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The Wastewater-Contaminated Treatment with Heavy Metals by Using a Sustainable Green Nanomaterial

Dhurgham Ali A. Al-Sultany
Biology Department, College of Sciences, Al-Qasim Green University, Babylon 51013, Iraq
Corresponding author email: taifdhurgham2010@gmail.com

Abstract---*The current research included treating wastewater with sustainable nanotechnology to remove some trace elements (arsenic, copper, baron, lead, and chromium) by using a nanomaterial extracted from potato plant waste in a sustainable, green, environmentally friendly way, with two different additions, the first adding 0.5 grams and the second adding 1 gram of nanocellulose. For two different periods (6 hours and 12 hours) for both quantities of nanocellulose. The results showed that nanocellulose has a great ability to remove the studied elements from wastewater after comparing their original concentrations that were in the water before treatment with nanocellulose. The results showed that increasing the amount of nanocellulose and increasing the time led to an increase in the removal rate, and this was clear from the results of the statistical analysis, which showed the presence of a positive significant correlation between the rate of removal of trace elements from waste water with increasing the amount of nanocellulose and increasing the time. When comparing the removal rates of the studied elements from wastewater with the PH values, it was found that the pH is the control of these rates, as the highest removal rates were at the neutral or close to acidic level, the pH between 5.5 and 7.5, and when the pH tends towards basicity (8 - 9.5) The removal rate decreased. The results also showed that the removal rate varies between the elements and this depends on the concentration of the element present in the water, its chemical composition, and the degree of its binding to the substance used for treatment.*

Keywords---*Nanocellulose, nanotechnology, potato plant, sustainable method, trace elements.*

Introduction

These days, human and environmental existence depends heavily on the sanitation and industrial water systems' treatment and purification. The majority of water on Earth, around 97.5%, is salty and unfit for human use of the remaining water, 2.5% is fresh water, of which less than 1% is fit for human consumption. Ten to twenty percent of the wastewater produced by human activity is treated and repurposed. As a result, billions of people worldwide lack access to sanitary facilities and clean drinking water (Ranade & Bhandari, 2014). Because of this, every person needs one to three liters of pure water annually. Nowadays, depending on whether water is limited and/or how many people flush the toilet, the amount varies from 5 to 120 liters per person per day. Home water demands include things like flushing the toilet, washing the car, watering the yard, and filling the swimming pool. As this water is typically contaminated, it needs to be cleaned before being used again (Kurunthachalam, 2014).

Improved wastewater treatment methods have been the result of developments in the domains of nanoscience and nanotechnology in recent decades. It has been demonstrated that the numerous paths based on nanotechnology are more efficient than conventional therapeutic methods (Yadav et al., 2022). Nanoparticles (NPs) possess a broad surface area-to-volume ratio, stronger chemical properties, and a smaller size. The NPs were traditionally created by physical and chemical means. These techniques required the use of expensive equipment, complex apparatus, and toxic chemicals. This had a negative impact on the environment and made the synthesis process costly and challenging (Jain et al., 2021).

Because of its lower material size, volume ratio concept, and larger surface area compared to chemical-based synthetic approaches, nanobioremediation is a more cost-effective and environmentally friendly solution. ecological

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and financial considerations. According to the findings, heavy metals and metalloids have harmful effects that can be mitigated with the use of biogenic nanoparticles (Sharma & Sharma, 2022). NM adsorbents make it simple to extract the HMs from the wastewater. Their increased specific surface areas and improved active sites aid in greater pollutant adsorption (Bognár et al., 2022).

Nanocelluloses have become a viable substitute for traditional materials used in wastewater treatment (Barhoum et al., 2020; Hassan et al., 2017). Industrial water treatment systems are advised to consider nanocellulose-based wastewater treatment materials as potential candidates because of their inherent qualities (Nnaji et al., 2018).

Because nanocellulose is an ecologically benign, harmless, sustainable, affordable, and highly effective material for a wide range of applications, including water treatment, its industrial-scale production and market are growing quickly on a global scale. Currently, a variety of nanocellulose products are offered on the market, which Markets & Markets projects will grow to USD 783 million by 2025. From 2020 to 2026, the size of the worldwide nanocellulose market is projected to increase at a compound yearly growth rate of 21.4% (Barhoum et al., 2019). Because HMs are non-biodegradable, extremely toxic even at low concentrations, and gather at each level of the food chain to destroy aqueous life and form a serious threat to human health, they are the most dangerous and a major environmental concern among the various water contaminants (Ali et al., 2017).

The sedimentary terrestrial zone is abundant in a variety of metallic and non-metallic elements. However, pollution and physical-chemical alterations are brought on by the increased concentrations of heavy metals (HM) in water bodies, for example, chromium, Cadmium, Arsenic, lead, Copper, Nickel, and zinc. Increased levels of heavy metals (HMs) in water bodies have negative impacts on both aquatic and terrestrial animals. These consequences include genotoxicity, oxidative stress, deactivation of cellular machinery or enzymes, and necrosis of individual cells (Razack & Duraiarasan, 2020).

The production of batteries, refining of petroleum processes, drainage with metal plating, mining operations, paint manufacture, and photography goods are among the many processes that release hazardous metal ions into the environment. These include Ni^{2+}, Ag^{+}, Cd^{2+}, Cu^{2+}, Pd^{2+}, Hg^{2+}, and U^{6+} (Abdelmouleh et al., 2004; El-Sayed, 2020). In light of this, developing environmentally friendly treatment methods is essential to ridding the industrial water system of dangerous heavy metals (Tan et al., 2018).

In the most sophisticated methods, NMs may identify, absorb, and immobilize HMs on a broad surface area as pollutants. Numerous distinctive characteristics of nanomaterial adsorbents include their nanoscale size, huge surface area, high reactivity, powerful mobility of the solution, robust mechanical qualities, porosity, hydrophilicity, dispersibility, and hydrophobicity (Nath & Banerjee, 2013). The current research aims to remove some heavy metals from wastewater by using sustainable, environmentally friendly nanocellulose naturally extracted from potato plant waste without adding chemicals.

Materials and Methods

Experimental work

Heavy element-contaminated water samples were taken from industrial wastewater treatment facilities. The produced nanocellulose material was then applied to the samples twice, once at a rate of 0.5 grams and once at a rate of 1 gram. To allow the contamination and the treated material to interact for as long as feasible and be eliminated, the created nanocellulose material was mixed with the contaminated water two separate times: for six hours and twelve hours. To achieve optimal removal efficiency, the pH of the water was adjusted to 5.5–7.5 and 8–9.5, respectively, using hydrochloric acid and sodium hydroxide.

Heavy metals analysis

Using a beaker, 50 ml of water was obtained, and then 5 ml of concentrated hydrochloric acid and 2 ml of concentrated nitric acid were added to the sample. After that, the sample was heated to between 90 and 100 °C for two hours, or until it was completely dry. After allowing the sample to cool, it was filtered, and distilled water was added to bring the volume up to 50 ml. Atomic absorption spectrometry (AAS) was then used to quantify the heavy metals (American Public Health Association, 2017).

Producing nanocellulose

Washing a known weight (1000 g) fresh potato sample with enough distilled deionized water was done. A sample was divided into tiny pieces. To ensure more homogeneity in the sample, a knife was cleaned using a solution of acetone and distilled deionized water. The purpose of this treatment was to stop contamination from being brought in by the instrument used to collect and prepare the sample (Hartmann, 2006).

The sample was then mechanically crushed to remove the potato. The generated extract sample was placed into a labeled dark container to avoid any potential oxidation caused by light or air. The extracted sample was then heated to (50 °C). To the extract sample, a few Citric acid, or lemon juice, was added in a few drops. Following ten minutes at 6000 rpm in an MSE Mistral 2000 Thermo Life Sciences centrifuge, the extracted sample was filtered with Whitman filter paper 42 (2.5 µm). After being cleaned with distilled deionized water, the precipitate was allowed to air dry at room temperature (De Gisi et al., 2016; Al-Kadhim et al., 2022).

Examination and Description of Nanocellulose Particles (NCP)

To verify the morphology of the nanoparticles' surface, which was detected using Atomic Force Microscopy (AFM) using the Scanning Probe Microscopy (SPM) technique, the generated nanocellulose particles were described using Fourier transform infrared (FTIR) to test the function of all groups across their polymeric structure.

The stretching of the (-OH) group was the cause of the absorption peak in the area of (3600-3100 cm-1) observed in the FTIR spectra, whereas the stretching of the (C-H) group was responsible for the peak that emerged at (3000-2800 cm-1). The band was located at (1651cm-1) on the other side of the absorbed water's bending (H-O-H). At (1400cm-1), the (C-H) group underwent symmetric bending.

The most distinctive peaks were found at the fingerprint area of the absorption band (856 cm-1), which is referred to as an "amorphous" absorption band and is linked to the stretching of the (C–O–C) group at β-(1→4)-glycosidic connections. The structure of amorphous (nanocrystalline) cellulose was validated by the IR spectra, as shown in the accompanying figures (1 and 2)

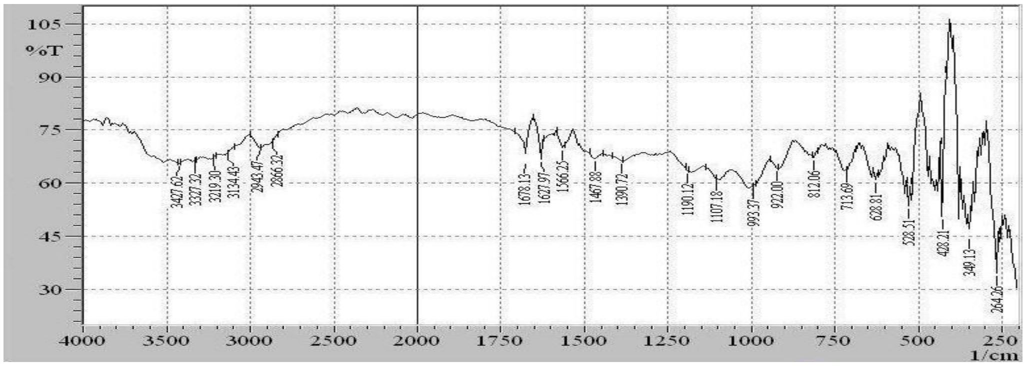

Figure (1). FTIR spectra for abstracted starch

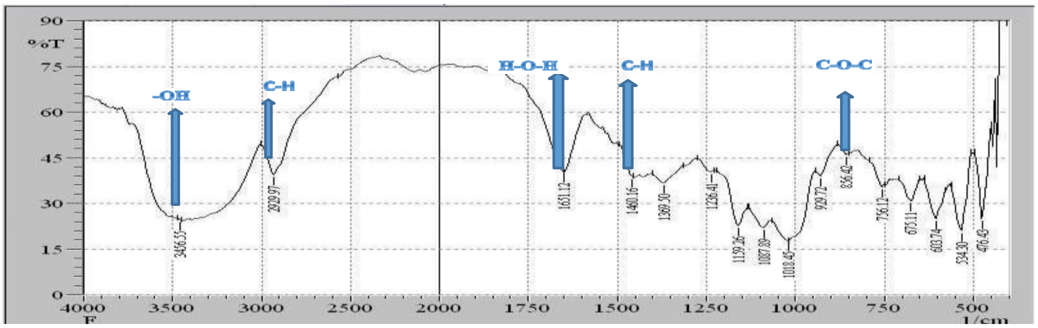

Figure (2). FTIR spectra for prepared Nano cellulose

The average diameter of the nanocellulose according to the granularity cumulation distribution chart was 23.44 nm, and the average height according to the height cumulation distribution chart was 12.714 nm, as shown in Figures (3–

4), respectively. These studies on SPM analysis and AFM measurements showed how the produced cellulose particles were at the nanoscale. Images 1-2 show the surface topology, roughness analysis, and parameters.

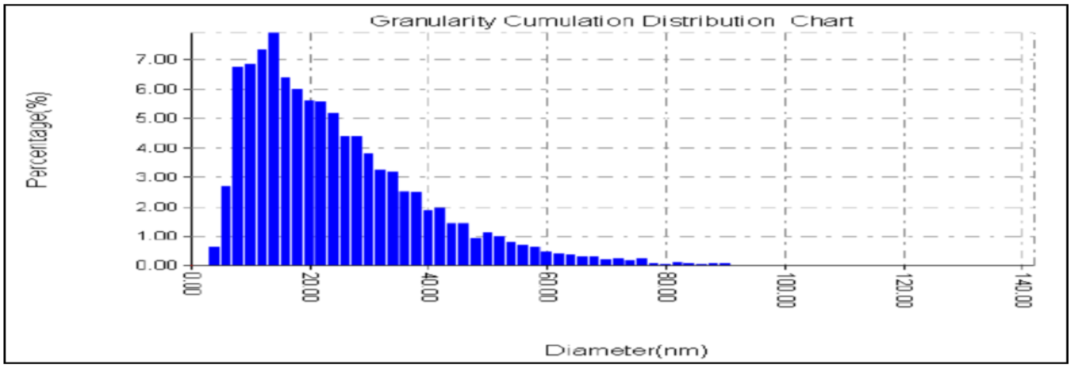

Figure (3) Granularity cumulation distribution of Nanocellulose particle

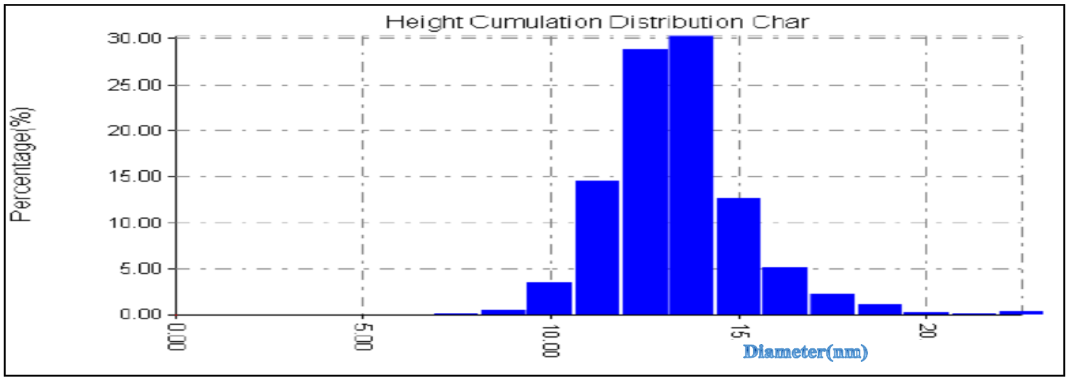

Figure (4). Height cumulation distribution of Nanocellulose particles

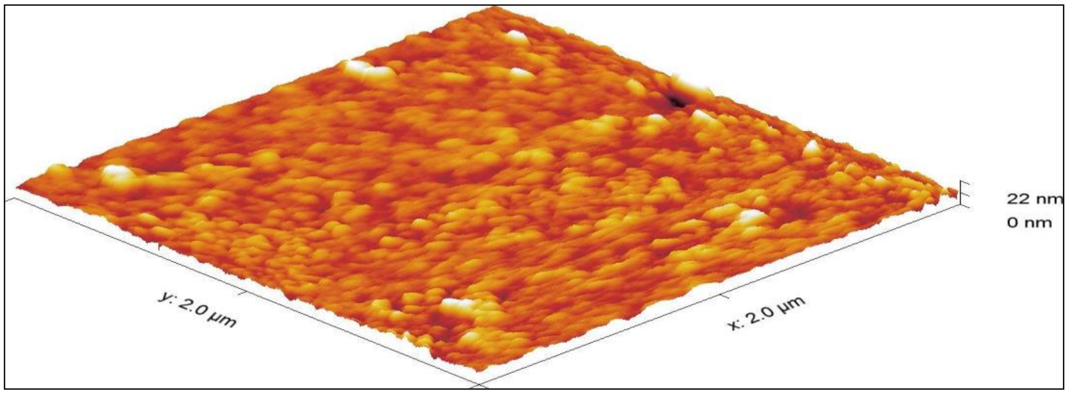

Image (1). Nanocellulose 3D-Surface topology

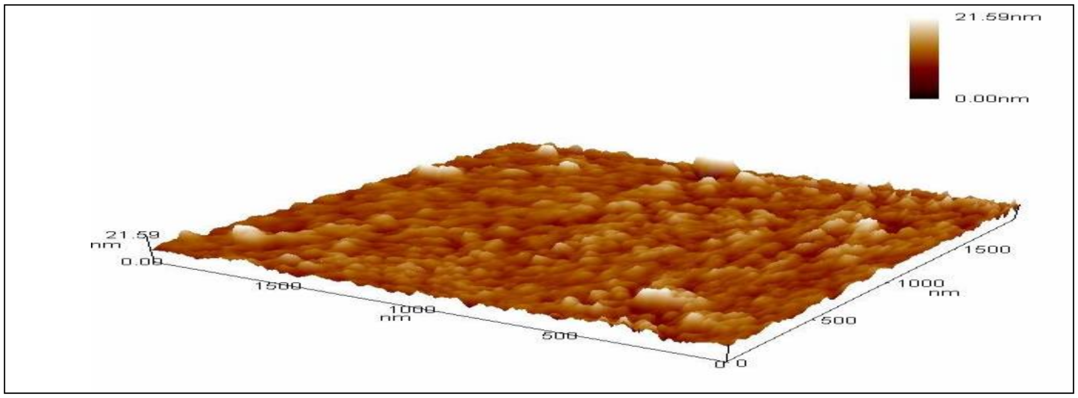

Image (2). SPM3D-nanocellulose surface

Statistical analysis

Means ±SD were used to express all the data. The mean separation was calculated using the least significant difference (LSD). The probability threshold of $P<0.05$ was chosen as the significant level.

Results and Discussion

In response to the pressing problem of water pollution caused by heavy metal ions, there is an increasing demand for green sorbents that can effectively remove these contaminants with ease of separation and regeneration (Sathasivam et al., 2023). Plants synthesize nanoparticles in a single step without the use of toxicants and with the help of natural capping agents. The main benefits of plant-based biosynthesis are its accessibility, safety during handling, and abundance of different metabolites that might facilitate the process. thus, it is thought that plants are a preferable choice for the production of nanoparticles because (Kumar & Rajeshkumar, 2018).

Metal ions can be reduced in an environmentally beneficial way by phytochemicals, which are compounds produced by plants. In addition to being stable and environmentally benign, plant-based nanoparticles are also made possible by the presence of proteins, polyphenols, and carbohydrates (Adil et al., 2015). In a little amount of time, plants finish the production of nanoparticles (Vijayaraghavan & Ashokkumar, 2017). Major biomolecules that contribute to the reduction of metals include amino acids, terpenoids, flavones, proteins, ketones, tannins, alkaloids, saponins, phenolics, and polysaccharides (Nath & Banerjee, 2013).

Figures 5 and 6 show the concentration of elements in wastewater after adding 0.05 and 1 grams of nanocellulose, respectively. The results of the current study demonstrated that the greater the amount of nanocellulose and the period of contact with water contaminated with heavy elements, the greater the removal rate. This was clear from the results of the statistical analysis, which showed a direct correlation between the amount of added nanocellulose and the removal rate, in addition to a direct correlation between the period of contact between nanocellulose and contaminated water and the removal rate at a probability level of $P\leq0.05$.

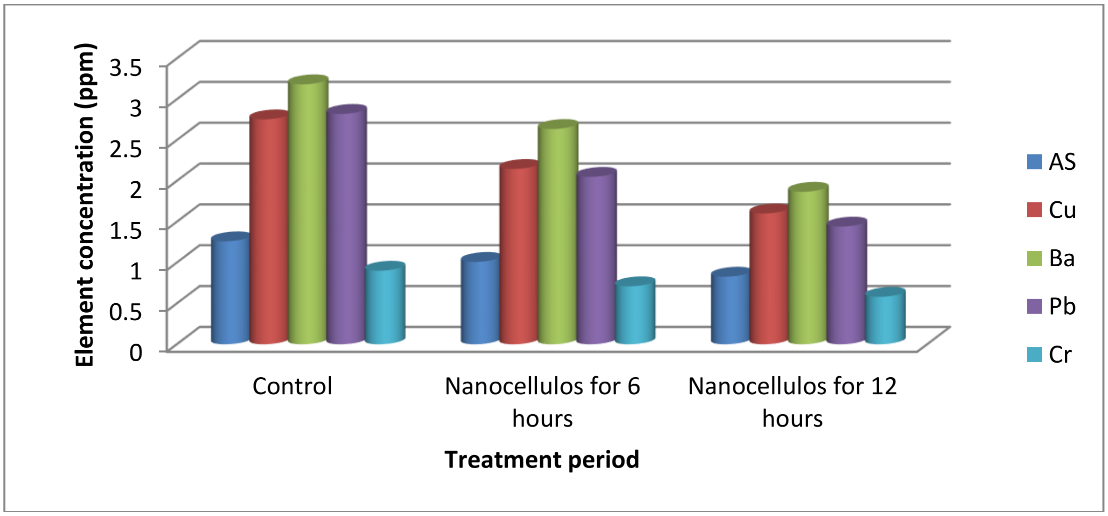

Figure (5). The concentration of elements in wastewater after adding 0.05 grams of Nanocellulose

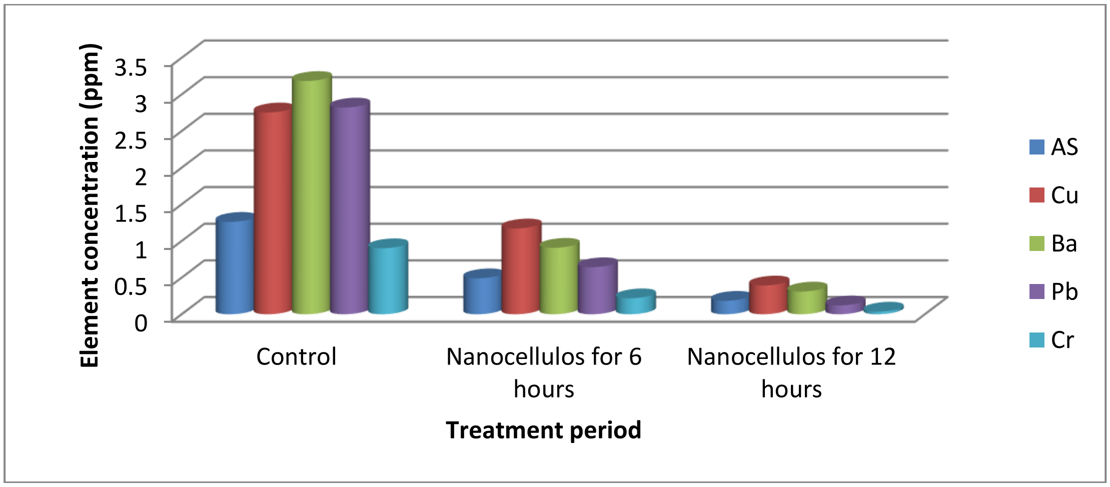

Figure (6) Concentration of elements in wastewater after adding 1 gram of Nanocellulose

This is due to the ability of nanocellulose to form covalent bonds and traps by cross-linking (González & Eugenia, 2023). Furthermore, nanoparticles have a large effective area of contact due to their tiny size. As a result, the adsorption and reactivity of nanoparticles are strong. This study shows that the considerable adsorption area, effective chemical reactions, and electrical conductivity of nanoparticles (NPs) contribute to the successful treatment of wastewater (Mbarek et al., 2022).

Because of its inherent hydrophilicity, cellulose interacts with water molecules more easily, making it a suitable material for use in water treatment procedures. Moreover, cellulose-based materials offer a broader range of uses in WW treatment because of their abundant supplies, low energy requirements, affordability, sustainability, and renewable nature (Sharma et al., 2023).

Due to their special qualities, which include having multiple -OH groups on their surface, which permits the insertion of chemical moieties, having a sizable specific surface area, having strong mechanical properties, being recyclable, and being biodegradable, nanocelluloses (NCs) have attracted a lot of interest as biosorbents (Sanad et al., 2023). Additionally, because of the high density of amide, hydroxyl, and carboxyl groups on its surface (Si et al., 2022).

Most common biopolymer found in the world is cellulose (Bethke et al., 2018). This biomaterial is a highly organized crystalline polysaccharide made up of glucose chains with linkages β-1,4 arranged in parallel arrays (Peng et al., 2020). Numerous investigations indicate that basic dimer repeats, or cellobiose (Kumar & Turner, 2015), are the cause of the distinctive high-order structure seen in cellulose. Moreover, the strong H-bonds that bind the many hydroxyl groups in cellulose provide its distinct physicochemical properties, including hydrophilicity, chirality, crystallinity, and biodegradability (Mischnick & Momcilovic, 2010).

Moreover, this naturally occurring polymer may be easily functionalized and altered by a range of chemical techniques employing different functional groups to improve and alter its physicochemical characteristics, thanks to the very dense OH groups on its surface structure. Because of this, cellulose is a flexible and adaptable substance (Thakur & Thakur, 2014; Al-Sultany et al., 2019).

The two main ways that biogenic nanoparticles interact with and remove heavy metals and metalloids are through adsorption and reduction. The two types of adsorption mechanisms are physical and chemical. Physical adsorption depends entirely on the existence of a permeable structure, whereas chemical adsorption needs functional groups to be present on the adsorbent's surface to remove heavy metals by chemically binding forces or electrostatic attraction. In contrast, the chemical adsorption approach is thought to be a superior technique for cleanup (Latif et al., 2020).

To put it simply, there are two ways in which heavy metals can be reduced: either directly by the nanoparticles, or by first adsorbing the metals onto the surface of the nanoparticles, after which they can be further reduced to lower valences. These nanoparticles readily undergo biodegradation with an increase in rate upon decrease to low hazardous levels (Wu et al., 2019).

Adsorbate and biosorbent, for example, are optimized based on factors such as reaction conditions, contact duration, pH, temperature, starting heavy metal ion concentration, and ionic nature (Pourfadakari et al., 2017; Al-Sultany et al., 2019).

Figures (7, 8, 9, and 10) also show the relationship between the percentage of removal of the studied heavy elements and the amount of addition of laboratory-made nanocellulose from potato plants, which was (0.5 and 1) grams, and the acidity function of the polluted water, which was in two stages: the first stage was acidic at pH (5.5–7.5), and the second stage was basic at pH (8–9.5). The results showed that at the acidic stage, the removal percentage was higher compared to the basic stage, and this is clear from the results of the statistical analysis.

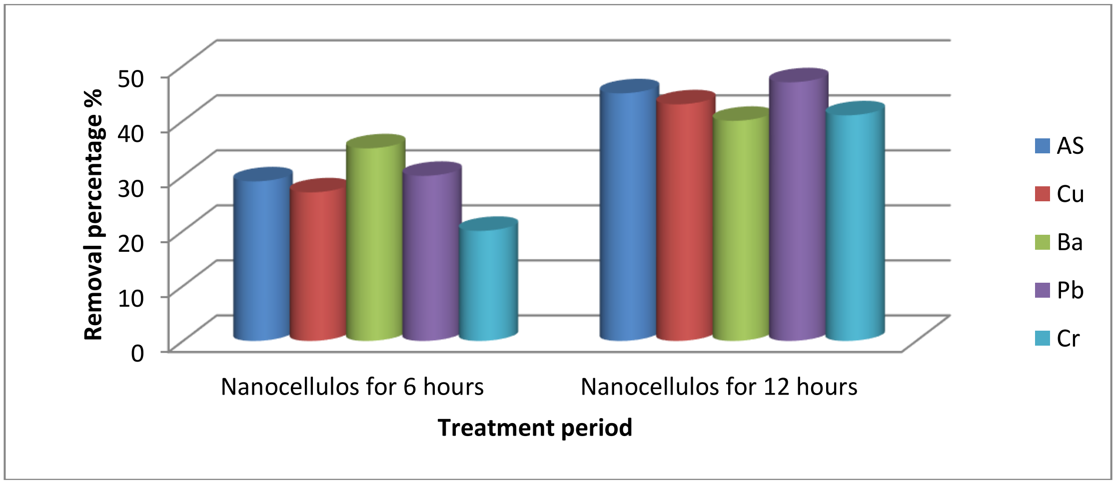

Figure (7) Percentage of elements removal from wastewater after adding 0.5 grams of nanocellulose at pH (5.5 – 7.5)

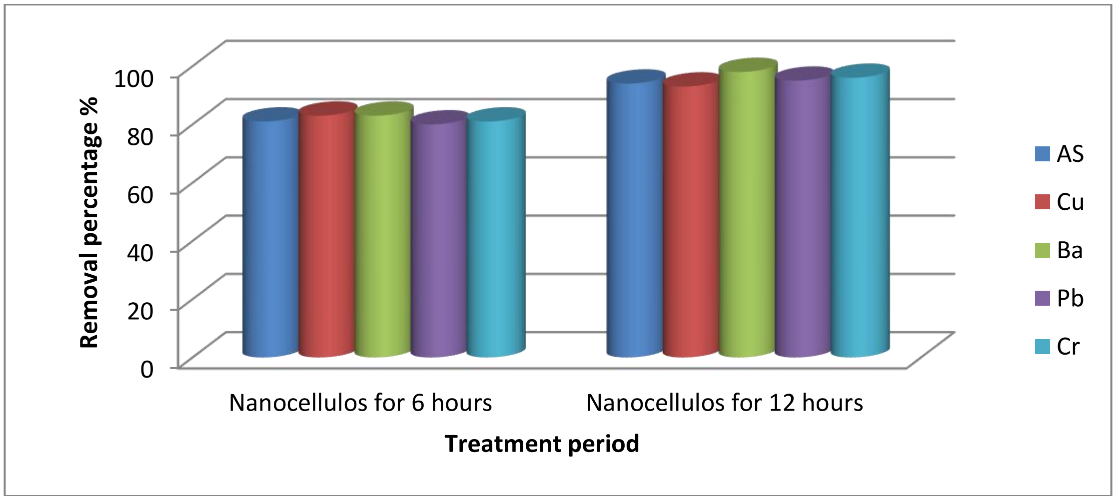

Figure (8). Percentage of elements removed from wastewater after adding 1 gram of nanocellulose at pH (5.5 – 7.5)

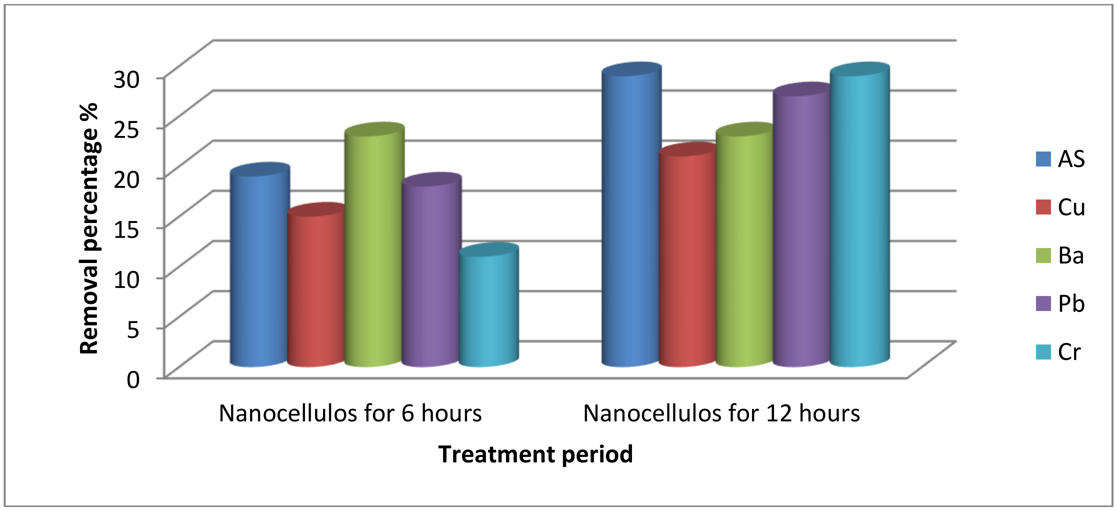

Figure (9). Percentage of elements removal from wastewater after adding 0.5 grams of nano cellulose at pH (8-9.5)

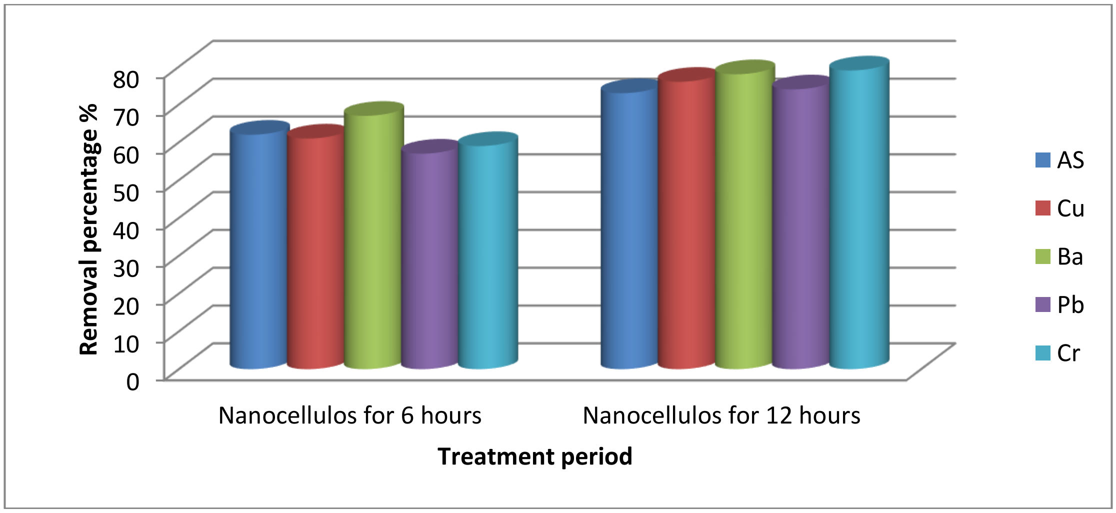

Figure (10). Percentage of elements removed from wastewater after adding 1 gram of nano cellulose at pH (8-9.5)

It was shown that the deprotonated functional groups at higher pH values compared to lower pH values result in greater binding at high pH values compared to low pH values, leading to improved sorption efficacy. The adsorption process is best explained as physisorption at low pH and chemisorption at high pH (Kim et al., 2021).

The size and texture of biogenic nanoparticles are influenced by the pH of the media. Since ambient circumstances maximize the rate at which metal ion reduction occurs, ambient pressure is optimal. The quality and kind of nanoparticles are influenced by the length of time the reaction media is incubated. Long-term storage, for example, may cause the nanoparticles to shrink or agglomerate, lose their homogeneity, or react with the environment (Peralta-Videa et al., 2016).

The kind and strength of the interactions between the adsorbents and the adsorption sites are determined by the charges on the adsorbent's surface. An essential metric It represents the zero-charge point (PZC), or pH of the adsorbent surface free of charge. While the adsorption of anionic molecules is beneficial when the pH of the solution is less than the adsorbent's pHPZC, the adsorption of cationic molecules is beneficial when the pH of the solution is higher. The adsorption effect is enhanced by additional carboxyl groups since they frequently produce more anions on the surface and a higher electrostatic attraction to metal ions (Ghorai et al., 2014). These studies also showed that changes in pH, contact duration, and metal ion concentration had an impact on heavy metal absorption (Chen et al., 2009).

Conclusion

Numerous remediation techniques have been developed over time to address the heavy metal pollution resulting from both industrial and human activities. Because the produced substance is non-toxic and has a high remediation efficiency, nano bioremediation has shown itself to be a game-changer. Using a greener strategy has resulted in a noteworthy decrease in hazardous effects and heavy metal pollution, as well as a reduction in total cost and remediation time.

A sustainable green method was used in the manufacture of nanocellulose material in the laboratory, and the nanosized was confirmed using some tests (FTIR, AFM, and SPM). This nanomaterial was used to remove some heavy metals (arsenic, copper, baron, lead, and chromium) from wastewater collected from wastewater treatment plants. The results of the current study showed that the ability of nanocellulose to be removed depends on its added quantity and the time of contact with wastewater, in addition to the pH of the removal medium. The greater the amount of nanocellulose and the time of contact in an acidic medium, the removal rate increases, and vice versa.

Funding
There is no funding to report.

Ethical approvals
This study does not involve experiments on animals or human subjects.

Data Availability Statement
The corresponding author may provide the data from this study upon request.

Conflicts of Interest
The authors declare no conflict of interest.

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