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Research Article

Removal of heavy metal ions from water using nanocellulose-based membranes derived from macroalgae *Chara corallina*

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Abstract

Chara corallina is a freshwater macroalgae found in aquatic-terrestrial boundary environments. Their cellulose fibers have a crystallinity and biosynthesis similar to those of terrestrial plants. The algal nanocellulose (NC) was prepared through a series of chemical treatments, including alkaline, bleaching, grinding, and acid hydrolysis. The X-ray diffraction (XRD) crystallinity index of nanocellulose was 85.64%. The cellulose nanocrystals are seen in the form of nanorods, and the specific surface area of the sample of NC found was 5.823 m^2g^{-1}. The study aimed to test the effectiveness of a nanocellulose composite membrane in removing heavy metal ions, specifically cadmium (Cd), nickel (Ni), and lead (Pb) ions, from an aqueous solution. A vacuum filtration unit was used for the experiment, where up to five filter layers of composite membranes were examined for their ability to remove heavy metal ions. The results showed that the highest removal rates of Cd^{2+}, Ni^{2+}, and Pb^{2+} ions were 98.20%, 95.15%, and 93.80%, respectively, when using five layers of membranes of NC with the adsorbent dose set at 20 ppm. Cellulose and its derivatives are essential in sustainable technology for wastewater treatment, as they demonstrate exceptional performance in removing various types of pollutants, including heavy metals, dyes, and other pollutants. Cellulose is preferred due to its low cost, biodegradability, eco-friendliness, and simple surface modification.

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Introduction

Air, water, and soil contamination by heavy metals is one of the world's most pressing environmental crises (Yousif et al., 2024). Heavy metal contamination is a major problem since these metals are poisonous, bioaccumulate easily, are abundant, and stay in the environment for a long time (AL-Heety et al., 2021a). Heavy metals enter soil and water via natural processes like weathering and rock erosion, in addition to anthropogenic sources, including waste disposal, industrial and mining operations, the application of fertilizers and pesticides, and urban and industrial activities (Rosariastuti et al., 2018; Badariah et al., 2023). Heavy metal pollution refers to the presence of any metallic chemical species in high densities that can be toxic in very low quantities (AL-Heety et al., 2021b). Wastewater from industries such as tanneries, mining operations, and metal plating contains heavy metals as pollutants, which can be lethal (Le et al., 2023). The accumulation and distribution of metals in sediment and river water have increased to an alarming degree; this has detrimental effects on biota, which may infiltrate the food chain and pose a health risk to humans (Badariah et al., 2023).

In order to process these wastes in a manner that is practical and affordable for the general public, technical studies on their management are essential

(Nurcholis et al., 2020). Over the past few decades, strict rules have been implemented regarding environmental protection and management. Various methods have been adopted to decontaminate industrial effluents, such as coagulation, chemical precipitation, adsorption, biosorption, ion exchange, membrane filtration, and electrochemical treatment (López et al., 2022). However, these technologies are often ineffective due to high operating and maintenance costs, as well as the requirement of highly skilled personnel to handle the management of the sludge generated during the process (Koul et al., 2022). Therefore, a sustainable technology with a less environmentally degrading approach is necessary. Nanotechnology has been used to remove pollutants from wastewater with high efficiency. Different nanoforms, such as nanomembranes, nanoadsorbents, nanopowders, and nanoparticles, are used to detect and remove undesired chemical and biological substances from wastewater (Goswami et al., 2021).

In this work, a nanomembrane prepared from cellulose nanocrystals was used to remove some heavy metal ions. Researchers have discovered that heavy metals can be removed from wastewater using membranes based on nanocellulose (Wang et al., 2013; Sehaqui et al., 2014; Goswami et al., 2021). Cellulose is a naturally occurring biopolymer that is found widely in nature. It is known for its biodegradable, biocompatible, and toxin-free properties, as well as its ability to regenerate (Carolin et al., 2023). Due to their large surface area, chemical accessibility, and ease of functional modification, cellulose nanomaterials have gained significant interest in the field of wastewater treatment (Salama et al., 2021). One of the most significant naturally occurring and sustainable polymers is cellulose.

Nanocellulose refers to cellulosic materials with a single dimension in the nanoscale range. There are three primary subcategories within it: nanocrystalline cellulose, bacterial nanocellulose, and cellulose nanofibers (Chen et al., 2019). Cellulose nanocrystals, which are made up of rod-shaped cellulose crystals and are also called "whiskers," are usually made using an acid hydrolysis method to get rid of the amorphous parts of a pure cellulose source (George and Sabapathi, 2015). Depending on the type of acid that has been used in cellulose treatment, the crystals that are produced by it usually exhibit varying charges. The crystals show a negative charge after being treated with HCl because ester groups are formed. CNC suspensions made from hydrochloric acid have great colloidal stability. Additionally, cellulose nanocrystals have special liquid-crystalline and optical characteristics (Vasconcelos et al., 2017). Most importantly, nanocellulose exhibits greater flexibility, porosity, and exceptional purity when obtained from algae (Trache et al., 2020).

Cellulose nanocrystals have special properties that make them useful in many areas. They can be used in composite materials, biomedical applications (Dumanli, 2017), hydrogels (De France et al., 2017), packing (Amara et al., 2021), and heavy metal adsorbents (Si et al., 2022). Extensive research has been conducted on freshwater algae due to their ability to eliminate contaminants from polluted water sources. Several species of algae, including *Oscillatoria limnetica, Pseudanabaena limnetica, Anabaena spiroides, Eudorina elegans*, and *Chlorella vulgaris*, are effective in adsorbing copper, cadmium, and lead (Sebeia et al., 2019).

Cladophora species have been successful in removing arsenic, cadmium, and selenium (Jasrotia et al., 2014). Furthermore, several studies have investigated the possibility of using different types of algae to remove dyes from water. For example, Kousha et al. (2012) documented the potential of using *Cystoseira indica* and *Gracilaria persica* biomass for the biosorption of Acid Black 1 from water solutions. Marzbali et al. (2017) studied the adsorption of Chrysophenine (Direct Yellow 12) from a water-based solution using Spirulina algae. Mokhtar et al. (2017) examined the process of biosorption of azo dye by the marine macroalga *Euchema spinosum*.

Materials and Methods

Collection of Chara corallina

During the spring season of 2023, *C. corallina* was collected from the Euphrates River shore located in Ramadi, Iraq. It was carefully washed several times with distilled water to remove unwanted materials, such as sand particles and debris. Then dried at 60°C for 24 hours. The seaweed samples were subsequently placed in sealed bags and stored at room temperature.

Extraction of cellulose

Cellulose was extracted from *C. corallina* using a method outlined by Reddy and Yang (2009). The process involved soaking 100 g of dried seaweed biomass in a 17.5% KOH solution (10:1 solution to biomass ratio) at 25°C overnight. The solid residue was then washed with distilled water, neutralized with a dilute acetic acid solution to eliminate any residual alkali, and air-dried. To remove residual green pigments, 400 mL of 4% hydrogen peroxide was used to suspend the sample for 16 hours at room temperature. After centrifuging the suspension at 5,000 rpm for 15 minutes, the residue was dried for 24 hours at 60°C. The resulting cellulose was tumbler-milled to obtain micrometer-sized particles of cellulose powder (Piras et al., 2019).

Preparation of nanocellulose

An acid hydrolysis method was used to produce nanocellulose. 10 g of bleached cellulose fibers were mixed with 100 mL of 40% hydrochloric acid using vigorous stirring, and the reaction was performed at 45°C for 40 minutes. To stop the reaction, 100 mL of cooled deionized water (10°C) was added to the

solution. The suspension was neutralized with 1% NaOH and centrifuged at 5,000 rpm for 15 minutes (Lima et al., 2023).

Fabrication of nanocellulose composite membrane

Nanocellulose-based membranes were fabricated following the method described in Agtasia et al. (2018). To form the membrane, 3.5 g of nanocellulose powder was mixed with 15 mL of 5% polyvinyl alcohol (PVA) and 10 mL of 5% polyethylene glycol (PEG). The liquid was stirred on a hot plate for 15 minutes and then placed on a glass plate in a thin layer. The mixture was left to dry naturally at room temperature for one hour. Next, the membranes were dried at room temperature to remove any residual moisture content. Finally, they were washed with 1% NaOH (Figure 1).

Figure 1. Preparation of nanocellulose-based membrane with polymers.

Characterization of nanocellulose

The nanocellulose was characterized using several techniques. The Fourier-transform infrared spectra were analyzed using the Bruker Alpha II Compact FT-IR Spectrometer. The morphology of the nanocellulose was studied using a Zeiss Sigma scanning electron microscope (SEM). The energy-dispersive X-ray spectrometer (EDX) was used on the EDXA apex to investigate the structure and morphology of the nanocellulose. The Empyrean PAN-analytical XRD technique was employed to investigate the crystalline structure of nanocellulose at room temperature. The crystallinity level (Crl%) was calculated using the Segal equation (El-Sheekh et al., 2023).

$$\text{Crl } \% = \frac{\text{I200} - \text{Iam}}{\text{I200}} \times 100 \qquad \text{eq. (1)}$$

Where I200 denotes the intensity of the crystalline peak observed at 2θ = 22° that corresponds to the (200) plane, and Iam represents the intensity of the local minimum of the curve seen at 2θ = 15° that corresponds to the amorphous phase of cellulose.

Heavy metal removal

The vacuum filtration unit shown in Figure 2 was used in this study. 100 mL of heavy metal solutions with a concentration of (20, 40, 60, 80, and 100 mg L^{-1} was poured into the filtration unit. One-, three-, and five-layer filters were used to evaluate their ability to trap heavy metal ions from solutions. After completion of the filtration process, approximately 5 mL of sample was collected, and the remaining heavy metals in the filtrate were determined by atomic flame spectrometry (Shimadzu, Japan). The adsorption percentage was calculated after estimating the remaining concentrations. This value represents the ratio between the difference in concentration of adsorbed material before and after adsorption (Ci – Cf), and the initial concentration of metal ions in the aqueous solution (Ci) and is represented by the equation (Nibret et al., 2019):

$$\text{Adsorption } \% = \frac{\text{Ci} - \text{Cf}}{\text{Ci}} \times 100 \qquad \text{eq. (2)}$$

where:

C_i is the initial concentration of the heavy metal ion in the solution (ppm).
C_f is the final concentration of the heavy metal ion in the solution (ppm).

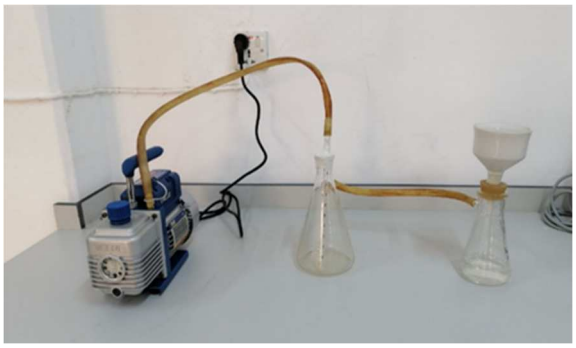

Figure 2. Vacuum filtration system used in this study.

Statistical analysis

Data were calculated as mean ± standard deviation based on three replicates. A one-way ANOVA test was performed to examine statistical hypotheses, and statistical significance was defined as p-values less than 0.05.

Results and Discussion

Cellulose extraction

Algal cellulose is a composite material consisting of semi-crystalline cellulose, hemicellulose, and lignin. It is a D-glucose polymer that exhibits a distinct X-ray diffraction (XRD) pattern akin to that of plant cellulose (Chen et al., 2016). Nevertheless, algal cellulose obtained from *C. corallina* features extensive microfibrils that are highly crystalline compared to the thin, randomly aligned microfibrils present in wood cellulose. Chemical treatment is required to remove the amorphous constituents from cellulose due to the chemical bonding of the carbohydrate groups of

hemicellulose and lignin within the cellulose mixture. The extraction process involves different steps that affect the chemical composition of the algal cellulose. The Chara algae, which was collected from its natural habitat along the shore of the Euphrates River, turned brown when air-dried. Alkaline treatment enables the hydrolysis of the ester bond between the lignin hydroxyl group and the hemicellulose carboxyl group. This process results in a reduction in hemicellulose content (Sheltami et al., 2012).

Lignin is naturally amorphous and can dissolve in hot alkalis. On the other hand, cellulose is resistant to strong alkalis. When Chara fibers are treated with 0.5 M sodium hydroxide, the cellulose or cellulose microfibrils remain attached to each other. This treatment partially separates the microfibrils from the fiber bundles, indicating that most of the lignin has been dissolved in the alkaline solution. Although a small amount of lignin usually remains after alkaline treatment, it is important to remove the remaining lignin through bleaching. When hydrogen peroxide is used to bleach algae, it turns white. The resulting white cellulose indicates that the majority of non-cellulosic components have been removed. It is worth noting that algae samples require a simple bleaching process because they have fewer dyes and components than terrestrial plant samples, which usually require several bleaching steps.

The production of nanocrystals from cellulose requires the use of intense acid hydrolysis. Hydronium ions infiltrate the non-crystalline regions of cellulose, resulting in the hydrolytic cleavage of glycosidic linkages (Le Gars et al., 2020). Through controlled circumstances, acid hydrolysis can selectively remove the non-crystalline portions of cellulose fibers while leaving the crystalline domains intact, resulting in the formation of crystalline nanoparticles. The choice of acid used for hydrolysis is an important factor that affects the outcome, in addition to the reaction time. Nanocrystals prepared with hydrochloric acid have a negatively charged surface, which is due to the esterification of the surface hydroxyl groups, and this has an impact on CNC characteristics and behaviors (Harun et al., 2022).

For the first time, the preparation of CNCs from *C. corallina* using HCl was reported in this paper. When hydrolyzed with HCl instead of H_2SO_4, fewer labile centers are formed, which may act as potential locations for adverse responses. Because amorphous cellulose has a lower molecular order than crystalline cellulose, it is more prone to HCl hydrolysis (Lorenz et al., 2017). The protonation of glucose units' glycosidic O by hydronium ions enhances the electrophilicity of the non-bonded carbon, leading to nucleophilic attack by water at the anomeric carbon. This reaction breaks the glycosidic bond, generating separate glucose units and regenerating the hydronium ion. The reaction is facilitated by utilizing concentrated acid to propel the reaction forward.

FT-IR of the nanocellulose

Figure 3 displays the FT-IR spectra of nanocellulose, which was produced from *C. corallina* by acid hydrolysis. The spectral analysis of the sample showed the presence of hydroxyl groups within the cellulose molecule. This was evident from the distinct bands observed in the spectral bands of 3,275 to 3,332 cm^{-1} which were found in cellulose I (CI).

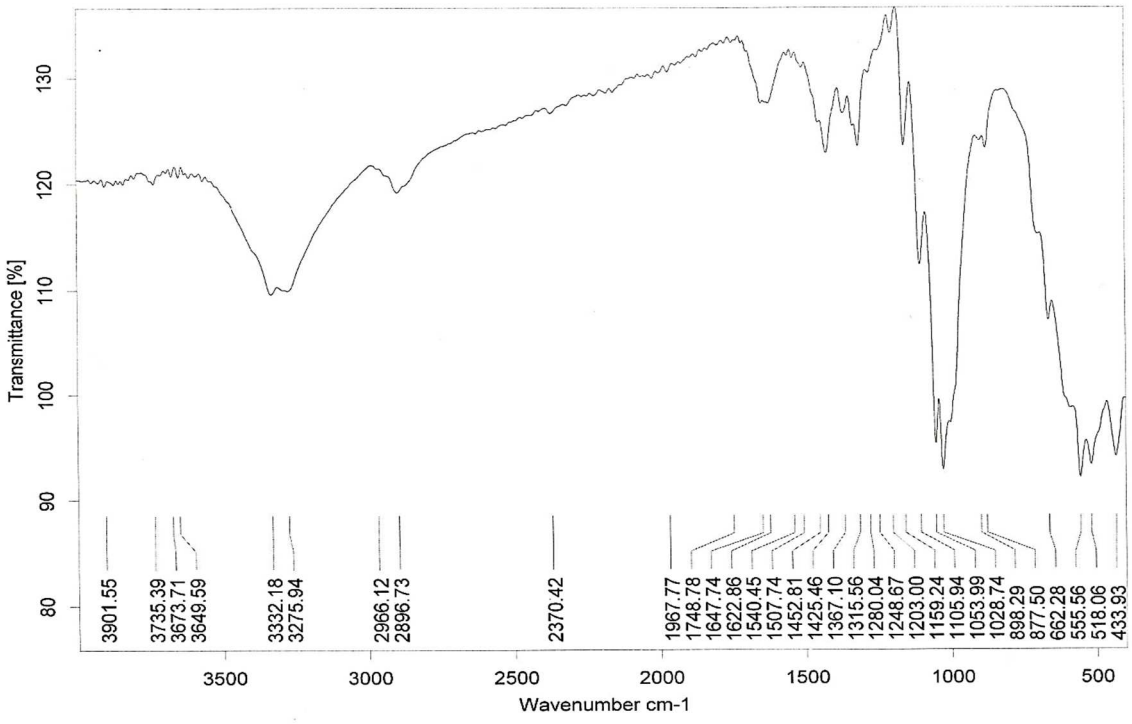

Figure 3. FTIR spectra of algal nanocellulose prepared via acid hydrolysis.

Additionally, bands from 3,649 to 3,901 cm^{-1} as well as two bands, were observed at 1,647 and 1,622 cm^{-1}, which were attributed to the bending vibration of adsorbed water. This feature is characteristic of hydrophilic materials that have a cellulosic nature. These insights provide valuable information about the physicochemical properties of the cellulose sample and its potential use in various applications (Battisti et al., 2018).

The stretching vibration of the carbon-hydrogen bond (methyl group) was observed at peaks at 2,896 and 2,966 cm^{-1}. Also, the band noticed at 1,452 cm^{-1} indicates the presence of methyl groups in cellulose. The bands ranging from 1,248 cm^{-1} to 1,425 cm^{-1} denote the plane bending of the stretching vibration in the C=O carbonyl groups, and the symmetric elongation of the C-O-C bonds represents the main peaks around 1,028-1,105 cm^{-1}. The band at 1,159 cm^{-1} was identified as an asymmetric extension of the COC of cellulose. The presence of a peak at both 877 and 898 cm^{-1} indicates the existence of a beta-glycosidic bond that connects glucose units (Fazio et al., 2020). The findings of the study suggest that the process of cellulose isolation from *C. corallina* was executed efficiently, yielding results that corroborate the existing literature (Wahlström et al., 2020; Saud et al., 2022; El-Sheekh et al., 2023).

XRD profiles and crystallinity

The acidolyzed cellulos's XRD profile differs from milled cellulos's (Figure 4). On the treated cellulose fibers, the primary peaks (peak 3) slightly moved to a higher 2 theta. When comparing the acidolyzed-treated cellulose sample to the milled cellulose sample, the number of peaks reduced, and the peak width rose, suggesting that some of the amorphous elements present in the milled fiber were eliminated and the crystallite size was decreased. The major peak, which was identifiable at about 22.5°, revealed the crystal polymorph I characteristic of the native cellulose (French, 2013). This indicated that the chemical treatments successfully extracted the crystalline cellulose and efficiently removed hemicellulose, lignin, and other non-cellulosic components, most of which exist in an amorphous phase. Following the chemical treatments, the XRD crystallinity index (CI) of these samples increased, reaching 74.20% for milled cellulose and 85.64% for acidolyzed cellulose. This aligns with the findings examined by Chen et al. (2016).

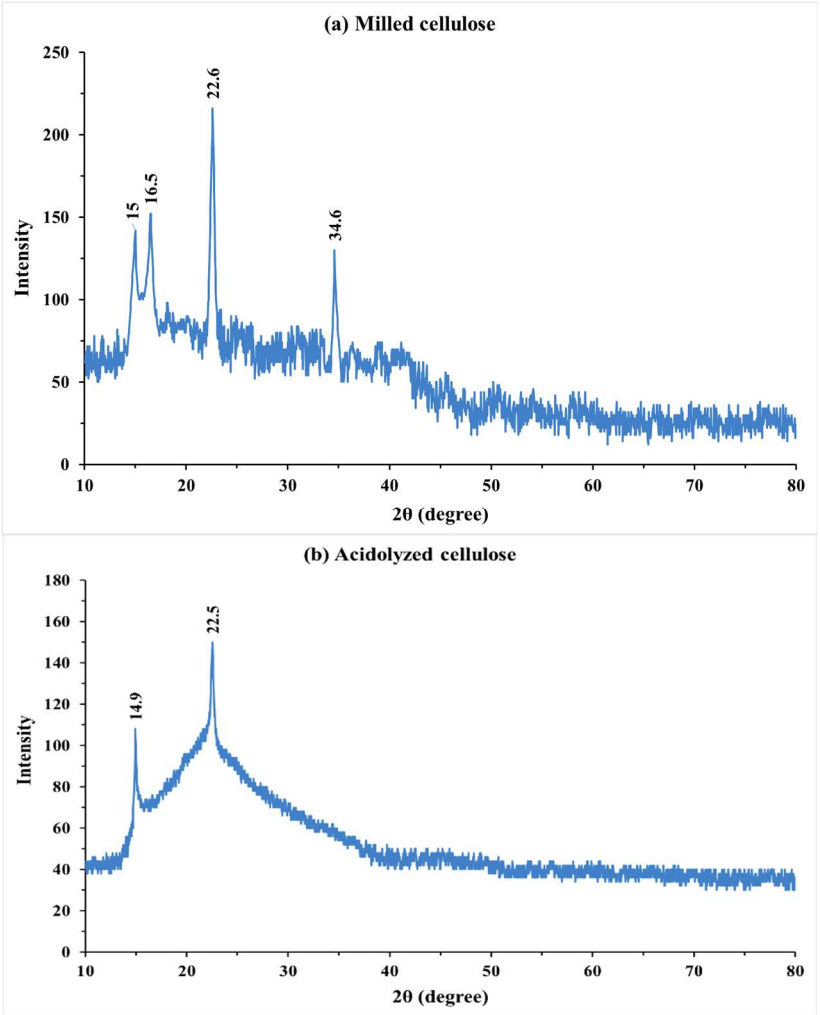

Figure 4. XRD profiles of (a) milled cellulose, and (b) acidolyzed cellulose from *C. corallina*.

Field emission scanning electron microscopy

The study employed FE-SEM to examine the alterations in surface morphology resulting from variations in the cellulose nanoparticle production technique. Figure 5 displays FE-SEM micrographs of membranes produced using the milling process using cellulose derived directly from algae. The FE-SEM pictures reveal that the molecules are composed of irregularly shaped particles with a coarse surface and cavities, suggesting a significant specific surface area. This occurs as a result of the degradation of the cellulose chains when subjecting the cellulose to intense pressure by passing it through a ball during the milling process. The images also revealed the clustering of the nanocellulose particles. A change in morphology was observed during the conversion of cellulose to nanocellulose using 40% hydrochloric acid. This process caused the fibers to disintegrate due to their extensive cross-linking, creating a sponge-like structure with microporous properties as nanorods of crystalline cellulose began to emerge. Hydrochloric acid hydrolysis caused the fibers to decompose and produce a network of microporous structures, Figure 6.

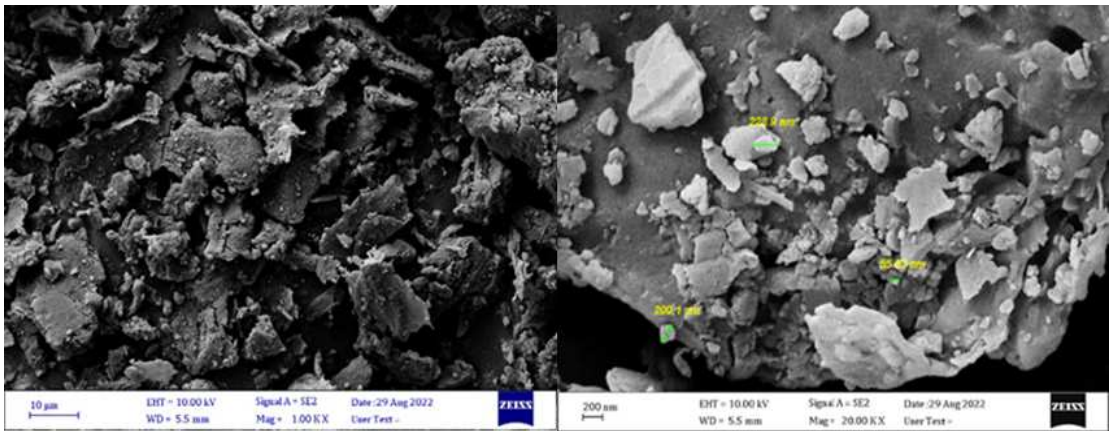

Figure 5. FE-SEM of cellulose nanoparticle formation by milling process.

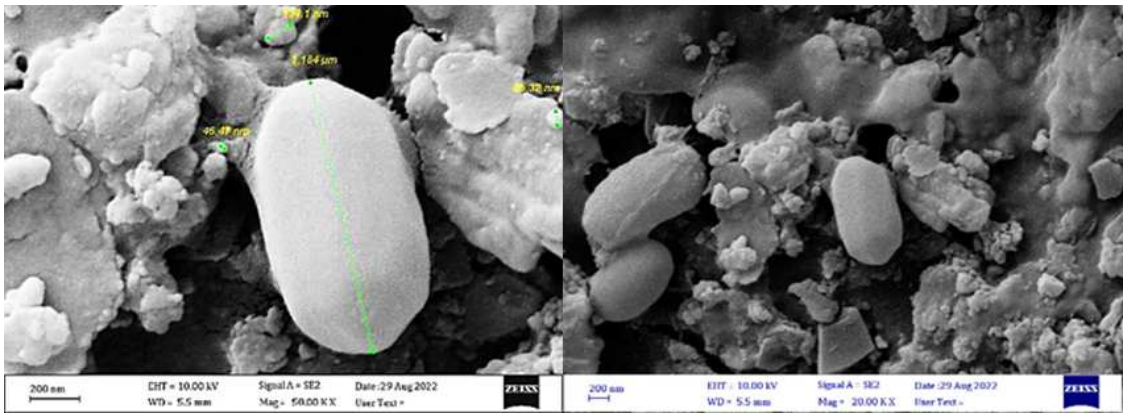

Figure 6. FE-SEM of cellulose nanoparticle formation by acid hydrolysis process.

BET analysis

The nanocellulose crystals have a high potential for gas adsorption due to their large surface area, which can be measured using the Brunauer-Emmett-Teller (BET) method. This method involves the use of dry samples and N_2 adsorption at 77 K to determine the surface area accessible to other molecules for interaction. By measuring the amount of sorbate in the monolayer or multilayer on the surface of the sorbent, the BET method can accurately determine the surface area of the nanocellulose crystals (Kondor et al., 2021). The BET calculation model determined the specific surface areas for acidic hydrolysis of nanocellulose and found that they were 5.823 m^2/g, and the average pore diameter was 23.995 nm.

Heavy metal ions removal

Figure 7 shows the experimental results for the removal of heavy metal ions (Cd^{2+}, Ni^{2+}, and Pb^{2+}) according to two variables, namely the number of layers of NC membranes used in the adsorption experiments and different concentrations of heavy metals from 20 to 100 ppm at optimal values of time, temperature, and pH. The selective sequence for the adsorption process by NC membranes was as follows: Five filters > three filters > one filter.

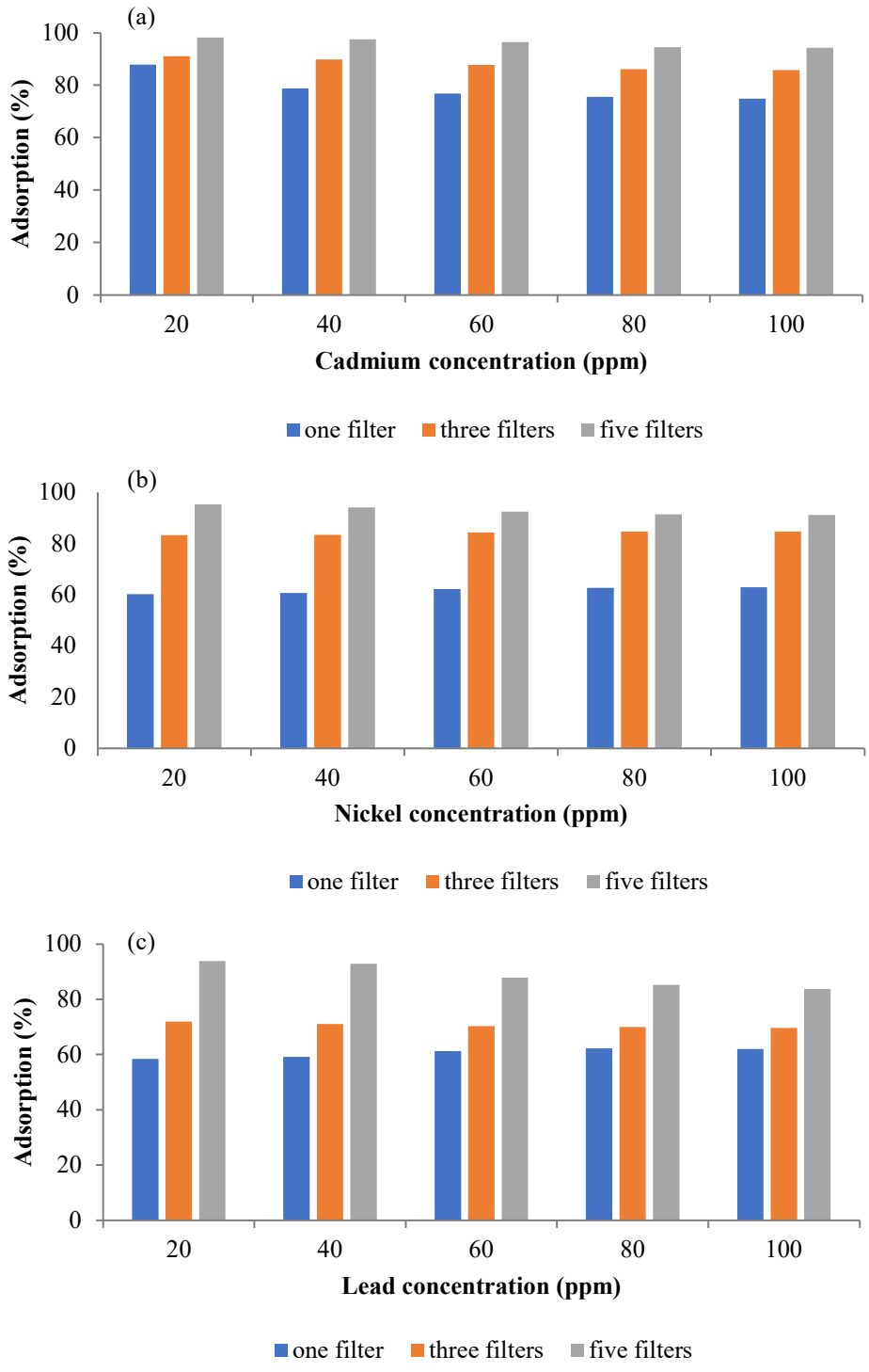

Figure 7. Adsorption efficiency of NC membranes for (a) Cd^{2+}, (b) Ni^{2+}, and (c) Pb^{2+}.

Hence, the adsorption of heavy metals on a single filter is the least due to the lower chemical activity of these functional groups on the NC surface. The highest adsorption percentage reached 97.90%, 95.15%, and 93.8% at a concentration of 20 ppm of Cd^{2+}, Ni^{2+}, and Pb^{2+}, respectively, when using five layers of membranes (4.7 g), while the lowest adsorption percentage was 74.81%, 60.20. %, and 58.4% at 20 ppm of Cd^{2+}, Ni^{2+}, and Pb^{2+}, respectively, using one layer of film (0.94 g). Due to the increase in heavy metal ion concentrations, the proportion of ions adsorbed on the adsorbent surface increases with the increase in the polymer dosage at the adsorbent binding sites until they reach equilibrium (Hassan et al., 2021). The increase in metal removal efficiency can be attributed to the fact that as the adsorbent dosage increases, more adsorbent surfaces or more adsorption sites are available for the adsorption of metal ions. The adsorption mechanism occurs through electrostatic interactions between metal ions and

carboxyl, carbonyl, and hydroxyl groups on the NC surface, which contribute to the adsorption process. The dosage of nanosorbents has a significant impact on the adsorption performance due to the availability of more binding sites on the surface of nanosorbents due to the complexation of metal ions (Pandey, 2021; Raji et al., 2023). Due to its enormous surface area and the abundance of accessible adsorption sites, the NC membrane showed a high adsorption percentage of 98.20% at a low initial Cd^{2+} ion concentration (20 ppm) and a lower adsorption percentage of 94.23% at a high initial Cd^{2+} ion concentration (100 ppm) when using five filter membranes. As a result, the removal percentage of the adsorbent dropped and approached adsorption equilibrium. Therefore, 20 ppm was the ideal Cd^{2+} ion concentration range for the ion removal (Figure 8).

At the optimum initial Ni^{2+} ion concentration of 20 ppm, adsorbents have shown a higher Ni^{2+} ion removal capacity of 95.15% than NC adsorbents. While 91.03% was the removal percentage when using a 100 ppm concentration of Ni^{2+}. Also, the removal percentage of Pb^{2+} decreased from 93.8 to 83.64 when nanosorbents were used to remove Pb^{2+} at concentrations of 20 to 100 ppm, respectively, as shown in Figure 8.

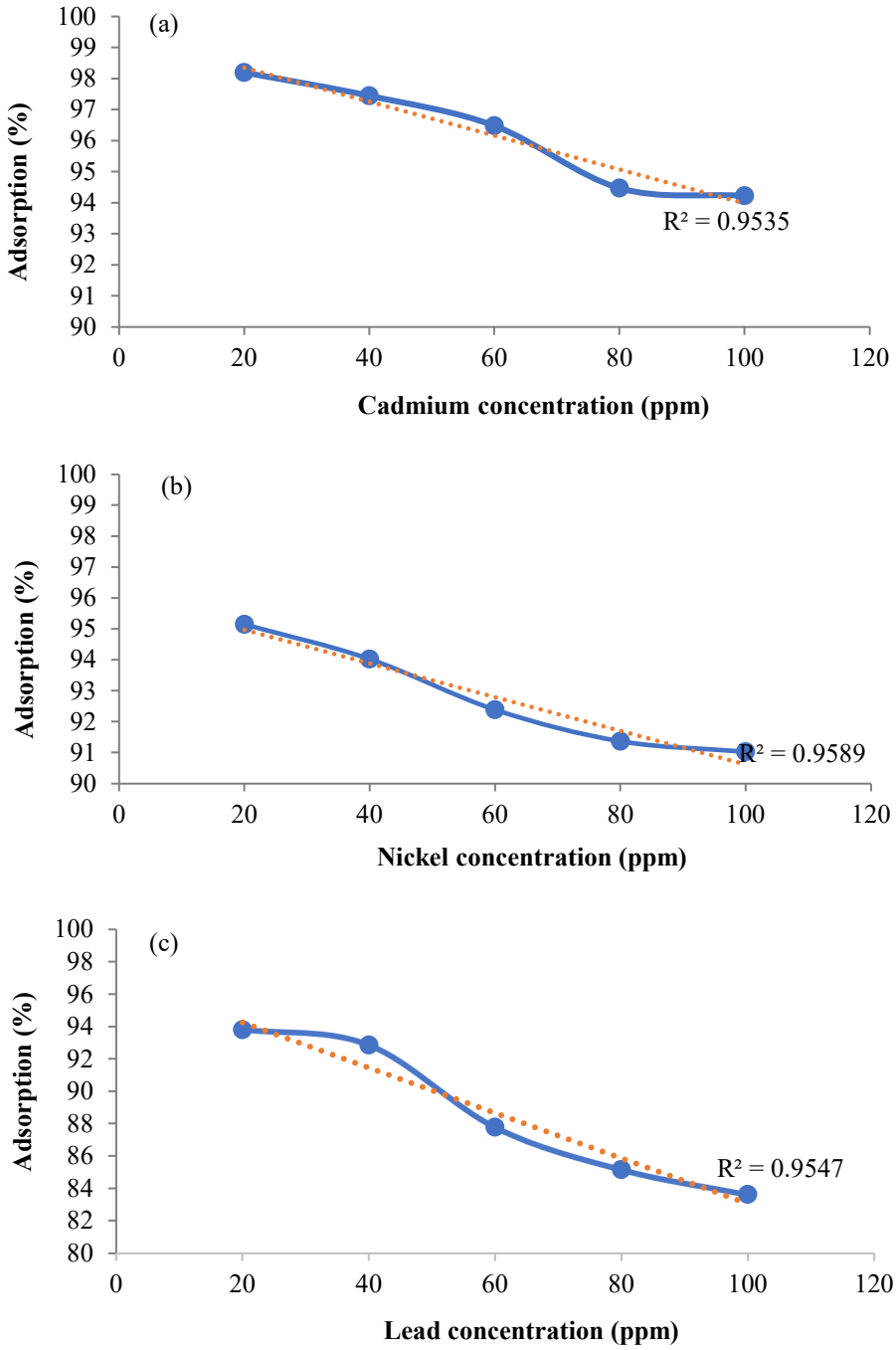

Figure 8. Effect of adsorbate concentration on the adsorption of (a) Cd^{2+}, (b) Ni^{2+}, and (c) Pb^{2+}.

In general, an increase in the initial concentration of metal ions results in a reduced percentage of adsorption for each metal ion on the adsorbent. However, at lower concentrations, the adsorbent's ample active sites facilitate the removal of a greater number of metal ions. As the concentrations increase, the adsorbents become saturated with metal ions, resulting in a greater number of unadsorbed ions (Sharifi et al., 2021).

Conclusion

Many algae species have been considered promising biosorbents. However, *C. corallina* biomass species have not been studied as an adsorbent. The main goal of this study was to extract cellulose from the *C. corallina* moss and then convert it into nanocellulose through a series of chemical and physical treatments. Additionally, the study aimed to fabricate filter membranes from nanocellulose and investigate the potential of these membranes to adsorb heavy metal ions in aqueous solutions. These membranes are exceptional since they can effectively and simultaneously remove several hazardous chemicals from contaminated water at the same time. This makes them a potential option for purifying drinking water. To attain an economical method, this study wants to take into account the possibilities of either pre-filtration or nanofiltration when significant quantities of nonorganic materials and natural colloids are present.

Acknowledgments

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References

Agtasia Putri, C., Yulianti, I., Desianna, I., Sholihah, A. and Sujarwata. 2018. Water hyacinth cellulose-based membrane for adsorption of liquid waste dyes and chromium. *Journal of Physics: Conference Series* 1008:012014, doi:10.1088/1742-6596/1008/1/012014.

AL-Heety, L.F., Hasan, O.M. and Al-Heety, E.A.M.S. 2021. Heavy metal pollution and ecological risk assessment in soils adjacent to electrical generators in Ramadi City, Iraq. *Iraqi Journal of Science* 1077-1087, doi:10.24996/ijs.2021.62.4.4.

Al-Heety, L.F., Hasan, O.M. and Al-Heety, E.A.M.S. 2021b. Assessment of heavy metal pollution of plants grown adjacent to power generators in Ramadi city. *IOP Conference Series: Earth and Environmental Science* 779(1):012023, doi:10.1088/1755-1315/779/1/012023.

Amara, C., El Mahdi, A., Medimagh, R. and Khwaldia, K. 2021. Nanocellulose-based composites for packaging applications. *Current Opinion in Green and Sustainable Chemistry* 31:100512, doi:10.1016/j.cogsc.2021.100512.

Badariah, B., Sukmawati, N., Heraningsih, S.F., Rainiyati, R., Riduan, A. and Putri, R.D. 2023. Heavy metal contamination of Batanghari River, Jambi, Indonesia: determination based on sediment enrichment factor value. *Journal of Degraded and Mining Lands Management* 10(4):4761-4768, doi:10.15243/jdmlm.2023.104.4761.

Battisti, R., Hafemann, E., Claumann, C.A., Machado, R.A.F. and Marangoni, C. 2018. Synthesis and characterization of cellulose acetate from royal palm tree agroindustrial waste. *Polymer Engineering and Science* 59(5):891-898, doi:10.1002/pen.25034.

Carolin C.F., Kamalesh, T., Kumar, P.S., Hemavathy, R. and Rangasamy, G. 2023. A critical review on sustainable cellulose materials and its multifaceted applications. *Industrial Crops and Products* 203:117221, doi:10.1016/j.indcrop.2023.117221.

Chen, W., Chen, F., Zhang, G., Liu, X., Kong, S., Cai, W., Wang, J., Du, L. and Wu, C. 2019. Fabrication of cellulose nanocrystal composite filter papers for rapid and highly efficient removal of bacteria from aqueous solutions. *Cellulose* 26(12):7027-7035, doi:10.1007/s10570-019-02620-9.

Chen, Y.W., Lee, H.V., Juan, J.C. and Phang, S.M. 2016. Production of new cellulose nanomaterial from red algae marine biomass *Gelidium elegans*. *Carbohydrate Polymers* 151:1210-1219, doi:10.1016/j.carbpol.2016.06.083.

De France, K.J., Hoare, T. and Cranston, E.D. 2017. Review of hydrogels and aerogels containing nanocellulose. *Chemistry of Materials* 29(11):4609-4631, doi:10.1021/acs.chemmater.7b00531.

Dumanli, A.G 2017. Nanocellulose and its composites for biomedical applications. *Current Medicinal Chemistry* 24(5):512-528, doi:10.2174/0929867323666161014l.

El-Sheekh, M.M., Yousuf, W.E., Kenawy, E.R. and Mohamed, T.M. 2023. Biosynthesis of cellulose from Ulva lactuca, manufacture of nanocellulose and its application as antimicrobial polymer. *Scientific Reports* 13(1), doi:10.1038/s41598-023-37287-7.

Fazio, A., La Torre, C., Caroleo, M.C., Caputo, P., Plastina, P. and Cione, E. 2020. Isolation and purification of glucans from an Italian cultivar of *Ziziphus jujuba* Mill. and in vitro effect on skin repair. *Molecules* 25(4):968, doi:10.3390/molecules25040968.

French, A.D. 2013. Idealized powder diffraction patterns for cellulose polymorphs. *Cellulose* 21(2):885-896, doi:10.1007/s10570-013-0030-4.

George, J. and Sabapathi, S.N. 2015. Cellulose nanocrystals: synthesis, functional properties, and applications. *Nanotechnology, Science and Applications* 45, doi:10.2147/nsa.s64386.

Goswami, R., Mishra, A., Bhatt, N., Mishra, A. and Naithani, P. 2021. Potential of chitosan/nanocellulose-based composite membrane for the removal of heavy metal (chromium ion). *Materials Today: Proceedings* 46:10954-10959, doi:10.1016/j.matpr.2021.02.036.

Harun, Z., Arsad, A., Pang, A.L., Zaini, M.A.A., Abdurrahman, M.D., Awang, N., Junin, R. and Mohsin, R. 2022. Acid hydrolysis and optimization techniques for nanoparticles preparation: Current review. *Applied Biochemistry and Biotechnology* 194(8):3779-3801, doi:10.1007/s12010-022-03932-6.

Hassan, M., Liu, Y., Naidu, R., Du, J., Qi, F., Donne, S.W. and Islam, M.M. 2021. Mesoporous biopolymer architecture enhanced the adsorption and selectivity of aqueous heavy-metal ions. *ACS Omega* 6(23):15316-15331, doi:10.1021/acsomega.1c01642.

Jasrotia, S., Kansal, A. and Kishore, V. 2014. Arsenic phyco-remediation by *Cladophora algae* and measurement of

arsenic speciation and location of active absorption site using electron microscopy. *Microchemical Journal* 114:197-202, doi:10.1016/j.microc.2014.01.005.

Kondor, A., Santmarti, A., Mautner, A., Williams, D., Bismarck, A. and Lee, K.Y. 2021. On the BET surface area of nanocellulose determined using volumetric, gravimetric and chromatographic adsorption methods. *Frontiers in Chemical Engineering* 3, doi:10.3389/fceng.2021.738995.

Koul, B., Yadav, D., Singh, S., Kumar, M. and Song, M. 2022. Insights into the domestic wastewater treatment (DWWT) regimes: A review. *Water* 14(21):3542, doi:10.3390/w14213542.

Kousha, M., Daneshvar, E., Sohrabi, M., Koutahzadeh, N. and Khataee, A. 2012. Optimization of C.I. acid black 1 biosorption by *Cystoseira indica* and *Gracilaria persica* biomasses from aqueous solutions. *International Biodeterioration and Biodegradation* 67:56-63, doi:10.1016/j.ibiod.2011.10.007.

Le Gars, M., Douard, L., Belgacem, N. and Bras, J. 2020. Cellulose nanocrystals: from classical hydrolysis to the use of deep eutectic solvents. *Smart Nanosystems for Biomedicine, Optoelectronics and Catalysis*, doi:10.5772/intechopen.89878.

Le, Q.H., Smida, K., Abdelmalek, Z. and Tlili, I. 2023. Removal of heavy metals by polymers from wastewater in the industry: A molecular dynamics approach. *Engineering Analysis With Boundary Elements* 155:1035-1042, doi:10.1016/j.enganabound.2023.07.034.

Lima, A.R., Cristofoli, N.L., Rosa da Costa, A.M., Saraiva, J.A. and Vieira, M.C. 2023. Comparative study of the production of cellulose nanofibers from agro-industrial waste streams of *Salicornia ramosissima* by acid and enzymatic treatment. *Food and Bioproducts Processing* 137:214-225, doi:10.1016/j.fbp.2022.11.012.

López, Y.C., Ortega, G.A. and Reguera, E. 2022. Hazardous ions decontamination: From the element to the material. *Chemical Engineering Journal Advances* 11:100297, doi:10.1016/j.ceja.2022.100297.

Lorenz, M., Sattler, S., Reza, M., Bismarck, A. and Kontturi, E. 2017. Cellulose nanocrystals by acid vapour: towards more effortless isolation of cellulose nanocrystals. *Faraday Discussions* 202:315-330, doi:10.1039/c7fd00053g.

Marzbali, M.H., Mir, A.A., Pazoki, M., Pourjamshidian, R. and Tabeshnia, M. 2017. Removal of direct yellow 12 from aqueous solution by adsorption onto spirulina algae as a high-efficiency adsorbent. *Journal of Environmental Chemical Engineering* 5(2):1946-1956, doi:10.1016/j.jece.2017.03.018.

Mokhtar, N., Aziz, E.A., Aris, A., Ishak, W. and Mohd Ali, N.S. 2017. Biosorption of azo-dye using marine macro-alga of Euchema Spinosum. *Journal of Environmental Chemical Engineering* 5(6):5721-5731, doi:10.1016/j.jece.2017.10.043.

Nibret, G., Ahmad, S., Rao, D.G., Ahmad, I., Shaikh, M.A.M.U. and Rehman, Z. U. 2019. Removal of methylene blue dye from textile wastewater using water hyacinth activated carbon as adsorbent: Synthesis, characterization and kinetic studies. *Proceedings of International Conference on Sustainable Computing in Science, Technology and Management (SUSCOM),* Amity University Rajasthan, Jaipur - India, February 26-28, 2019, doi:10.2139/ssrn.3358101.

Nurcholis, M., Nursanto, E., Sakti, H.E.B., Yudiantoro, D.F. and Haryanto, D. 2020. Coagulation and adsorption techniques for purification of the amalgamation slurry waste. *Journal of Degraded and Mining Lands Management* 7(2):2001-2010, doi:10.15243/jdmlm.2020.072.2001.

Pandey, L.M. 2021. Surface engineering of nano-sorbents for the removal of heavy metals: Interfacial aspects. *Journal of Environmental Chemical Engineering* 9(1):104586, doi:10.1016/j.jece.2020.104586.

Piras, C.C., Fernández-Prieto, S. and De Borggraeve, W.M. 2019. Ball milling: a green technology for the preparation and functionalisation of nanocellulose derivatives. *Nanoscale Advances* 1(3):937-947, doi:10.1016/j.jece.2020.104586

Raji, Z., Karim, A., Karam, A. and Khalloufi, S. 2023. Adsorption of heavy metals: Mechanisms, kinetics, and applications of various adsorbents in wastewater remediation - A review. *Waste* 1(3):775-805, doi:10.3390/waste1030046.

Reddy, N. and Yang, Y. 2009. Extraction and characterization of natural cellulose fibers from common milkweed stems. *Polymer Engineering and Science* 49(11):2212-2217, doi:doi.org/10.1002/pen.21469.

Rosariastuti, R., Barokah, U., Purwanto, P. and Supriyadi, S. 2018. Phytoremediation of Pb contaminated paddy field using a combination of *Agrobacterium* sp. I3, compost and ramie (*Boehmeria nivea*). *Journal of Degraded and Mining Lands Management* 5(4):1381-1388, doi:10.15243/jdmlm.2018.054.1381.

Salama, A., Abouzeid, R., Leong, W.S., Jeevanandam, J., Samyn, P., Dufresne, A., Bechelany, M. and Barhoum, A. 2021. Nanocellulose-based materials for water treatment: adsorption, photocatalytic degradation, disinfection, antifouling, and nanofiltration. *Nanomaterials* 11(11):3008, doi:10.3390/nano11113008.

Saud, A., Saleem, H. and Zaidi, S.J. 2022. Progress and prospects of nanocellulose-based membranes for desalination and water treatment. *Membranes* 12(5):462, doi:10.3390/membranes12050462.

Sebeia, N., Jabli, M., Ghith, A., Elghoul, Y. and M Alminderej, F. 2019. Production of cellulose from Aegagropila Linnaei macro-algae: Chemical modification, characterization and application for the bio-sorption of cationic and anionic dyes from water. *International Journal of Biological Macromolecules* 135:152-162, doi:10.1016/j.ijbiomac.2019.05.128.

Sehaqui, H., de Larraya, U.P., Liu, P., Pfenninger, N., Mathew, A.P., Zimmermann, T. and Tingaut, P. 2014. Enhancing adsorption of heavy metal ions onto biobased nanofibers from waste pulp residues for application in wastewater treatment. *Cellulose* 21(4):2831-2844, doi:10.1007/s10570-014-0310-7.

Sharifi, M.J., Nouralishahi, A., Hallajisani, A. and Askari, M. 2021. Magnetic chitosan nanocomposites as adsorbents in industrial wastewater treatment: a brief review. *Cellulose Chemistry and Technology* 55(1-2):185-205, doi:10.35812/cellulosechemtechnol.2021.

Sheltami, R.M., Abdullah, I., Ahmad, I., Dufresne, A. and Kargarzadeh, H. 2012. Extraction of cellulose nanocrystals from “mengkuang” leaves (*Pandanus tectorius*). *Carbohydrate Polymers* 88(2):772-779, doi:10.1016/j.carbpol.2012.01.062.

Si, R., Pu, J., Luo, H., Wu, C. and Duan, G. 2022. Nanocellulose-based adsorbents for heavy metal ions. *Polymers*, 14(24):5479, doi:10.3390/polym14245479.

Trache, D., Tarchoun, A.F., Derradji, M., Hamidon, T.S., Masruchin, N., Brosse, N. and Hussin, M.H. 2020.

Nanocellulose: From fundamentals to advanced applications. *Frontiers in Chemistry* 8, doi:10.3389/fchem.2020.00392.

Vasconcelos, N.F., Feitosa, J.P.A., da Gama, F.M.P., Morais, J.P.S., Andrade, F.K., de Souza Filho, M.D.S.M. and Rosa, M.D.F. 2017. Bacterial cellulose nanocrystals produced under different hydrolysis conditions: Properties and morphological features. *Carbohydrate Polymers* 155:425-431, doi:10.1016/j.carbpol.2016.08.090.

Wahlström, N., Edlund, U., Pavia, H., Toth, G., Jaworski, A., Pell, A.J., Choong, F.X., Shirani, H., Nilsson, K.P.R. and Richter-Dahlfors, A. 2020. Cellulose from the green macroalgae Ulva lactuca: isolation, characterization, optotracing, and production of cellulose nanofibrils. *Cellulose* 27(7):3707-3725, doi:10.1007/s10570-020-03029-5

Wang, R., Guan, S., Sato, A., Wang, X., Wang, Z., Yang, R., Hsiao, B.S. and Chu, B. 2013. Nanofibrous microfiltration membranes capable of removing bacteria, viruses and heavy metal ions. *Journal of Membrane Science* 446:376-382, doi:10.1016/j.memsci.2013.06.020.

Yousif, Y.M., Mutter, T.Y. and Hassan, O.M. 2024. Health risks and environmental assessments of heavy metals in road dust of Ramadi, Iraq. *Journal of Degraded and Mining Lands Management* 11(2):5301-5306, doi:10.15243/jdmlm.2024.112.5301.