanomaterials and polymers as support matrices, polyurethane (PU) was found to be promising due to its excellent properties such as UV resistance, enhanced mechanical property, and high abrasion resistance [9]. Polyurethanes rely on petrochemicals as the source of the raw materials. However, environmental apprehensions have increased the need for more sustainable and eco-friendly alternatives. Recent studies in PU research are focused on the replacement of petro-based polyols and isocyanates with bio-based resources such as polysaccharides (starch and sugars), wood (lignocellulose), proteins, and vegetable oils [10, 11]. Vegetable oils are widely studied as a source of bio-polyol due to their ready availability, easy processing, and possess required chemical functionality. Polyols derived from vegetable oils are found to be a promising replacement for petroleum-derived polyols. Over recent years, renewable nanofillers such as nanocellulose in the form of cellulose nanocrystal or cellulose nanofiber are extensively studied because of their high surface area with abundant active sites on their surface [12–14]. Nanocellulose shows similar and comparable properties with that of carbon-based, inorganic nanofillers in polymer nanocomposites and it acts as a suitable alternative to other nanofillers because of their sustainability and other advantages over conventional fillers [15].

Deriving biobased polyurethane and the use of nanocellulose as filler in the polyurethane matrix creates a lower environmental impact compared to petroleum-based polymer nanocomposites. Biobased polyurethane nanocomposites are garnering attention in wastewater remediation such as the removal of textile dyes, metals ions, and organic pollutants from wastewater and their adsorption efficiency is on par with existing adsorbents used in the wastewater treatment process [16–19]. In the present work, bio-based polyurethane nanocellulose nanocomposites were prepared from cottonseed oil as a source of bio-polyol and nanocellulose was derived from pineapple leaves and further its surface was functionalized by silyl groups to improve its compatibility with polymer. Bio polyol with relatively low OH functionality of 2 is prepared from cottonseed oil using a one-pot synthesis by controlling the time of the hydroxylation. In situ polymerization of biobased porous polyurethane nanocomposite with silylated nanocellulose was carried out and the synthesized composites were used as adsorbents for the removal of Rhodamine B. The optimum conditions for effective adsorption such as the temperature of the stimulated wastewater medium, pH of the stimulated wastewater medium, and the amount of silylated nanocellulose loading (wt%) within the polyurethane matrix were estimated and reported.

Experimental

Materials and Sample Preparation

Cottonseed oil (CSO) was purchased from a local oil mill (Bengaluru, India), 30% hydrogen peroxide (H2O2), formic acid (HCOOH), diethyl ether (C2H5–O–C2H5), sodium chloride (NaCl), sodium sulphate (Na2SO4) were acquired from S.D Fine Chemicals, India and these chemicals are used as received without any further purification for the preparation of low functional polyol from the cottonseed oil. Pineapple leaves were collected from fields and cut, sun-dried, and milled to a fine powder. Sodium hypochlorite(NaClO), Sodium hydroxide(NaOH), acetate buffer of pH 4.5, sulphuric acid (H2SO4) (99%), 100% acetic acid (CH3COOH), ethanol (C2H5OH) were purchased from S.D fine chemicals, India and 3-Aminopropyltriethoxysilane (APTES) were procured from Sigma Aldrich, India for extraction of nanocellulose from pineapple leaves followed by its surface modification via silylation. Methylene diphenyl diisocyanate (MDI), DABCO (1,4-diazabicyclo[2,2,2]octane), and Polyethylene glycol (PEG-6000) were purchased from TCI Chemicals, Chennai, and Karnataka Fine Chemicals, Bangalore, India respectively. The textile dye for simulated wastewater [Rhodamine–B (Rh–B)] was bought from Rolex Chemical Industries, India.

Preparation of Low Functional Polyol (Formiated Epoxy Cottonseed Polyol (FECSP)) from CSO

CSO (50 g) was taken in an RB flask to which formic acid (13 ml) was added and mixed for 10 min. The reaction is followed by the dropwise addition of hydrogen peroxide (29 ml) to the mixture and stirred at room temperature. As the incorporation of hydrogen peroxide is finished, the temperature was changed to 65 °C, and the mixture were mixed for about 80 min for the hydroxylation to be completed. Then, the mixture was cooled and left overnight in the open air to remove the excess peroxide if present. Followed by washing the mixture with organic solvent (diethyl ether) by vigorous shaking, the obtained organic layer was rinsed with Na2CO3 (10% wt/vol) and a small amount of NaCl until the organic layer got neutralized. After drying the organic layer with Na2SO4, it was heated at 45 °C to remove the diethyl ether and stored in a tight glass container [20].
Extraction of Nanocellulose and its Surface Modification by Silylation

To the fine powder of milled pineapple leaves (10 g) about 200 ml of NaOH solution (4 wt%) was added and stirred for 2 h at 100 °C for removal of the lignin content. Then the solution was rinsed with water until the complete removal of alkali. The delignified powder was bleached further with the help of NaClO (10 wt%) and acetate buffer of pH 4.5 for 4 h at 90 °C. After complete removal of the lignin present, it was washed several times until neutral pH of 7 was achieved and filtered to obtain cellulose. The extracted cellulose was acid hydrolysed to get nanocellulose. Then, cold sulphuric acid (64 wt%) was treated with cellulose for about 1 h at 45 °C. By adding tenfold water, the hydrolysis was stopped, and then this suspension was centrifuged for 10 min and washed with distilled water until neutral pH was achieved. Then the suspension was ultrasonicated for 10 min, rinsed with acetone, and dried at 50 °C [21]. The silylated nanocellulose preparation from pineapple leaves was carried out as per the literature, reported elsewhere [22, 23]. APTES and water were mixed in a 1:100:5 v/v/w ratio to nanocellulose. The pH of the solution was adjusted to 4 by dropwise addition of CH3COOH, followed by continuous stirring till the pH was stabilized to 4, then nanocellulose was added to the solution. The mixture was magnetically stirred for 2 h at 500–550 rpm and then the obtained slurry was centrifuged. The precipitate was centrifuged again with deionized water followed by ethanol to eliminate the unreacted APTES and dried at 80 °C for 15 min.

Optimization of Adsorption Parameters Using Taguchi Methodology

The dye adsorption of the prepared composites is mainly governed by the parameters at which adsorption occurs such as pH and temperature of the dye solution, amount of silylated nanocellulose in the composites, etc. Levels for the amount of silylated nanocellulose were 1 wt%, 3 wt%, and 5 wt%. Levels for the pH of the dye solutions were 5, 7, and 9, and the levels for temperatures were 30 °C, 40 °C, and 50 °C. Taguchi methodology was adopted to optimize these parameters to achieve maximum adsorption efficiency [25]. 33 = 27 runs are required in a full factorial experiment if the number of factors and levels are 3 each. Taguchi’s factorial approach requires only 9 runs and offers an edge over a full factorial experiment in terms of time and cost. To optimize the parameters, % removal of dye was considered as the performance property and a larger is better category is taken for Signal to noise ratio calculations. Adsorption of dye from the Rhodamine dye solution was carried out for 5 min in all the trials. The maximum adsorption efficiency of the nanocomposites per gram of silylated nanocellulose was calculated by carrying out the adsorption for 8 h by measuring the amount of dye removed after adsorption.

Characterization

Fourier transform infrared spectroscopy (FT-IR, Alpha, 200619) was carried out for CSO, FECSP, nanocellulose, silylated nanocellulose, and flexible polyurethane derived from FECSP and its composite using silylated nanocellulose. Nuclear Magnetic Resonance Spectroscopy (Bruker NMR, AV400 (400 MHz)) was performed for CSO and FECSP. Morphology studies were carried out using Scanning Electron Microscope (SEM, TESCAN-VEGA3 LMU) under an accelerated electron beam with 10 kV for polyurethane composites and 25 kV energy for nanocellulose [20, 26]. To view the individual nanocellulose fibers distinctly, Field Emission Scanning Electron Microscope (FESEM) was used. It was scanned in JEOL JSM-7100F SEM under an accelerated electron beam with 30 kV energy. The adsorption nature of the prepared composites for the Rh-B in the wastewater medium was studied using a UV–Visible Spectrometer (UV-2600 Shimadzu). Acid value, hydroxyl value, and OH functionality of the oil and bio polyol were determined using the reported methods [27–29].

Results and Discussions

FTIR Analysis of Oil and Polyol

In the spectra of CSO, the bands for triglycerides such as carbonyl ester groups at 1743 cm⁻¹, and –CH₂ stretching of
aliphatic hydrocarbons at 2910 and 2853 cm\(^{-1}\) are observed. In the spectra of FECSP, two bands are observed at 3499 cm\(^{-1}\) (broad, –OH str) and 868 cm\(^{-1}\) for epoxy groups. The absence of the band at 3012 cm\(^{-1}\) corresponding to hydrogen of =CH group indicates the conversion of double bonds of cottonseed oil to epoxy groups and hydroxy groups. The peak for hydroxyl groups (3499 cm\(^{-1}\)) is predominant in the spectra of FECSP when compared to the spectra of CSO [30]. The FT-IR spectra of CSO and FECSP are presented in Fig. 1.

**NMR Analysis of Oil and Polyol**

Figure 2a shows NMR spectra of cottonseed oil (CSO). The characteristic peak for the terminal CH\(_3\) in CSO is observed at 0.85 ppm. The peaks corresponding to all acyl chains (–CH\(_2\)–CH\(_2\)–COOH), and allyl methylene protons (–CH\(_2\)–CH=CH–) present in CSO are observed at 1.6 ppm and 2.0 ppm respectively. The peak at 2.7 ppm is multiple proton signals corresponding to methylene protons between two C=C bonds (HC=CH–CH\(_2\)–CH=CH–CH\(_2\)). The peaks corresponding to protons of glycerol α-position (–CH\(_2\)–O–COR) and CH=CH– of methine protons of the glycerol backbone are observed at 4.1–4.2 ppm and 5.2–5.4 ppm respectively [31].

In Fig. 2b, the intensity of the peak at 5.4 ppm has decreased compared to Fig. 2a indicating the transformation of double bonds. The presence of new peaks at 2.9–3.0 ppm accounts for the formation of epoxy groups (–CHOCH–CH\(_2\)–CHOCH) and the formation of peaks at 8.15 ppm and 1.6 ppm indicates the formation of formiate groups (–CHOR–) and the methylene protons adjacent to epoxy group (–CH\(_2\)–CH\(_2\)–CHOCH–). The peak at 2.0 ppm shows the methylene alpha group and acyl group (CH\(_2\)–CH\(_2\)–C=OO–). Thus, the NMR spectra confirm the formation of formiated epoxy cotton seed polyol (FECSP).

**Physico-Chemical Characteristics of Oil and Polyol**

It is very essential to note the difference in the double bonds in the fatty acid chains of the oil as it is fundamental in determining the possible OH groups which will be introduced into the oils after its conversion to polyol [32, 33]. Acid value and a hydroxyl value of the cottonseed oil (CSO), the Formiated of epoxy cottonseed polyol (FECSP) was determined by standard methods as mentioned by Ranote et al. [34] and shown in Table 1. These results confirm the formation of low functional polyol (FECSP) from cottonseed oil which determines the flexibility of the prepared polyurethane nanocellulose nanocomposites.

**SEM Analysis of Nanocellulose**

The morphology of extracted nanocellulose from pineapple leaves is studied using SEM and FESEM in Fig. 3, which depicts the surface features of nanocellulose at different magnification. The structure of cellulose fibers is observed in the lower magnification. At higher magnification, when individual fibers are focused, defibrillation of cellulose fibers in the nanoscale order is observed which confirms the formation of nanocellulose [35].

**FTIR Analysis of Nanocellulose and Silylated Nanocellulose**

The FT-IR spectra of nanocellulose derived from pineapple leaves (NC-PL) and Silylated nanocellulose (SNC) are shown in Fig. 4. The major constituents of pineapple leaves are cellulose, hemicellulose, and lignin [36]. The characteristic IR peak for lignin lies between 1200 and 1300 cm\(^{-1}\) and that of hemicelluloses at 1730–1830 cm\(^{-1}\) is absent in spectra [37] which indicates the complete elimination of lignin and hemicellulose during delignification and bleaching. The major characteristic peak of cellulose at 3336 cm\(^{-1}\) shows the presence of hydroxyl groups. The other important peaks
are 2902 cm$^{-1}$ for C–H stretching of cellulose, 1428 cm$^{-1}$ for bending vibrations of the C–H and C–O groups of the rings in cellulose [38], and 1035 cm$^{-1}$ for stretching frequency of C–H and C=O group of cellulose. In addition to this, an absorption band is detected at 898 cm$^{-1}$ which indicates the existence of $\beta$-glycosidic linkages. As the absorption bands in the spectra represent the characteristic bands of the cellulose, it can be confirmed that the structure of the cellulose is preserved during pre-treatment and acid hydrolysis [39]. After the surface modification of nanocellulose

Fig. 2  $^1$H-NMR pattern of a Cottonseed oil (CSO) and b Formiated epoxy cottonseed polyol (FECSP)
with APTES, the intensity of hydroxyl groups is decreased which is attributed to the conversion of a significant amount of hydroxyl groups on the surface of nanocellulose to silyl groups. A new band was seen at 1548 cm\(^{-1}\) which accounts for the N–H bending vibration of primary amine attributed to the functionalization on the surface of NC [23]. Apart from this, the bands of Si–O–Si and Si–O–C cellulose bridges around 1135 and 1150 cm\(^{-1}\) were found to be overlaid with C–O–C vibration bands of cellulose in the sample spectra which makes it difficult to be visible in the FT-IR spectra [40]. In the previous study, the authors performed an XRD analysis of nanocellulose derived from pineapple leaves and the results confirmed the prepared nanocellulose showing typical cellulose structure I with a small amount of cellulose structure II [22].

**SEM Analysis of Polyurethane Composites**

The obtained porous polyurethane and its cell structures are shown in Fig. 5. With the increase in the percentage of loading of silylated nanocellulose, significant changes in the cell size, and the pore structure are observed. In Fig. 5a the pore sizes are small and appear as a combination of both open and closed cell structures, with a relatively low number of open cells [41]. The average pore size of CSO-PU with (a) 1 wt% of Si-NC was found to be 222 µm, (b) 3 wt% of Si-NC was found to be 403 µm, and (c) 5 wt% of Si-NC was found to be 749 µm which indicates that the incorporation of nanocellulose increases the pore size and impacts the structure of pores during the in-situ polymerization. This is also one of the reasons for the flexible nature of the prepared polyurethane nanocellulose composites. These increased open structures are expected to increase the adsorption capacity of the PU composites [40].

**FTIR Spectra of Neat Polyurethane and Composites Derived from FECSP**

Figure 6 represents the FT-IR spectra of neat polyurethane and polyurethane derived from FECSP with 3 wt% of silylated nanocellulose. In Fig. 6a, the absence of the stretching band of free isocyanate (–N=C=O) at 2500–2270 cm\(^{-1}\) confirms the formation of polyurethane linkages. The important FTIR characteristic features were found to be the presence

| Sample | Acid value (AV) (mg KOH/g) | Hydroxyl value (HV) (mg KOH/g) | Epoxide content | OH functionality | Inference |
|--------|--------------------------|-------------------------------|----------------|-----------------|-----------|
| CSO    | 0.3798                   | 2                             | –              | –               | Low AV and HV values indicate that CSO did not undergo any hydrolytic/free oxidation process and is in accordance with the reported literature [35] |
| FECSP  | 1.702                     | 90                            | 1.345          | 2.04            | AV and HV of FECSP was found to be higher than that of CSO indicating that successful formation of hydroxyl groups onto the CSO [22]. With the help of epoxide content from the NMR data, OH functionality was found to be 2.04 |

![Fig. 3 FESEM images of a individual nanocellulose fiber and b defibrillated nanocellulose at higher magnification](image-url)
1 of bands at 3345 cm$^{-1}$ for $–$NH stretching of the urethane group, 2930–2841 cm$^{-1}$ for symmetric and anti-symmetric stretching vibrations of CH$_2$, 1734 cm$^{-1}$ for stretching vibrations of $–$C=O from urethane groups, 1596 cm$^{-1}$ assigned to $–$C=C stretching in the aromatic ring structure of MDI, 1546 cm$^{-1}$ for $–$NH bending, 1220 cm$^{-1}$ for stretching of $–$C–N and 1085 cm$^{-1}$ for stretching of $–$C–O in the urethane group ($–$NHCOO). The FTIR spectra confirm the formation of polyurethane [42, 43]. In the present study, most of the bands appeared nearly similar in neat PU and PU/Si-NC indicating that the incorporation of silylated nanocellulose does not involve any chemical interaction with polyurethane. From the previous literature, it is known that there could be physical interactions between polyurethane and nanocellulose due to van der Waal’s forces and weak hydrogen bonding [11].

Adsorption Studies

Optimisation of Adsorption Conditions Using Taguchi Methodology

The percentage removal of the Rh-B dye from the effluent was determined using a UV–Visible spectrometer. For the optimization, the initial concentration of dye solution was 10 ppm and about 50 ml of dye solution was taken and 2 g of the prepared adsorbent (polyurethane-silylated nanocellulose composites) in the form of small beads were added to the dye solution for the adsorption. Table 2 depicts the % removal of Rh-B dye by the prepared adsorbent.

Table 2 depicts the S/N ratios of adsorption conditions based on the analysis of % of Rh-B dye removal by the prepared adsorbent and ANOVA results for the adsorption of Rh-B using the synthesized adsorbent and the ANOVA analysis was carried out with a level of confidence 95%. ‘Larger is better category’ is taken for the signal to noise ratio calculations.

The main factor affecting the adsorption characteristics of the composites was found to be the loading of silylated nanocellulose and this factor possesses a rank of 1. As the loading of silylated nanocellulose increases, the S/N ratio also increased and the optimum loading of silylated nanocellulose in these experiments is considered as 5 wt%. This could be due to the availability of more active sites of adsorption for the dye at higher loading. The second factor that was found to affect the amount of adsorption is pH. Maximum adsorption occurred at a pH of 9 and pH has a major role as it influences the surface charge of the adsorbent, molecular structure of the dye, etc. [44]. The delta value for the factor temperature is comparatively smaller which indicates that temperature change has very less influence on the adsorption by synthesized adsorbent as their S/N values did not vary significantly. The optimized conditions for the adsorption of Rh-B dye by the prepared adsorbent are loading of silylated nanocellulose at 5 wt%, pH, and temperature of the solution as 9 and 30 °C respectively.

R$^2$ value associated with these sets of the experiment is 99.30% and this higher value indicates that experimental data is fitting with a general linear model. The percentage contribution of the parameters on the % dye removal conforms with the rank of conditions which were calculated using S/N ratios given in Table 3. As per the percentage contribution values in Table 3, the effect of change in the loading of silylated nanocellulose at 5 wt%, pH, and temperature of the solution as 9 and 30 °C respectively.

Long-Term Adsorption Studies

The optimized conditions for the adsorption of Rh-B dye by the prepared polyurethane composite are 5 wt% of silylated
nanocellulose, the temperature of dye solution as 30 °C, and pH of 9. The maximum adsorption efficiency of the adsorbent was studied. About 2 g of 5 wt% of silylated nanocellulose-filled polyurethane was added to 100 ppm Rh-B solution (50 ml) and the experiment was carried out under optimized conditions. The adsorption was continued for 8 h the maximum adsorption capacity was determined. Fig 7 represents the polyurethane composites before and after the adsorption of Rh-B.

The maximum adsorption capacity of the prepared adsorbent for Rh-B dye was found to be 597 mg/g of silylated nanocellulose which is one of the highest reported values among the nanocellulose-filled nanocomposites [45, 46]. Table 4 represents the recently reported values of adsorption capacity of different adsorbents for Rh-B dye in comparison with the present study [47–51]. The plausible mechanisms for the removal of Rh-B dye using the prepared biobased adsorbent are shown in Fig. 8. In achieving the maximum adsorption by the prepared adsorbent, it was found that the pH of the dye solution played a major role as a higher pH as the Rh-B exists in a zwitterion state. The enhanced adsorption was observed could be attributed to Rh-B, which exists as zwitterion and electrostatic attraction could exist between carboxyl groups of dye and amine groups of silyl groups present on the surface of the composite or covalent bonding [52]. It could be even weak hydrogen bonding between the hydroxyl groups of the silylated nanocellulose to the aromatic ring of the Rh-B molecule [53].

![SEM images of CSO-PU with a 1 wt% of Si-NC b 3 wt% of Si-NC c 5 wt% of Si-NC](image-url)
Conclusion and Future Aspects

In the present study, flexible biobased porous polyurethane–silylated nanocellulose composites were prepared and used to study its adsorption behavior. Low functional polyol (OH functionality of 2) was synthesized from cottonseed oil via one-pot synthesis. FTIR studies indicate the formation of polyol from cottonseed oil, polyurethane formation from the obtained polyol when reacted with MDI, and modification of nanocellulose obtained from pineapple leaves into silylated nanocellulose upon silylation using APTES. NMR studies of polyol were obtained to confirm the OH functionality of the polyol as 2, which is the contributing factor to the formation of flexible polyurethane. SEM indicates the increase in the number of open-cell structures and pore size with the increase in nanocellulose content and FESEM indicates defibrillation of cellulose fibers. Dye adsorption conditions for effective removal of Rh-B such as loading of silylated nanocellulose (wt%), pH, and temperature of the dye solution which was optimized using the Taguchi methodology. The loading of silyated nanocellulose within the polyurethane matrix was found to have a more key influence on the rate of adsorption than the pH and temperature of the dye solution. The optimized parameters are 5 wt% of silyated nanocellulose in the polyurethane matrix, pH of 9, and temperature of 30 °C. The maximum adsorption capacity of the prepared adsorbent was found to be 597 mg/g of nanocellulose which is one of the highest reported values among the nanocellulose-filled adsorbents. Preliminary studies on the desorption of dye from the PU nanocomposites show that the desorption of dye is possible by reducing the pH of the water in which the desorption is done. The reusability of the PU nanocomposite for the repeated adsorption of Rhodamine dye is to be explored in detail which is one of the future aspects of this study.

Table 2 % removal of Rh-B dye using the prepared adsorbent (FECSP derived PU-SiNC composites)

| Expt. trials | Silylated nanocellulose (wt%) | pH | Temperature (°C) | % removal of Rhodamine B after 5 min of adsorption (%) |
|--------------|-------------------------------|----|------------------|-------------------------------------------------------|
| Run 1        | 1                             | 5  | 30               | 63.2                                                  |
| Run 2        | 1                             | 7  | 40               | 65.6                                                  |
| Run 3        | 1                             | 9  | 50               | 69.8                                                  |
| Run 4        | 3                             | 5  | 50               | 62.2                                                  |
| Run 5        | 3                             | 7  | 30               | 71.0                                                  |
| Run 6        | 3                             | 9  | 40               | 81.4                                                  |
| Run 7        | 5                             | 5  | 40               | 82.0                                                  |
| Run 8        | 5                             | 7  | 50               | 91.0                                                  |
| Run 9        | 5                             | 9  | 30               | 95.0                                                  |
Table 3  S/N ratios for % removal of Rh-B dye by prepared adsorbent (FECSP derived PU-SiNC composites) and ANOVA parameters

S/N ratios for % removal of Rh-B dye

| Levels     | Loading of silylated nanocellulose | pH     | Temperature |
|------------|------------------------------------|--------|-------------|
| S/N ratios | Level 1                            | 36.41  | 36.72       | 37.80       |
|            | Level 2                            | 37.04  | 37.51       | 37.26       |
|            | Level 3                            | 39.00  | 38.21       | 37.39       |
|            | Delta                              | 2.59   | 1.49        | 0.55        |
|            | Rank                               | 1      | 2           | 3           |

ANOVA parameters considering % removal of Rh-B dye as performance property

| Source                   | DF | Seq SS   | Adj SS   | Seq MS | F       | P       | % contribution |
|--------------------------|----|----------|----------|--------|---------|---------|----------------|
| Silylated nanocellulose content | 2  | 880.44   | 880.44   | 440.22 | 106.39  | 0.009   | 74.9           |
| pH                       | 2  | 251.05   | 251.05   | 125.52 | 30.34   | 0.032   | 21.3           |
| Temperature              | 2  | 36.41    | 36.41    | 18.20  | 4.40    | 0.185   | 3.1            |
| Error                    | 2  | 8.28     | 8.28     | 4.14   | 0.7     |         | 0.7            |
| Total                    | 8  | 1176.17  |          |        |         |         |                |

S = 2.03415 R2 = 99.30% R2(Adj) = 97.19%

Fig. 7  Before and after photographs of the prepared polyurethane composites after adsorption of Rh-B

Table 4  Recent reported values of adsorption capacity of different adsorbents for Rh-B dye in comparison with the present study

| Adsorbent                                                      | Adsorption capacity (mg/g) | References |
|----------------------------------------------------------------|---------------------------|------------|
| Hierarchical mesoporous cellulose/activated carbon composite  | 33.4                      | [47]       |
| Activated sugar-based carbon                                   | 123.46                    | [48]       |
| Acid modified banana peels                                     | 9.5220                    | [49]       |
| Aleurites moluccana (WAM)                                      | 117                       | [50]       |
| Soy based polyurethane nanocellulose composite                 | 271                       | [51]       |
| Prepared adsorbent                                             | 597                       | This work  |
Possible routes of Adsorption mechanism

![Possible routes of Adsorption mechanism](image)

**Author Contributions** AC conducted all experimental work and prepared original manuscript draft, SV contributed for preparation of nanocellulose, JGV contributed in the synthesis of polyurethanes, JAG supervised the research, initial plan and contributed in writing the manuscript, TNP contributed in the research plan, conceptualization and editing the manuscript. All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

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**Declarations**

**Conflict of interest** The authors declare that they have no conflict of interest.

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