SLJoAS Sri Lankan Journal of Applied Sciences
Research Article
www.sljoas.uwu.ac.lk/index.php/sljoas

Production of low-cost nanocellulose bio adsorbent for water purification

K.G.H. Mekala[a], S.M.P.A. Koliyabandara[a*]
[a] Civil and Environmental Technology Department, Faculty of Technology, University of Sri Jayewardenepura, Homagama 10200, Sri Lanka
[a,*]Civil and Environmental Technology Department, Faculty of Technology, University of Sri Jayewardenepura, Homagama 10200, Sri Lanka

*** Corresponding author email address**: arundathi@sjp.ac.lk

(Received 10th April 2024; accepted 28th August 2024)

Abstract

Chemical contaminants like heavy metals, dyes, and organic oils pose a significant threat to both the environment and human health. Currently, around 2 million tons of waste are discharged into water systems daily, leading to approximately 14,000 deaths due to chemical exposure. Existing methods for reducing these contaminants to safe levels are costly, energy-intensive and not sustainable. A promising solution involves using a combination of biosorption and nanotechnology to remediate these chemical pollutants. This study presents a comprehensive investigation on the production of low-cost nanocellulose bioadsorbents for water purification. Three nanocellulose samples were prepared from rice husk, pineapple leaves, and a composite of both materials. Furthermore 3 nanocellulose membranes were developed using obtained nanocellulose samples. The effectiveness of these samples in removing Remazol Brilliant Blue dye, a common water contaminant, was evaluated by studying the impact of contact time, adsorbent dosage, and pH value. The results demonstrated that the nanocellulose bioadsorbents possessed significant adsorption capacity for Remazol Brilliant Blue dye, highlighting their potential for water purification applications. The nanocellulose bio adsorbent derived from using rice husk shown 57% removal efficiency and the nanocellulose derived from pineapple leaves shown 44% removal efficiency. The 3rd sample made as a composite of both rice husk and pineapple leaves exhibited 61.95% removal efficiency, indicating a synergistic effect between rice husk and pineapple leaves. The adsorption capacity increased with longer contact times and higher adsorbent dosages led to improved dye removal efficiency. The pH of the solution also influenced the adsorption performance. Reusability studies were performed in various runs, and it was confirmed that the nanocellulose bioadsorbents could be effectively recovered using the solvent NaOH and reused up to three runs to adsorb Remazol Brilliant Blue dye in aqueous solutions with a considerable reduction in adsorption efficiency. These findings contribute to the field of water purification by offering a low-cost, eco-friendly solution for the removal of Remazol Brilliant Blue dye and potentially other contaminants. Future research directions may include scaling up the production process and assessing the bioadsorbents' performance with real world industrial wastewater samples. This study demonstrates the promising capabilities of low-cost nanocellulose bioadsorbents derived from rice husk and pineapple leaves, both individually and in combination, as effective and sustainable alternatives for water purification.

Keywords: Nanocellulose, Wastewater, Water purification, Bioadsorbent,

1. Introduction

Water scarcity and pollution pose significant challenges to global well-being, emphasizing the urgent need for sustainable and cost-effective water purification technologies. There is severe pollution of the water and land due to industrialization, population growth, and fast urbanisation [1]. Approximately two million tonnes of waste are discharged into the water system each day [2]. Pollutants including organic chemicals, heavy metals, oil emulsions, dyes, and microbes are mostly found in wastewater. Chemical pollutants pose a major hazard to human health and the environment, including organic oils, dyes, and heavy metals. Every day, exposure to certain toxins in the environment claims the lives of almost 14,000 people. The majority of the existing methods for removing these toxins to safe levels are costly, energy-intensive, and not sustainable [2].

An innovative and environmentally friendly method of eliminating these chemical pollutants is provided by the fusion of nanotechnology and biosorption [2]. The adsorption method is regarded to be the simplest and most practical of the various treatment techniques used for chemical decontamination [3]. Any cellulose with a dimension of 100 nanometers (nm) or less is referred to as nanocellulose [5]. Its intriguing qualities make it a material that can be used in many situations. Because nanocellulose's surface chemistry can be functionalized, it's a great material for adsorbing chemical contaminants [6]. Adsorption capacity of nanocellulose is 40 times greater than its weight [7]. Its reactivity, processability, biodegradability, and reversibility are all quite varied [8]. Although many other approaches have been researched, cellulose nanomaterials

(CN) offer an affordable, environmentally friendly, and renewable way to meet this demand with low carbon footprint [9].

Pineapple leaves and rice husk are two potential sources of nanocellulose that can be used for the production of low-cost and sustainable adsorbents. Pineapple leaves are a byproduct of the pineapple industry and are a rich source of cellulose. The cellulose content in pineapple leaves ranges from 70 to 76%, with hemicellulose and lignin being the other major components. Pineapple leaves can be processed by various methods to obtain nanocellulose, including acid hydrolysis, enzymatic hydrolysis, and mechanical treatments. Acid hydrolysis is a widely used method that involves the treatment of pineapple leaves with strong acids such as sulfuric acid or hydrochloric acid to break down the cellulose fibers into nanocellulose. Rice husk is an agricultural waste generated during rice production and is a potential source of nanocellulose. The cellulose content in rice husk ranges from 30 to 35%, with silica being the other major component. The resulting nanocellulose obtained from pineapple leaves and rice husks can be used as a bio adsorbent for water purification. The high surface area of nanocellulose allows for the effective adsorption of various contaminants from water, including heavy metals, dyes, and organic compounds. The production of nanocellulose bio adsorbent from pineapple leaves and rice husk is a low-cost and environmental freindly solution to the growing problem of water pollution. Overall, the production of low-cost nanocellulose bio adsorbent for water purification using pineapple leaves and rice husk is a promising research topic that can address the growing demand for safe and clean water while also promoting sustainable development

2. Materials and methods

2.1 Materials

The rice husk and pineapple leaves used as raw material were obtained from Southern province, Sri Lanka. Sodium hydroxide was used for alkali treatment. Hydrogen peroxide and Sodium hydroxide were used as bleaching agents while Sulfuric acid was used for acid hydrolysis. Remazol Brilliant Blue dye used for testing purposes. Remazol Brilliant Blue-R (RBBR) is a vinyl sulphone-based formazan dye also known as Reactive blue 19. The discharge of unreacted dye residues directly into water sources can cause environmental pollution as well as serious harm to organisms in aquatic life due to their toxicity, carcinogenicity, and non-biodegradability; the latter allows for their accumulation within bodies of water which can lead to a reduction in the amount of dissolved oxygen. As a result, the effluents containing toxic RBBR dye have to be treated effectively and their concentrations must be reduced to an acceptable level before discharging into the river. It is a challenging task to remove RBBR due to the stability of its complex aromatic molecular structure which often bio-accumulates in the human body and the aquatic ecosystem when the dye is discharged directly with wastewater.

Various treatment methods, such as Flocculation, membrane filtration, electrochemical methods, ozonation, fungal degradation, Fenton process, and photo degradation, are some examples of successful treatment systems that have been used to treat the toxic substances present in the effluent. However, these technologies have several disadvantages, such as high capital and operating cost, the complexity of the treatment processes, the sludge disposable problem, and the need for chemicals, which may in turn pollute the water. Due to these limitations, there is a vital need for a more environmentally friendly and cost-effective method.

2.2 Preparation of nanocellulose bio-adsorbent

2.2.1 Alkali treatment

The alkali treatment was adapted from Nurain et al. [10]. Dust, stones, and other debris were removed from the raw material after it had been collected. 10 g of cleaned raw material was measured. The measured sample was treated with an alkali solution (4 wt% NaOH) at reflux temperature for 2 hours. After that the mixture was filtered to separate the solid residue, which mainly consist of cellulose fibres, from the liquid phase. The solid residue was washed thoroughly with distilled water to remove any residual alkali and dissolved impurities. This treatment was performed thrice. At the end of alkali treatment, the sample was washed with distilled water until pH 7 was reached, filtered and then dried in an incubator at 60°C for 1 hour.
This treatment was done for all three samples of RH, PL & RHPL. When preparing RHPL sample ratio of pineapple leaves and risk husk was taken as 1:1.

2.2.2 Bleaching process

The smooth surface of the untreated fibre becomes rougher after alkali treatment. This could mean that some of the non-cellulosic outer layer, which is made up of impurities like hemicellulose, lignin, pectin, wax, and others, has been partially removed. Natural fibres are

.

Fig. 1. Bleached RHPL composite

known to have a protective layer of wax and pectin on their surface. Lignin functions as a binder in the fibre components by forming a bridge bond with the cellulose ester. The bundles of rice husk fibres split into individual fibres following the bleaching process. For the bleaching process described by Zhixuan et al. [11], Known amount of distilled water was added into a glass container. 8% NaOH was added while stirring. After that 5% Hydrogen peroxide was added to this solution. The solution was stirred gently to ensure uniform mixing. Placed the alkali treated sample in the bleaching solution, ensuring it is completely submerged. The mixture was continuously stirred for 24 hours at 55 °C temperature using a magnetic stirrer. After that suspension was diluted to stop the reaction and allowed to settle for 1 hour until the suspension was layered. The clear top layer was decanted off and then repeatedly washed with distilled water until pH was neutral. At the end obtained solid cellulose was separated using a filter paper. Fig. 1 shows the RHPL composite that obtained at the end of bleaching process.

2.2.3 Acid hydrolysis

After the fibers were bleached and alkali treated, they underwent acid hydrolysis treatment. The amorphous portion of cellulosic microfibrils was predicted to be cut transversely by this, maintaining the straight crystalline domains separate. Eventually, the treatment ought to cause the fibers' size to decrease from the micron to the nanoscale. The acid hydrolysis was adapted from Lurima et al. [12]. Prepared 40% (w/w) sulfuric acid mixture in a glass beaker and added 2g of pretreated sample to this mixture while rapidly mixing. This mixture was continuously stirred using a magnetic stirrer at 50 °C temperature and 250 rpm for 40 minutes. After that suspension was diluted to stop the reaction and allowed to settle for 1 hour until the suspension were layered. The clear top layer was decanted off and then repeatedly washed with distilled water until pH was neutral. Separated the solid nanocellulose material from the nanocellulose suspension using vacuum filtration technique. After that the nanocellulose was dried at 60 °C for 2 hours using an incubator and nanocellulose bio-adsorbent was obtained. Fig. 2 shows the obtained nanocellulose bio adsorbent.

Fig. 1: Composite nanocellulose bio-adsorbent which was prepared using both rice husk and pineapple leaves

2.3 Nanocellulose membrane production

A nanocellulose dispersion was prepared by dispersing 2 g of nanocellulose in 25 ml of distilled water. Filtration apparatus was set up by attaching a vacuum filtration funnel to a filtration flask. A filer paper was placed on the funnel to serve as the support for the nanocellulose membrane. Pored the nanocellulose dispersion onto the filter paper in the filtration funnel. A vacuum was applied to the filtration flask to create a pressure difference, causing the nanocellulose dispersion to pass through the filter paper while retaining the nanocellulose particles on the membrane surface. At the end carefully removed the nanocellulose membrane and dried in the incubator at 40 °C temperature. Fig. 3,4 and 5 shows the prepared nanocellulose membranes.

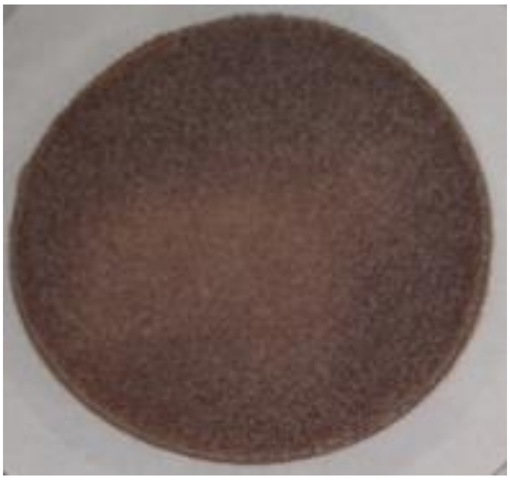

Fig. 3. Rice husk nanocellulose membrane

Fig 4: Pineapple leaves nanocellulose membrane

Fig 5 : RHPL nanocellulose membrane

2.4 Characterization

2.4.1 Zeta potential analysis

Zeta potential analysis provides valuable information about the surface charge of the nanocellulose particles, which is important for understanding their stability and potential interactions in aqueous environments. Prior to analysis, the nanocellulose bio adsorbent samples were prepared by dispersing 0.1g of the material in 25 ml of deionized water. Subsequently, the prepared nanocellulose suspension were carefully loaded into the zeta potential analyzer cell. Surface charge of the nanocellulose particles was measured.

2.5 Batch adsorption studies

Batch adsorption studies were conducted to evaluate the impact of dosage, contact time and pH value on the adsorption performance of the nanocellulose bio adsorbent for the removal of Remazol Brilliant Blue dye from aqueous solutions. These studies provide insights into the optimal operating conditions for maximizing dye adsorption efficiency.

For evaluate the impact of dosage, 3 beakers were prepared, and 20 ml of the dye solution was added in to the each beaker. After that 0.1 g, 0.3 g and 0.5g dosages of nanocellulose bio adsorbents were introduced to each beaker. The initial dye concentration was prepared as 20 mg/L and kept it for 180 minutes. Nanocellulose bio adsorbents were separated from the dye solution using a filter paper and the residual dye concentration was measured in the solution using the spectrophotometric analysis.

For evaluate the impact of contact time, 3 beakers were prepared and 20 ml of the dye solution with 20 mg/l of constant concentration was added in to each beaker. After that 0.1 g of nanocellulose bio adsorbent was added to each of beaker. In time intervals of 60 minutes, 120 minutes and 180 minutes, the residual dye concentration in the solution was measured using the spectrophotometric analysis.

For evaluate the impact of pH value, 3 beakers were prepared and 20 ml of the dye solution with 20 mg/l of constant concentration was added in to each beaker. After that 0.1 g of nanocellulose bio adsorbent was added to this each beaker. Adjusted the pH of the dye solutions 4-10 pH by using 0.1 M Acetic acid and 0.1 M Sodium hydroxide. After 180 minutes, nanocellulose bio adsorbents were separated from the dye solution using a filter paper and the residual dye concentration was measured in the solution using the spectrophotometric analysis.

At the end of this batch experiments adsorption capacities and removal efficiencies of nanocellulose bio adsorbents were calculated. Assessed the impact of dosage, contact time, and pH on the removal efficiency and determined the optimal conditions for maximum dye removal.

The quantity of the Remazol Brilliant Blue dye adsorbed on nanocellulose adsorbents at equilibrium (qe) was estimated by the Equation (1).

$$\textit{Adsorption capacity} = \frac{(Co - Ct)\,V}{M} \qquad \text{Equation 1}$$

The removal efficiency of Remazol Brilliant Blue dye calculated by the Equation (2).

$$\textit{Removal efficiency} = \frac{(Co - Ct)\times 100\%}{Co} \qquad \text{Equation 2}$$

Where Co is the initial concentration of RBBR in the aqueous solution (mg/L), Ct is the dye concentration in the solution at a time ‘t’ (mg/L), V is the total volume of the dye solution (L), and W denotes the weight of dry nanocellulose bio-adsorbent (g). To ensure that the results are reproducible, all the experiments were repeated in triplicate, and the average values obtained from these experiments are reported in results and discussion.

2.6 Reusability study

An adsorption study was conducted to determine the efficiency of the adsorbent in removing dye from the solution. After completing the adsorption study, nanocellulose bio adsorbents were rinsed with distilled water. After that bio adsorbents were separated using a filter paper and dried it at 60 °C for one hour using the incubator. Then the adsorbents were regenerated by eluting the dye from the adsorbent using distilled water, 0.1 M NaOH and 0.1 M HCl. The adsorption and desorption steps were repeated for 3 cycles to test the reusability of adsorbents. The efficiency of the adsorbent after each cycle were monitored by measuring the amount of dye adsorbed by the adsorbent and comparing it with the initial adsorption capacity.

3. Results and discussion

3.1 Characterization

3.1.1 Zeta potential analysis

The zeta potential analysis is an essential technique for evaluating the surface charge and stability of nanoparticles or bio adsorbents. Table 1 shows the results obtained from zeta potential analysis.which is not covered by the author contribution or funding sections. This may include administrative and technical support, or donations in kind (e.g., materials used for experiments).

Table 1: Results obtained from zeta potential analysis

Nanocellulose bio-adsorbent sample	Mobility	Zeta potential (mV)
Rice husk nanocellulose bio-adsorbent	-0.86	-11.01
Pineapple leaves nanocellulose bio-adsorbent	-0.11	-1.43
RHPL nanocellulose bio-adsorbent	-2.98	-37.85

According to the above results the zeta potential of rice husk nanocellulose was determined to be -11.01 mV, indicating a significantly negative surface charge. The zeta potential of the pineapple leaves nanocellulose bio adsorbent was determined to be -1.43 mV. The composite nanocellulose bio-adsorbent, derived from rice husk and pineapple leaves, was analyzed, and the zeta potential was determined to be -37.85 mV.

This can be attributed to the presence of ionizable functional groups, such as carboxyl or hydroxyl groups, on the surface of the nanocelluse. The substantial negative zeta potential suggests a high density of negative charges on the nanocellulose surface.

The RH+PL composite shows large zeta potential values compared to their components even though the cellulose is the main component from both RH and PL. The observed large zeta potential values in the RH+PL composite can be attributed to the interactions between the nanocelluloses from rice husk (RH) and palm leaves (PL). The zeta potential is indicative of the surface charge and stability of the particles in suspension, and a high zeta potential often suggests better stability due to strong electrostatic repulsion between particles. Although cellulose is a common component in both RH and PL, the structural characteristics of nanocellulose from these sources can differ. The specific surface area, morphology, and surface charge density of the nanocelluloses can significantly influence the zeta potential. The combination of nanocelluloses from RH and PL may lead to synergistic effects that alter the overall surface charge. This could be due to the differing surface functional groups or the presence of additional components in RH or PL that interact with the nanocellulose. The different surface chemical properties of RH and PL nanocelluloses can result in unique interactions when combined. For instance, if the RH nanocellulose has a higher density of surface hydroxyl groups compared to the PL nanocellulose, this can lead to a significant alteration in the overall zeta potential when they are combined.

The magnitude of the zeta potential value of rice husk and RHPL composite nanocellulose bio adsorbent indicates a robust surface charge, resulting in a significant electrostatic repulsion between nanocellulose bio-adsorbent particles. This repulsion helps maintain the colloidal stability of the nanocellulose suspension, minimizing the chances of particle aggregation or flocculation. The magnitude of the zeta potential value of pineapple leaves nanocellulose bio adsorbent is relatively low, indicating a weak surface charge. It is important to note that zeta potential values closer to zero suggest a decreased electrostatic repulsion between particles, which could lead to higher chances of aggregation or flocculation.

The negative zeta potential suggests that nanocellulose adsorbents can exist as stable individual particles or small clusters in solution, which is advantageous for its applications in various fields. The negative zeta potential of the nanocellulose also has potential implications for its interaction with positively charged species. This property makes the nanocellulose potentially useful as an adsorbent material for removing cationic contaminants, such as heavy metal ions or dyes, from aqueous solutions.

3.2 Batch adsorption studies

3.2.1 Effect of initial pH value

Table 4 in the appendices shows the results obtained from adsorption study on effect of pH value. Fig. 6 demonstrates that the RBB dye removal efficiency of rice husk nanocellulose bio adsorbent increased from 39.44% to 56.05% over pH range between 4 to 10. The reason for this is dyes are negatively charged at lower pH values (acidic conditions). Usually organic dye molecules become neutral or positively charged when they are in an acidic medium due to neutralization of negative charges or protonation. RBB dye contains specific functional groups that may not follow the general trend observed for other organic dyes. Unlike some dyes that lose their negative charge due to protonation in acidic environments, RBB dye's structure might retain its anionic charge due to the nature of its functional groups. For instance, sulfonic acid groups, which are common in RBB dyes, can remain negatively charged even in acidic conditions due to their strong acid dissociation constants. In the case of RBB dye, the protonation of the dye's functional groups might not lead to a neutral or positively charged state because these groups are less susceptible to protonation in acidic media compared to other dyes. The specific pKa values of the functional groups in RBB dye influence their behavior. The dye may remain negatively charged if the pH is not sufficiently low to protonate these groups. Other factors such as the dye concentration, the presence of salts or buffering agents, and the exact pH of the medium can influence the charge state of the dye. Our study took these factors into account, which may explain the observed behaviour of RBB dye.

When the pH is increased, the negative charge on the dye molecules decreases, reducing the repulsive forces between the dye and the adsorbent surface. This allows for stronger electrostatic interactions between the dye and the adsorbent, leading to increased adsorption and removal efficiency. Fig. 7 shows that highest removal efficiency of pineapple leaves nanocellulose was showed at pH equal to 4. It has 43.45% removal efficiency. Fig. 8 demonstrates that the removal efficiency of RBB dye decreased from 60.32% to 26.35% by RHPL composite nanocellulose bio adsorbent over a pH range between 4 and 10. At pH 4, between the anionic dye molecules and the protonated binding sites of the adsorbent, there is a significant electrostatic interaction. The presence of excess OH- ions on the adsorbent surface will deprotonate the active sites as the pH of the solution rises, increasing the number of negatively charged sites and possibly increasing the electrostatic repulsion between the dye molecules and the adsorbent surface. Additionally, competition between the excess hydroxyl ions and the negatively charged dye ions for the adsorption binding sites are the reason for the lower RBB de-colorization efficiency at basic pH [13].

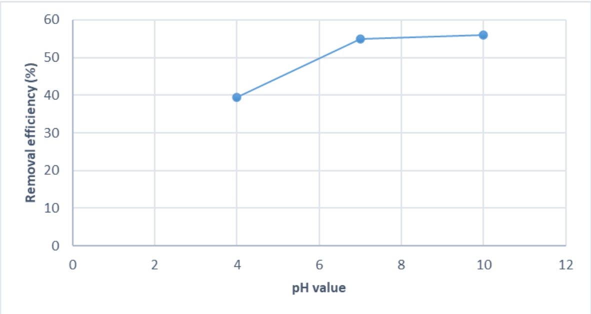

Fig. 6: Impact of pH on the removal efficiency of rice husk nanocellulose bio adsorbent (adsorbent dosage: 0.1 g; contact time: 3h; dye volume: 20 ml; initial dye concentration: 20 ppm)

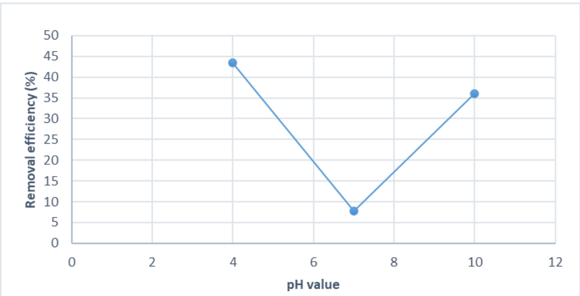

Fig. 7: Impact of pH on the removal efficiency of pineapple leaves nanocellulose bio adsorbent (adsorbent dosage: 0.1 g; contact time: 3h; dye volume: 20 ml; initial dye concentration: 20 ppm)

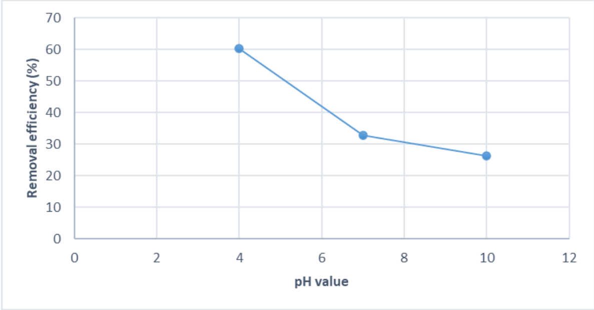

Fig. 8: Impact of pH on the removal efficiency of RHPL nanocellulose bio adsorbent (adsorbent dosage: 0.1 g; contact time: 3h; dye volume: 20 ml; initial dye concentration: 20 ppm)

3.2.2 Effect of adsorbent dosage

Accounting for a cost-effective system, it is important to evaluate the optimum dosage of adsorbent required to efficiently remove the color from wastewater. The effect of nanocellulose bio adsorbent dosage on color removal of RBB dye was studied by varying the dosage from 0.1 to 0.5 g and obtained results are showed in table 5 in the appendices.

Fig. 9 shows that the decolorization efficiency of rice husk nanocellulose bio adsorbent is increased from 56.05% to 57.00%, but the dye concentration at equilibrium (Ce) decreased from 8.79 to 8.60 mg/L with the increase in the adsorbent dosage from 0.1 to 0.5 g. Fig. 10 shows that the decolorization efficiency of pineapple leaves nanocellulose bio adsorbent is increased from 43.45% to 44%, but the dye concentration at equilibrium (Ce) decreased from 11.31 to 11.2 mg/L with the increase in the adsorbent dosage from 0.1 to 0.5 g. Fig. 11 shows that the decolorization efficiency of RHPL composite nanocellulose bio adsorbent is increased from 60.3% to 61.95%, but the dye concentration at equilibrium (Ce) decreased from 7.93 to 7.60 mg/L with the increase in the adsorbent dosage from 0.1 to 0.5 g. This may be due to increased adsorbent surface area and the availability of more binding sites for the adsorption of RBB dye molecules.

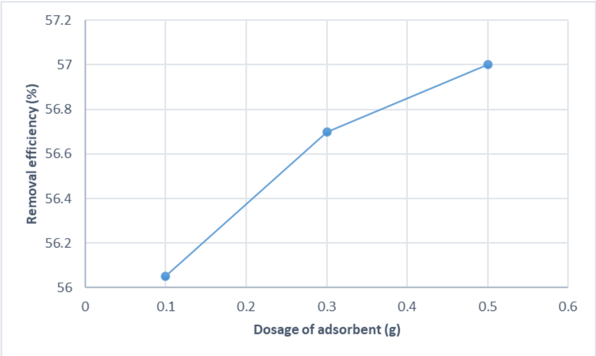

Fig. 9: Impact of adsorbent dosage on the removal efficiency of Rice husk nanocellulose bio adsorbent (contact time: 3h; dye volume: 20 ml; initial dye concentration: 20 ppm)

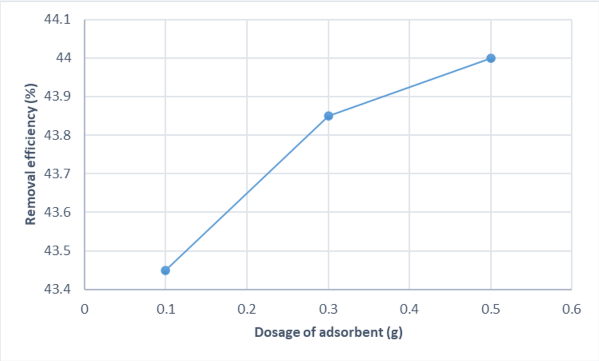

Fig. 10: Impact of adsorbent dosage on the removal efficiency of pineapple leaves nanocellulose bio adsorbent (contact time: 3h; dye volume: 20 ml; initial dye concentration: 20 ppm)

On the other hand, it was found that the equilibrium adsorption capacity, qe, of rice husk nanocellulose bio adsorbent decreased from 2.24 mg/g to 0.45 mg/g with the increase in the adsorbent dosage. The equilibrium adsorption capacity, qe, of pineapple leaves nanocellulose bio adsorbent decreased from 1.74 mg/g to 0.35 mg/g with the increase in the adsorbent dosage.

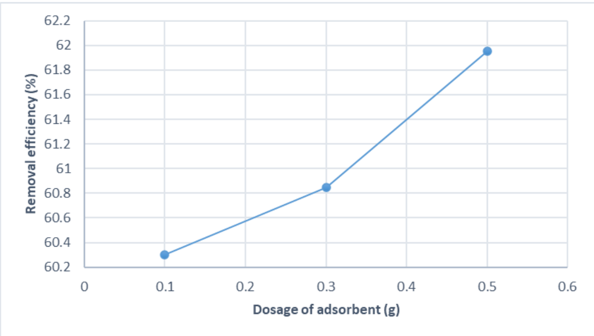

Fig. 11: Impact of adsorbent dosage on the removal efficiency of RHPL composite nanocellulose bio adsorbent (contact time: 3h; dye volume: 20 ml; initial dye concentration: 20 ppm)

The equilibrium adsorption capacity, qe, composite nanocellulose bio adsorbent of RHPL decreased from 2.41 mg/g to 0.49 mg/g with the increase in the adsorbent dosage. The primary cause of this is the decline in the flux between the dye concentration at the adsorbent surface and that in the solution. As a result, when the dosage of the adsorbent increases, the competition for the available active sites for dye adsorption decreases. This suggests that there may be a large number of particles of adsorbent in solution as the number of particles increases. This could lead to the overlapping of adsorbed species or adsorption binding sites, causing the particles to aggregate and reducing the number of adsorption active sites per unit mass of the adsorbent [14].

3.2.3 Effect of contact time

The effect of contact time on colour removal of RBB dye from using nanocellulose bio adsorbent was studied by varying the contact time from 1 to 3 hours and obtained results are showed in table 6 in the appendices. The impact of time variation for removal of Remazol Brilliant Blue dye (RBB) during batch adsorption is shown in Fig. 12, 13 and 14. Similar to the beginning, there is a greater concentration of bulk solution, maximum driving forces, and maximum rates. However, as time goes on, the majority of the active sites become bound to dye molecules, reducing the amount of active sites that are free. It might result in fewer collisions that are successful, which would lower the rate of adsorption. The adsorption rate is high upon introduction of the adsorbent, but it gradually decreases over time. More dye molecules can come into contact with the adsorbent when adsorption is given more time, which increases removal efficiency.

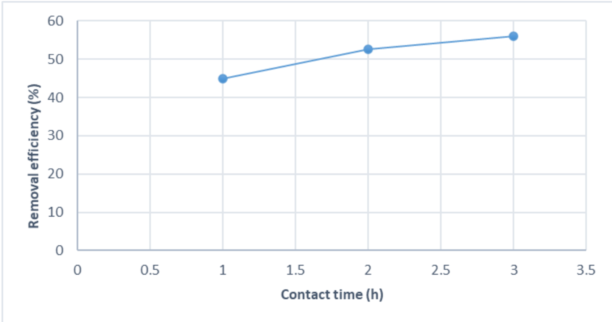

Fig. 12: Impact of contact time on the removal efficiency of Rice husk nanocellulose bio adsorbent (adsorbent dosage: 0.1 g; dye volume: 20 ml; initial dye concentration: 20 ppm)

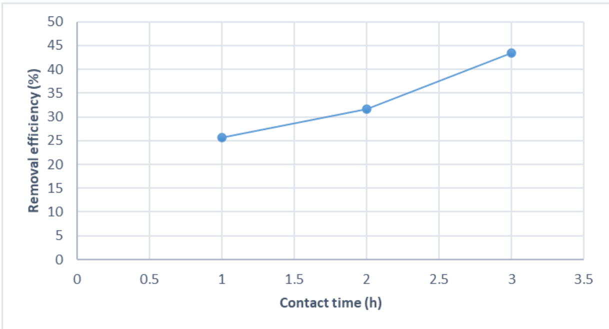

Fig. 13: Impact of contact time on the removal efficiency of pineapple leaves nanocellulose bio adsorbent (adsorbent dosage: 0.1 g; dye volume: 20 ml; initial dye concentration: 20 ppm)

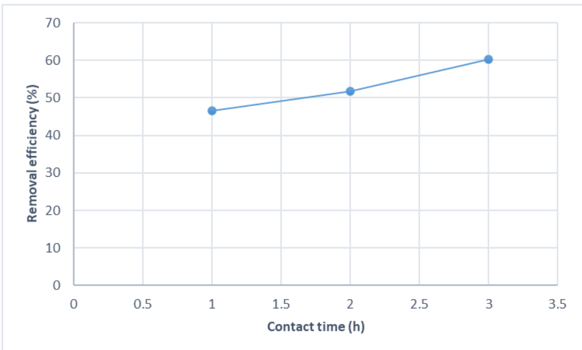

Fig. 14: Impact of contact time on the removal efficiency of RHPL composite nanocellulose bio adsorbent (adsorbent dosage: 0.1 g; dye volume: 20 ml; initial dye concentration: 20 ppm)

Fig. 12 shows that removal efficiency of rice husk nanocellulose bio adsorbent increased from 45% to 56.05% by increasing the contact time to 3 hours. Fig. 13 shows that removal efficiency of pineapple leaves nanocellulose bio adsorbent increased from 25.60% to 43.45% by increasing the contact time to 3 hours. Fig. 14 shows that removal efficiency of RHPL composite nanocellulose bio adsorbent increased from 46.65% to 60.32% by increasing the contact time to 3 hours.

3.3 Reusability study

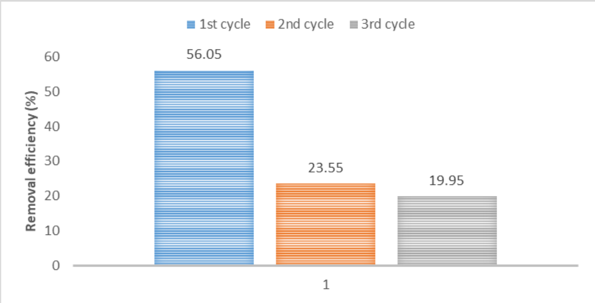

Fig. 15: Reusability of RH nanocellulose bio adsorbent for the adsorption of RBB dye in various runs (temperature: 293 K; contact time: 3 h; dye concentration: 20 ppm; dye volume: 20 ml; adsorbent dosage: 0.1 g)

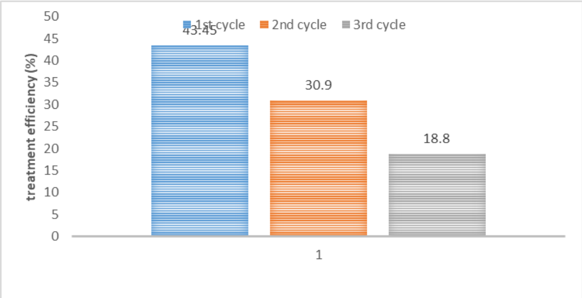

Fig. 16: Reusability of PL nanocellulose bio adsorbent for the adsorption of RBB dye in various runs (temperature: 293 K; contact time: 3 h; dye concentration: 20 ppm; dye volume: 20 ml; adsorbent dosage: 0.1 g)

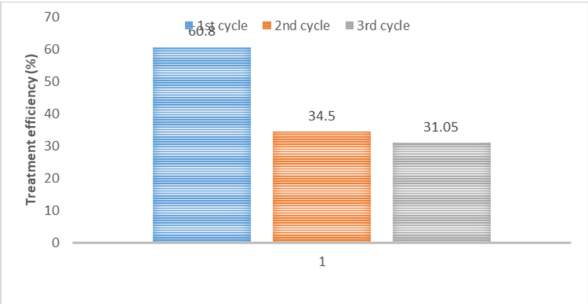

Fig. 17: Reusability of RH + PL composite nanocellulose bio adsorbent for the adsorption of RBB dye in various runs (temperature: 293 K; contact time: 3 h; dye concentration: 20 ppm; dye volume: 20 ml; adsorbent dosage: 0.1 g)

The reusability of nanocellulose bio adsorbents derived from rice husk, pineapple leaves, and their composite was assessed through multiple adsorption cycles, revealing trends that align with existing literature on cellulose-based adsorbents.

For rice husk nanocellulose, removal efficiency decreased from 56.05% in the first cycle to 23.55% in the second cycle and 19.95% in the third cycle (Fig. 15). The adsorption capacity similarly dropped from 2.24 mg/g to 0.94 mg/g and 0.79 mg/g. This reduction in performance is consistent with the findings of Nguyen et al. (2021), who reported a decline in the adsorption capacity of rice husk-derived bioadsorbents due to fouling and the saturation of active sites [15]. These effects are common in studies evaluating the reusability of plant-based adsorbents [16].

Pineapple leaves nanocellulose showed a decrease in removal efficiency from 43.45% in the first cycle to 30.90% in the second cycle, and further to 18.80% in the third cycle (Fig. 16). The adsorption capacity also decreased from 1.74 mg/g to 1.23 mg/g and 0.73 mg/g. This trend mirrors the observations of Rodriguez et al. (2020), who documented similar reductions in efficiency and capacity for pineapple leaf-derived cellulose due to residual pollutant accumulation and surface fouling [17].

The composite bioadsorbent demonstrated removal efficiencies of 60.80% in the first cycle, decreasing to 34.50% in the second cycle and 31.05% in the third cycle (Fig. 17). The adsorption capacity also fell from 2.41 mg/g to 1.38 mg/g and 1.24 mg/g. Although the composite bioadsorbent performed better than the individual materials, it still exhibited a decline in performance with repeated use. But the reduction of removal efficiencies and reduction of adsorption capacities between 1st, 2nd, and 3rd cycles are mostly similar for Rice husk and composite material. The improvement in performance of the composite bio-absorbent can be attributed to several factors beyond just the initial cycle performance. The composite bio-absorbent may exhibit enhanced overall performance due to synergistic effects between the rice husk and the additional component(s) present in the composite. The composite might provide better structural integrity and resistance to degradation over multiple cycles, which might not be fully captured in the immediate cycle performance. The combination of materials could enhance the available surface area or improve accessibility to active sites, which might contribute to better initial adsorption or more efficient removal even if the reusability trends are similar.

Overall, while the nanocellulose bioadsorbents derived from rice husk, pineapple leaves, and their composite show potential for pollutant removal, the progressive decline in effectiveness underscores the need for further optimization of regeneration and desorption techniques. Future research should focus on improving these aspects and evaluating the bioadsorbents in real-world water samples to better understand their practical applications.

3.4 Cost analysis

In this study, 0.1 g of nanocellulose bio adsorbent was used to treat 20 ml of dye mixed water. Therefore 5 g of nanocellulose bio adsorbent need to treat 1 L of water. Table shows the cost analysis for produce 5 g of nanocellulose bio adsorbent which need for treat 1 L of water.

Table 2: Cost analysis for prepared 5 g of nanocellulose bio adsorbent

Factor	Quantity	Cost (Rs.)
Raw Material Costs		
• Rice husk		-
• Pineapple leaves		-
Processing Costs		
• Chemicals		
Sodium hydroxide	2 g	154.20
Hydrogen peroxide (6%)	60 ml	120.00
Sulfuric acid	50 ml	523.00
• Energy		
Magnetic stirrer	1.55 KWh	23.70
Incubator	0.49 KWh	7.49
Weighing scale	0.01 KWh	0.15
• Water	250 ml	-
• Waste disposal		-
Equipment Expenses		-
Labor costs		-
Purification and Characterization Costs		-
Overhead Costs		-
Market and economic factors		-
Total	**Rs. 828.54**	

*The costs associated with equipment usage, labor, purification and characterization, overhead costs and, price associated with market and economic factors have been neglected.

Table 3: Cost analysis for treat 1 liter of water using coagulation and flocculation

	Amount	Unit price (Rs)	Cost (Rs)
Aluminum sulfate (alum)	100 g	2580/kg	258.00
Polyethylene oxides	200 ml	2800/L	560.00
Power	1.4 KWh	32.65/unit	45.71
Total			**Rs. 863.71**

Coagulation and flocculation is the commonly used method in the treatment of textile wastewater, especially for dye removal. Common coagulants used in textile wastewater treatment include Aluminum sulfate (alum), Ferric chloride, and Polyaluminum chloride. The coagulation process helps in reducing the color of wastewater by precipitating the dye molecules.

After coagulation, flocculants are added to promote the formation of larger and denser flocs. Flocculants are long-chain polymers that provide binding forces to the destabilized particles, allowing them to come closer and form larger aggregates. The commonly used flocculants in textile wastewater treatment are Polyacrylamides and Polyethylene oxides.

Usually, for treat 1 L of water 200 g of Aluminum sulfate (alum) and 300 ml of Polyethylene oxides need to be added. And also this coagulation and flocculation need minimum 200 rpm rapid mixing for treatment process [18]. Therefore it needs electricity and it increases the cost furthermore. Table 3 shows cost analysis for treat 1 L of water, using coagulants and flocculants. According to this analysis the cost of Rs 828.54 to treat 1 L of water using our nanocellulose bio adsorbent appears to be relatively lower compared to the commonly used coagulants and flocculants, which costs Rs 863.71. This suggests that our nanocellulose bio adsorbent may provide a cost advantage over the conventional coagulation and flocculation. If we consider large-scale water treatment operations or continuous water treatment needs, even a slight difference in the cost per L can lead to substantial savings.

Nanocellulose bio adsorbents are typically derived from renewable sources, such and are biodegradable. They offer a more sustainable alternative to conventional coagulants and flocculants, which are often derived from non-renewable resources or involve chemical synthesis. Using bio-based materials reduces the environmental impact associated with water treatment processes. Traditional coagulants often require the addition of chemicals, such as aluminum or iron salts, to promote flocculation and coagulation of impurities in water. In contrast, nanocellulose bio adsorbents can minimize the need for chemical additives, reducing the chemical usage and associated costs in the water treatment process. This can lead to a more environmentally friendly and sustainable approach to water treatment. The use of nanocellulose bio adsorbents in water treatment processes can result in reduced sludge generation compared to conventional coagulants and flocculants. The adsorption properties of nanocellulose bio adsorbents enable the formation of compact and denser flocs, leading to lower sludge production. This can simplify the waste management process and reduce disposal costs. Nanocellulose bio adsorbents can be regenerated and reused multiple times, depending on the nature of the adsorbent and the contaminants being targeted. The ability to regenerate and reuse the bio adsorbents further enhances their cost-effectiveness and sustainability in water treatment applications.

4. Conclusions

This study investigated the production and application of low-cost nanocellulose bioadsorbents derived from rice husk and pineapple leaves, both individually and in combination. Three distinct nanocellulose samples were prepared: one from rice husk, one from pineapple leaves, and a composite of both materials. Additionally, nanocellulose membranes were synthesized and evaluated for their adsorptive properties.

The effectiveness of these bioadsorbents was assessed using Remazol Brilliant Blue dye, with investigations into the effects of contact time, adsorbent dosage, and pH value on adsorption capacity. Results indicated that adsorption capacity increased with prolonged contact time and higher adsorbent dosage. pH influenced adsorption efficiency variably among the bioadsorbents: rice husk-derived nanocellulose showed enhanced removal efficiency with increasing pH from 4 to 10, whereas pineapple leaf-derived nanocellulose exhibited optimal performance at pH 4. The composite sample demonstrated decreased removal efficiency with increasing pH.

Reusability studies revealed that the bioadsorbents could be effectively regenerated using NaOH and reused up to three cycles, though with a notable reduction in adsorption efficiency. The composite nanocellulose bioadsorbent generally exhibited superior adsorption performance compared to the individual materials.

Future work should focus on evaluating the nanocellulose membranes for water permeability, rejection efficiency, and adsorption capacity across a range of contaminants. Additionally, testing the bioadsorbents in real water samples containing complex contaminant mixtures, such as wastewater or industrial effluents, will provide a more realistic assessment of their practical applications. This research contributes to advancing water purification technologies by presenting a cost-effective, environmentally friendly solution for the removal of contaminants such as Remazol Brilliant Blue.

5. Acknowledgement

The authors wish to acknowledge the Faculty of Technology, University of Sri Jayewardenepura for facilitating the research project.

References

[1] Zhang, Haijun, Yu Gao, Peipei Qian, Zhangji Dong, Wenjin Hao, Dong Liu, and Xuchu Duan. "Expression analysis of Rab11 during zebrafish embryonic development." BMC Developmental Biology 19 (2019): 1-8.

[2] Mohd Basri, Mohd Salahuddin, Nor Nadiah Abdul Karim Shah, Alifdalino Sulaiman, Intan Syafinaz Mohamed Amin Tawakkal, Mohd Zuhair Mohd Nor, Siti Hajar Ariffin, Nur Hamizah Abdul Ghani, and Faiqa Shazeaa Mohd Salleh. "Progress in the valorization of fruit and vegetable wastes: Active packaging, biocomposites, by-products, and innovative technologies used for bioactive compound extraction." Polymers 13, no. 20 (2021): 3503.

[3] Rashed, Mohamed Nageeb. "Adsorption technique for the removal of organic pollutants from water and wastewater." Organic pollutants-monitoring, risk and treatment 7 (2013): 167-194.

[4] Bolisetty, Sreenath, Mohammad Peydayesh, and Raffaele Mezzenga. "Sustainable technologies for water purification from heavy metals: review and analysis." Chemical Society Reviews 48, no. 2 (2019): 463-487.

[5] Yasim-Anuar, Tengku Arisyah Tengku, Hidayah Ariffin, Mohd Nor Faiz Norrrahim, Mohd Ali Hassan, Takayuki Tsukegi, and Haruo Nishida. "Sustainable one-pot process for the production of cellulose nanofiber and polyethylene/cellulose nanofiber composites." Journal of cleaner production 207 (2019): 590-599.

[6] Vandamme, Dries, Samuel Eyley, Guy Van den Mooter, Koenraad Muylaert, and Wim Thielemans. "Highly charged cellulose-based nanocrystals as flocculants for

harvesting Chlorella vulgaris." Bioresource technology 194 (2015): 270-275.

[7] Chen, Yu-Jin, Gang Xiao, Tie-Shi Wang, Qiu-Yun Ouyang, Li-Hong Qi, Yang Ma, Peng Gao, Chun-Ling Zhu, Mao-Sheng Cao, and Hai-Bo Jin. "Porous Fe3O4/carbon core/shell nanorods: synthesis and electromagnetic properties." The Journal of Physical Chemistry C 115, no. 28 (2011): 13603-13608.

[8] Mahfoudhi, Norhene, and Sami Boufi. "Nanocellulose as a novel nanostructured adsorbent for environmental remediation: a review." Cellulose 24 (2017): 1171-1197.

[9] Chenampulli, Sangeetha, G. Unnikrishnan, A. Sujith, Sabu Thomas, and Tania Francis. "Cellulose nano-particles from Pandanus: viscometric and crystallographic studies." Cellulose 20 (2013): 429-438.

[10] Nurain Johar, Ishak Ahmad and Alain Dufresne. "Extraction, preparation and characterization of cellulose fibres and nanocrystals from rice husk." Industrial Crops and Products 37(2012) 93-99.

[11] Zhixuan Wang, Jiaying Li, John P. Barford, Klaus Hellgradt and Gordon McKay. "A comparison of chemical treatment metods for the preparation of rice husk cellulosic fibers." International Journal of Environmental & Agriculture Research (IJOEAR) Vol-2, Issue-1(2016) 2454-1850.

[12] Lurima Uane Soares Faria, Bruna Jeanne Soares Pacheco, Gislaine Couto Oliveira and Jaqueline Lacerda Silva. "Production of cellulose nanocrystals from pineapple

[13] C. Debamita, Nakul Rampal, J.P. Gautham and P. Vairavel. "Process optimization, isotherm, kinetics, and thermodynamic studies for removal of Remazol Brilliant Blue-R dye from contaminated water using adsorption on guava leaf powder." Desalination and Water Treatment 185 (2020) 318–343.

[14] P. Vairavela, V. Ramachandra Murtyb and S. Nethajia. "Removal of Congo red dye from aqueous solutions by adsorption onto a dual adsorbent (Neurospora crassa dead biomass and wheat bran): optimization, isotherm, and kinetics studies". Desalination and Water Treatment 68 (2017) 274–292.

[15] Nguyen, T. T. "Reusability and regeneration of rice husk-based bioadsorbents for wastewater treatment." Journal of Environmental Management, 290 (2021), 112527.

[16] Ahmad, M. "Cellulose-based bioadsorbents: A review on their regeneration and performance." Journal of Hazardous Materials, 366 (2019), 389-406.

[17] Rodriguez. "Pineapple leaf-derived nanocellulose for dye removal: Performance and regeneration studies." Carbohydrate Polymers, 234 (2020), 115853.

[18] Meena Solanki, S. Suresh, Shakthi Nath and Kanchan. "Treatment of real textile wastewater using coagulation technology." International Journal of ChemTech Research, 5(2013), 610-615.