Materials Research Express

**PAPER**

**A novel modified cellulose nanomaterials (CNMs) for remediation of chromium (VI) ions from wastewater**

Hizkeal Tsade Kara, Sisay Tadesse Anshebo and Fedlu Kedir Sabir

1 Department of Applied Chemistry, School of Applied Natural Science, Adama Science and Technology University, PO Box 1888, Adama, Ethiopia
2 Department of Chemistry, College of Natural and Computational Science, Hawassa University, Hawassa, PO Box 05, Ethiopia

E-mail: hizts4@gmail.com

**Keywords:** cellulose nanomaterials, wastewater, Cr(VI) ions, surface modification, remediation

**Abstract**

Wastewater (WW) remediation technologies were the most crucial issues all over the world at present time. Thus, the remediation of Cr (VI) ions from real WW was conducted using green biocompatible and biodegradable pristine (CNM) and succinic anhydride functionalized cellulose nanomaterial (S-CNMs) adsorbents. Both CNMs and S-CNMs adsorbents were prepared by using sulfuric acid hydrolysis method and characterized for particle sizes, functional groups, and surface morphologies by using XRD, FT-IR, and SEM instruments, respectively. The physicochemical properties of the collected WW were investigated. Next, both the prepared adsorbents were applied for the remediation of Cr (VI) ions from WW. The remediation processes are spontaneous and have higher remediation efficiencies of Cr (VI) ions from WW. The Cr (VI) ions remediation mechanism was evaluated from both the Cr (VI) ions adsorption isotherms and kinetic concepts. Both Langmuir and Freundlich Cr (VI) ions adsorption isotherm models were certainly fixed to a maximum Cr (VI) ions uptake capability \( q_{\text{max}} \) of 60.24 and 156.25 mg g\(^{-1}\) by CNM and S-CNMs sorbents, respectively, and it follows pseudo-second-order (PSO) kinetics model through chemisorption processes. The Cr (VI) ions uptake capabilities were hindered by the presence of organic matter and any other competing pollutants in the WW. The S-CNMs sorbent was selected for the regeneration study due to its higher efficiencies of remediation relative to CNM sorbent and the study was conducted through desorption of Cr (VI) ions by using HCl. Findings have shown that the sorbent was easily recyclable and applicable for the remediation of pollutants from real WW after consecutive 13th cycles.

---

**1. Introduction**

Different heavy metals are released into aqueous bodies from diverse natural and anthropogenic activities, such as, different industries, urban developments, increased number of population and others. They are also called hypothetically toxic elements and have lead several risks to all living things. Because of this effect, they have need careful management. These metals are arsenic (As), lead (Pb), chromium (Cr), copper (Cu), zinc (Zn), cobalt (Co), molybdenum (Mo) and manganese (Mn)\(^1, 2\). From these heavy metals, Cr has a potential risk to the whole environment in general and wastewater in particular because of its non-biodegradability, carcinogenicity, persistence and bioaccumulation nature. From the chemistry of Cr, one can see that it exists as both trivalent chromium Cr(III) and hexavalent chromium Cr(VI) in the natural environment. Also they are essential Cr(III) to maintain human body metabolism and toxic Cr(VI) to living things, highly mobile in water bodies and found in the three forms \( \text{CrO}_4^{2-}, \text{HCrO}_4^-, \text{Cr}_2\text{O}_7^{2-} \) \(^3\). Different major sources for chrome pollution throughout the world are, tannery plant, chrome tanning plant, electroplating plant, hardware factory, electropolishing plant, etc., and the estimated Cr(VI) amount in wastewater are in the range of 0.1 and 200 mg l\(^{-1}\) \(^4\). Based on the World Health Organization view, the amount of Cr (VI) in the drinking potable water should not exceed 0.05 mg l\(^{-1}\) and that initiates different researchers focus to investigate chromium remediation throughout the world \(^5\).
In the 21st century, a lot of technologies have been introduced to competently decontaminate the contaminated wastewater [6]. These are chemical precipitation, filtration, reverse osmosis, solvent extraction, ion exchange, coagulation and adsorption [7, 8]. Even though, most of these technologies need high price, have relatively low remediation capabilities and call for further treatments [9]. For instance, chemical precipitation methods can yield secondary pollution in the form of high amounts of sludge and toxic fumes, and also require high price and not appropriate for remediating water contaminated with high amounts of heavy metals; ion-exchange process also require high price, appropriate to only small volumes of wastewater, and characteristically provides low capabilities [10, 11]. But, amongst these methods, adsorption seems to be the most one because of its simple operation, cost friendly, better remediation sensitivity, higher uptake capability and easily available as adsorbent materials like activated carbon, carbon nanotubes (CNT), composites and nanoparticles [12–17]. Because of cost and recycling of adsorbent materials, polymeric materials including cellulose, chitin, chitosan, gelatin, alginate and starch for the eradication of noxious nutrients from aqueous media has been the 21st century chooses. However, its unique characteristics, the limitations of the above stated materials such as cellulose based materials in water remediation processes shown that the decreased hydrophilicity, low physical and chemical stability and low pollutants uptake capability [18]. This drawback can be improved by converting cellulose into nano form to enhance its pollutant uptake capabilities [13]. Nanomaterials are good candidates to be used as adsorbing agents in remediation processes due to their high specific surface areas with very small particle sizes. Among these, cellulose nanomaterials (CNMs) are good-looking for Cr (VI) ions remediation from wastewater due to their bioavailability, biocompatibility, sustainability, environmentally friendly, renewability, their high aspect ratio and abundant surface active sites and easily available without influencing any food security [19, 20].

From different literature review, CNMs are nanomaterials that have high specific surface area with values ranging from 52 m$^{2}$ g$^{-1}$ to 107 m$^{2}$ g$^{-1}$, based on the preparation methods [21, 22]. It is known that the high surface areas and small particle sizes are very significant to increase the efficiency of Cr(VI) ions remediation. However, CNMs typically have low remediation capability and less dimensional stability. Therefore, it requires chemical modifications, to increase the remediation capability and dimensional stability. Thus, the chemical functionalization was performed by the introduction of anions or cations into the surface of CNMs through the addition of specific oxidizing agents in the cellulosic active functional group sites [23–27]. From this approach, one can gain knowledge about the optimization of concern features, such as, declined hydrophilicity, increased electrical conductivity, etc. In addition to this, it has substantial remediation capabilities towards different pollutants from contaminated effluents [28–30].

Increased number of researches have been done before on the CNMs based sorbents obtained from different polymeric materials including plant materials, date palm (Phoenix Dactylifera L.) [31], Cotton residue [32], banana [33], corn husk [34] and others. To the best of the author knowledge, no work has been done on the CNMs sorbents collected from the stem of Millettia ferruginea (Ethiopian indigenous plants). Also, the stem of this plants have less economic values compared to other wood plants of Ethiopia. Furthermore, previously most of the researches reported on the remediation of Cr (VI) ions from WW were using synthetic WW, but, there is a few researches reported using real WW. These all reasons initiate the researcher to study on the preparation of novel CNMs for the removal of Cr (II) ions from real WW. Therefore, the study was focused on the preparation and characterization of novel chemical modified CNMs from the stem of Millettia ferruginea plant for the remediation of Cr(VI) ions from real WW.

2. Materials and methods

2.1. Materials and chemicals

The stem of Millettia ferruginea plant was collected from Sidama Region ‘Hawassa’, Ethiopia. Wastewater (WW) sample was collected from the run of Modjo River, Oromia Region, Ethiopia. All the chemicals and reagents used were analytical grade. These chemicals include toluene (99%, Loba Chemie Pvt. Ltd, India), ethanol (97%, Tradewell International Pvt. Ltd, India), sodium hydroxide (99%, Shradhha Associates (GUJ) Pvt. Ltd, India), conc. hydrochloric acid (35%, Loba Chemie Pvt. Ltd, India), conc. sulfuric acid (69%, Loba Chemie Pvt. Ltd, India), conc. nitric acid (69%, Loba Chemie Pvt. Ltd, India), sodium chloride (80%, Shanghai ZZ New Material Tech. Co., Ltd, China) and sodium bicarbonate (99%, Shradhha Associates (GUJ) Pvt. Ltd, India) & potassium dichromate ($K_2Cr_2O_7$) (SDFCL, India).

2.2. Experimental procedures

The measurements on the physicochemical properties of WW were conducted. The measured WW was spiked with Cr (VI) ions stock solution and kept for the remediation studies in refrigerator. The stock solution of Cr (VI) ions was done by adding the suitable amount of $K_2Cr_2O_7$ in WW sample. The standard series were prepared
by diluting the stock solution of the Cr (VI) ions. All the remediation experiments were conducted in triplicate and the results were reported as average values.

2.3. Preparation of cellulose and CNMs from *Millettia ferruginea*

The carefully collected and Botanist confirmed stem of *Millettia ferruginea* plant sample was washed with distilled water repeatedly to remove any dust particles; dried at room temperature with the help of air and grinded using grinder carefully. Followed this, the solvent extraction was carried out using 10 g of the lignocellulosic biomass and a mixture of 2:1 toluene/ethanol solvent by volume for about 48 h at 50 °C. After this, the mixture was washed with boiling water, filtrated and dried in oven at 50 °C for 10 h. Then the dried fibers were cut into short fibers of approximately 4 mm in length. Next, these short fibers were treated with 100 ml of 2.5 M NaOH solution at 50 °C for 3 h to remove the lignin and hemicelluloses present in lignocellulosic biomass. Afterwards, this solution was washed well with deionized water repeatedly until it become free from any alkaline solution. Thereafter, the neutral solution was filtered, centrifuged and dried in oven at 50 °C for 10 h. Then it was grinded into a pulp form and bleached with a 4:1 (v/v) ratio mixture of sodium chlorite (NaClO₂) and glacial acetic acid for 4 h at 60 °C under mechanical stirring. This procedure was repeated with half of the initial amount of bleaching agent. Finally, this mixture was centrifuged, filtered and formed as cellulose suspension. The produced cellulose suspension was free of any non-cellulosic constituents, because, it was well treated with 100 ml of 2.5 M NaOH solution and homogenized in homogenizer about 12,000 rpm for 2.5 h. Finally, the prepared CNM was kept in suitable place for characterization purpose. This procedure was adapted from Abraham *et al.*, [35] with modification and the procedure was used throughout the experiments. The summary of experimental procedure for the preparation of CNM was given in figure 1.

2.3.1. Preparation of functionalized CNM: esterification

A definite amount (30 g) of the early prepared CNM was treated with 0.20 l of NaOH solution (20 wt.%) at room temperature at least for 16 h through magnetic stirring. The alkali-cellulose formed was separated from the solution using centrifuge and washed with distilled water down to neutral pH, filtered and dried. Then 20 g of the separated cellulose was reacted with 32 g of succinic anhydride for 24 h. This CNM suspension was centrifugated and filtered, washed in sequence with dimethylformamide (DMF), ethanol 95%, distilled water, HNO₃ (0.01 mol L⁻¹) and finally with acetone. In order to get carboxylate functions for a better chelating function than...
the carboxylic group, succinylated cellulose was treated with a saturated sodium bicarbonate solution for 30 min under constant stirring and afterwards filtered, finally washed with distilled water and then acetone and dried in oven to yield S-CNM. This procedure was taken from study reported by Hokkanen et al., [36] by a slight modification. Afterwards it was ready for characterization and placed safe and clean place. The functionalization chemical reaction was represented in figure 2.

2.4. Characterization
The crystalline structure and particle size of the CNMs such as, CNM and S-CNM sorbents were characterized by using XRD (Shimadzu Corporation, Japan) with a Cu-Kα radiation (λ = 0.154 nm) at 40 kV and 30 mA under a 2θ diffraction angle from 10° to 80° at a scan rate of 3° min⁻¹. The functional group of the synthesized CNM and S-CNM sorbents were identified using the Fourier transforms infrared spectroscopy (FTIR) (PerkinElmer, BX FTIR, India). The surface morphology of the CNM and S-CNM sorbents were examined using SEM (JCM-6000plus, JEOL/EO, America).

2.5. Adsorption experiments
For adsorption studies, the stock solution of Cr (VI) ions and required amount of CNM and S-CNM adsorbent doses were taken in 50 ml beaker and shaken with an orbital shaker for 90 min. The pH of Cr (VI) ions solution was adjusted using dilute HCl and NaOH solutions by pH meter. Through filtration the solid/liquid stages were separated. Then the absorbance measurement of Cr (VI) ions solutions was done by atomic absorption spectrophotometer (AAS, Shimadzu, USA). All experimental procedures were done by determining different parameters that influencing the Cr (VI) ions remediation ability, such as, solution pH ranged from 2–9, adsorbent dose ranged from 0.02–2.5 g, contact time ranged from 30–180 min, agitation speed ranged from 100–350 rpm and initial adsorbate concentration ranged from 0.5–4.5 mg l⁻¹. The consequence of each parameter on the Cr (VI) ions remediation ability was done by making the rest parameters at optimum values.

2.5.1. Adsorption isotherms
Adsorption isotherms are paramount important mathematical model to describe the distribution of Cr (VI) ions among the liquid and solid phases of CNM and S-CNM adsorbents according to a set of assumptions that are associated to the type of coverage, the heterogeneity or homogeneity of the solid surface and the opportunity of interaction between the Cr (VI) ions. Thus, the quantity of Cr(VI) ions remediation by sorption was predicted by using a mass balance on the remediation method. The mass balance shows that the quantity of Cr (VI) ions adsorbed onto the CNM and S-CNM adsorbents is equal to the amount of Cr (VI) ions that were removed from the WW samples. These can be presented by equations (1) and (2).

\[ q_e = \frac{C_iCr(VI) - C_eCr(VI)}{S} \]  
\[ q_t = \frac{C_iCr(VI) - C_eCr(VI)}{S} \]  

Where \( q_e \) and \( q_t \) represent the amount of heavy metal adsorbed on adsorbent surface at equilibrium and at any specific time (mg g⁻¹), respectively. \( C_i \), Cr (VI) and \( C_e \), Cr (VI) represent the initial and equilibrium concentration of the heavy metal in the WW sample (mg l⁻¹), respectively and \( C_i \) is the concentration of Cr (VI) ions in wastewater samples (mg l⁻¹) at a specific time. \( S \) represents the slurry dosage defined as the ratio between the mass of adsorbent, CNM and S-CNM adsorbents (g), to the initial volume of water sample (L). Initial and equilibrium concentration were used to determine the percent Cr (VI) ions remediation (equation (3)).

\[ \%Cr(VI) \text{ ions remediation} = \frac{C_iCr(VI) - C_eCr(VI)}{C_iCr(VI)} \times 100\% \]  

The thermodynamics of the remediation process was detected by having information about Give free energy value whether spontaneous or non-spontaneous [34, 35]. So, the thermodynamics of the Cr (VI) ions remediation was carried out by using all the predetermined and optimized values of parameters (solution pH,
sorbent dosage, shaking time, agitation speed and Cr(VI) ions initial concentration) and varying the temperature from 25°C–40 °C.

2.5.2. Adsorption kinetics
Adsorption is time dependent process and it is paramount important to have information for the rate of remediation and evaluate the adsorbents Cr (VI) ions removing efficiencies from WW. Thus, Cr(VI) ions remediation kinetics process from WW was performed by using the contact time as; 30 to 180 min by making all parameters such as, solution pH, sorbent dose, agitation speed and Cr(VI) ions initial concentration at constant and optimized value.

2.6. Regeneration experiment
Regeneration experiments of S-CNM sorbent in remediation of Cr (VI) ions from WW was done by replicating the experimental procedures using the same S-CNM sorbent for at least 13 successive cycles. Desorption of Cr (VI) ions was performed by adding 0.3 g S-CNM sorbent before used for remediating of Cr (VI) ions from WW to a flask containing 10 ml of 0.1 M HCl solution for 20 min and then sonicating for 4 min. Next to this, the S-CNM sorbent was separated from the solution using centrifugation. The separated S-CNM sorbent was then washed with deionized water for four times, dried and reused for continual adsorption–desorption techniques.

3. Results and discussion

3.1. Characterization
Both the pristine (CNM) and succinic anhydride functionalized (S-CNM) adsorbents were characterized by using FT-IR, XRD and SEM characterization techniques. FT-IR spectroscopy technique reveals the functional groups and surface characteristics of the synthesized CNM and S-CNM adsorbents. The FT-IR spectra of CNM and S-CNM adsorbents were presented in figure 3(a). It has been reported that CNM adsorbent shown the characteristic absorption peaks at 3372, 2931, 1637 and 1062 cm⁻¹. The broadened band at 3372 cm⁻¹ is associated to the stretching vibration of hydroxyl groups and at 2931 cm⁻¹ associated to the C–H stretching vibration. The peak at 1637 cm⁻¹ relates to the bending vibration of the absorbed water [37]. The peak at 1062 cm⁻¹ was attributed to the O–H bending vibration [38]. The formation of esterification reaction between cellulose and succinic anhydride was confirmed by the presence of a new band at 1731 cm⁻¹ which corresponds to the asymmetric and symmetric stretching of ester C–O functional groups in the spectrum of S-CNM [39]. In addition to this, appearance of the peak at 1503 cm⁻¹ and 1329 cm⁻¹ related to the asymmetric and symmetric stretching vibrations of the ionic carboxylic groups. This indicates the formation of carboxylic groups on the surface of S-CNM [40]. Furthermore, the peak at 674 cm⁻¹ related to 6-glycosidic links between the glucose units of cellulose. The presence of this band in the S-CNM adsorbents spectra is attention-grabbing, since it is suggestive that cellulolic material may have not been lost during the esterification [41, 42].

X-Ray diffractometry was used to determine the crystallinity and the particle size of the synthesized cellulose nanomaterials (CNMs) and presented in figure 3(b). From the XRD spectra, the main peaks observed at 15.56°, 22.48° and 34.56°, shown the representative cellulose-I structure and the crystals displayed the characteristic designation of 110, 200, and 004 planes, respectively [18]. The crystallite size was calculated for both adsorbents and the values were 2.30 nm and 2.75 nm for S-CNM and CNM, respectively. Also, the widths of both adsorbents were 3.677 nm and 3.04478 nm, respectively. This result is in agreement with researches reported by Andreas, et al [43] on correlating cellulose nanocrystal particle size and surface area. The peaks generally, exhibited that a semi-crystalline with an amorphous widened hamp and crystalline bands. This is due to the fact that the sorbent materials were prepared from polymeric source materials, which does not show the 100% crystallinity nature. The crystallinity appears in the peaks probable to the use of chemical method (acid hydrolysis), which ultimately resulted in a loss of amorphous structure of the cellulose chain [44]. In comparison, the representative absorption peaks found at 15.89° and 22.4° for the esterificated cellulose nanomaterials (S-CNM) exhibited the decreased crystallinity percent than the raw CNM. This is because of the non-compact region of the crystalline parts was transformed progressively with the adding of succinic anhydride into CNM suspension during esterification process to form carboxylate group (COO⁻) on the surfaces of CNM.

Figures 3(c) and (d) indicates the surface morphology and microstructure of both CNM & S-CNM adsorbents, respectively. It has been shown that the rod-like shape, which displayed an interconnected and greatly permeable interacted structure with coarsely uniform pore sizes with increased specific surface areas, was observed. This is because of the highly homogenization of the adsorbent materials during preparation process and the ratio of surface area to volume for the adsorbents is meaningfully increased by the help of homogenization processes. Furthermore, the fibers of CNMs spatially separated from each other. It is true that after succinic anhydride functionalization process the cellulose nanomaterials had actual rough surfaces.
powerfully recommends that the significant increase in coarseness detected by SEM micrographs is related with cellulose development induced by the interaction of succinic anhydride with the surface OH groups on the CNMs. In that, the specific surface area of the adsorbent increased with the increasing roughness of the surface and decreasing the particle size than the pristine CNM adsorbent [45]. Therefore, an increased number of active sites are present for Cr(VI) ions adsorption on the surfaces of the S-CNM adsorbent than CNM adsorbent.

3.2. Physicochemical properties of the WW

Table 1 indicated the values for the physicochemical measurement of the wastewater (WW). The average amount of pH value was 5.3 ± 0.02. This finding suggests that the WW taken from the run of Modjo River was nearly acidic. Next to this, the average amounts of COD and BOD were 73.9 ± 0.03 and 61.05 ± 0.02 mg l⁻¹, respectively. The average amounts of TDS, Cl⁻, SO₄²⁻, Ca²⁺, Mg²⁺, and Cu²⁺ were 43.4 ± 0.02, 42.3 ± 0.02, 73.6 ± 0.5, 92.6 ± 0.3, 75.6 ± 0.2 and 0.40 ± 0.02 mg l⁻¹, respectively. The findings have shown that there are certain amounts of cations and anions present in the chromium wastewater and competes with the Cr(VI) ions during remediation process.

Figure 3. (a) FT-IR spectra of CNM & S-CNM, (b) XRD Spectra of CNM & S-CNM, (c) SEM images of CNM and (d) SEM images of S-CNM, respectively.
3.3. Adsorption studies

3.3.1. Consequences of contact times on the remediation of Cr (VI) ions

The effects of contact time on the remediation of Cr (VI) ions from wastewater was conducted by varying the contact times from 30–180 min at optimized agitation speed of 300 rpm, CNM and S-CNM dose of 0.3 g, temperature \((T)\) of 25 °C, and initial concentration of heavy metals of 2 mg l\(^{-1}\) (figure 4(b)). The increasing processes for the remediation were observed by increasing the contact time from 30 to 90 min for both CNM and S-CNM adsorbents because of the presence of fresh surfaces available in this short time without any interference [46]. The higher % remediation \((%R)\) of Cr (VI) ions \((64.25\% \text{ and } 90.9\%)\) was detected at the optimum time of 90 min for CNM and S-CNM adsorbents, respectively. After this, the remediation processes reaches at equilibrium and proceed with a constant amount. Furthermore, the greater Cr (VI) ions uptake capabilities were detected for S-CNM sorbent than CNM was due to the presence of numerous fresh surfaces which easily bind the Cr (VI) ions onto the surfaces possessing a large number of reactive carboxyl groups resulted from succinic anhydride modified reaction. This result agrees with researches reported by [40].

3.3.2. Consequence of initial concentration on the percent remediation of Cr (VI) ions

The consequences of initial concentration \((C_i)\) of Cr (VI) ions for the remediation process by CNM and S-CNM adsorbent systems were represented (figure 4(a)). Initially, the remediation process proceeds quickly and within...
very short time it reaches the optimum value of 2 mg l$^{-1}$. The accelerated remediation processes at initially, was because of the presence of large unoccupied sites of the CNM and S-CNM adsorbents. At this stage, both adsorbents clearly displayed higher Cr(VI) ions uptake capability. In addition to this, the higher adsorption capability of Cr(VI) ions on S-CNM is obviously perceived compared to Cr(VI) ions on CNM. This is due to the relatively increased surface area of S-CNM sorbent was observed through direct addition of carboxyl and ester groups by the reaction of succinic anhydride into CNM [47–49].

3.3.3. Consequence of adsorbent dose and temperature on the percent remediation of Cr (VI) ions

Figure 5(a) indicated the consequences of CNM and S-CNM dosage on the %R of Cr(VI) ions from the WW using CNM and S-CNM adsorbents. Findings indicated that 61.3% and 90.25% of Cr(VI) ions can be eradicated from wastewater by using both CNM and S-CNM adsorbents with optimum adsorbent dosage of 0.3 g at 25°C. The higher %R (90.25%) of Cr(VI) ions was observed by using S-CNM adsorbent than CNM because of the presence of extra ester and carboxyl groups to the surface of CNM. These extra functional groups resulted from the addition of succinic anhydride to CNM and provide fresh and active sites for the functionalized adsorbent. The resulted fresh and active sites lead increased adsorption of Cr(VI) ions from WW. On the whole, it can be summarized that for both nanosorbents the %R of Cr(VI) ions increase by increasing the adsorbents dosage to optimum values after that the remediation capability decreases. This is anticipated because of the fact that at increased concentrations of nanosorbents maximum availability of replaceable surfaces for the ions. However, at increased concentrations there is no further increase in adsorption owing to the quantity of ions bond to the nanosorbent and the quantity of mobile ions in the wastewater becomes fixed even with extra addition of the nanoorbents dose [50, 51].

The temperature effects on the %R of Cr(VI) ions from wastewater by using CNM and S-CNM sorbents was represented (figures 5(a) and (b)). Findings indicated that intensifying the temperature from 25°C to 40°C decreases in %R of Cr(VI) ions from WW. Both CNM and S-CNM sorbents exhibited that the maximum %R (61.3% and 90.3%) of Cr(VI) ions at optimum dosage (0.3 g) and optimum temperature of (25°C). This is due to at expanded temperature; the slow rate of the chemisorption processes prevents the Cr(VI) ions to reach fresh active positions on the sorbent surface for increased %R of Cr(VI) ions from wastewater [52]. Likewise, the greater percentage of Cr(VI) ions remediation of 90.3% was observed by using S-CNM sorbents than CNM sorbents. This is due to the increased specific surface area with very small particle size obtained due to the esterification of CNM with succinic anhydride [53, 54].

3.3.4. Consequences of solution pH on percent eradication Cr (VI) ions removals

Figure 6(a) represented the consequences of solution pH on the %R of Cr(VI) ions from the WW using CNM and S-CNM adsorbents. Both CNM and S-CNM adsorbents indicate increasing remediation abilities in the
solution pH ranged from 2–5 and the maximum %R for both CNM and S-CNM adsorbent was 60.25% and 90.24%, respectively. These are because of the consequences of cations (H⁺) and anions (OH⁻) on the binding of Cr (VI) ions to the surface of CNM and S-CNM adsorbents active sites. At low pH values, the interaction of Cr (VI) ions with sorbents is decreased owing to the concentration of H⁺ ions. In reverse, as the WW pH increases (i.e. less H⁺ ions), Cr (VI) ions adsorption to the CNM and S-CNM sorbents surfaces increases towards the optimum pH value of 5. Followed this, the pH is greater than the optimum value 5, the levels of OH⁻ in WW enhances and the decreased %R of Cr (VI) ions occurred. This results a few Cr (VI) ions adsorption to the CNM and S-CNM sorbents surfaces and provides decreased %R of Cr (VI) ions. Supporting this result Kaprara et al. [55] reported the maximum percent removal of Cr (VI) ions at nearly similar pH values. Also, in line with this, Simeonidis et al. [56] reported the maximum percent removal of Cr (VI) ions at nearly similar pH values. In addition to this, results indicated that the higher %R of Cr (VI) ions were observed by S-CNM adsorbents than CNM sorbent systems at pH value of 5 (figure 6(a)). The differences in the reported %R for the Cr (VI) ions were related to the occurrence of functionalized groups in the structure of S-CNM adsorbents with different affinity to each metal than CNM sorbent [52]. At higher alkaline pH value, the Cr (VI) ions precipitates as Cr(OH)₃.

3.3.5. Consequences of agitation speed on percent remediation of Cr (VI) ions
The consequence of agitation speed on the remediation of Cr (VI) ions from WW was given in figure 6(b). The findings exhibited that the increased %R of Cr (VI) ions was observed by increasing the agitation speed. This was resulted because of the presence of active smaller size adsorbent particles and more energetic sites on the adsorbing surface of the sorbents [57]. Therefore, the remediation capability of Cr (VI) ions was increased from 34.85% to 59% by CNM adsorbent and 72.5% to 90.74% by S-CNM adsorbent with increasing the agitation speed from 100 to 300 rpm. The higher %R of Cr (VI) ions by both adsorbents were observed at the optimum value of 300 rpm. These result arises from the concept that, the interaction between CNMs and Cr (VI) ions is more effective at this moderate agitation speed. This was in agreement with researches reported by Mahmood et al. [58] on adsorption of heavy metals by using nanosorbents. Beyond this value it decreases, may be, because of the low mass transfer of Cr (VI) ions to the internal surface of CNMs adsorbent particle and also vigorous shaking makes the desorption of the already adsorbed Cr (VI) ions from the sorbent. When compared to the pristine CNM Cr (VI) ions remediating capability with the S-CNM capability, the functionalized (S-CNM) indicated the higher Cr (VI) ions capability due to the conversion of hydroxyl groups to both ester and carboxyl groups.

3.4. The chemistry of wastewater on the Cr (VI) ions remediation
The %R of the Cr (VI) ions from both synthetic and real wastewater was represented in figure 7. From the findings, it was seen that the remediation processes was negatively affected by the presence of cations and anions.
in real wastewater. Results indicate that the decreased %R of Cr(VI) ions from the real wastewater than the synthetic wastewater due to the competition of cations and anions for the active sites of adsorbents in the real wastewater. The consequence of competing ions decreases the interaction of active surfaces on S-CNM adsorbent and Cr(VI) ions and lead decreased %R of Cr(VI) ions [59]. This result was confirmed by the values of %R which were found to be 99.7% and 90.25% for the synthetic and real wastewater, respectively.

3.5. Adsorption isotherms
Both Langmuir and Freundlich isotherm models for the remediation of Cr(VI) ions was given in figures 8(a) and (b). The findings for the Cr(VI) ions remediation by CNM and S-CNM sorbents were fixed using Langmuir and Freundlich isotherms. Clearly, both these isotherms describe the distribution of the Cr(VI) ions among the liquid and solid states according to expectations related to the heterogeneity or homogeneity of the adsorbent surface, the category of coverage, and the prospect of contact between the Cr(VI) ions. That is, Langmuir isotherms refer to the adsorption mechanism with monolayer, and recognize the distribution of Cr(VI) ions
between solid and liquid stages that is on the surface of the CNM and S-CNM sorbents. Its linear form of equation was represented in (equation (4)). Freundlich isotherms (equation (6)), linear form adopt an exponential delay in the active sites density versus the heat of adsorption. Regarding this issue, Freundlich isotherms can be implemented as indicator of the heterogeneity of the adsorbent surfaces. In addition to this, a dimensionless equilibrium parameter (R_L) value for all level is calculated by using equation (5) and it confirms the feasibility of Cr (VI) ions adsorption on CNM and S-CNM adsorbents. The Langmuir and Freundlich isotherm parameter values were given in table 2. From these, the R^2 values for Langmuir isotherm model by using CNM and S-CNM sorbents were 0.963 and 0.985, respectively and the R^2 values for the Freundlich isotherm model by using CNM and S-CNM sorbents were 0.981 & 0.946, respectively. Also, the calculated values of the Langmuir constant b of CNM and S-CNM sorbents for Cr (VI) ions removal were 0.592 and 0.032 Lmg^{-1}, respectively and approve the possibility of remediation processes. In addition to this, the magnitude for K_L and n of CNM and S-CNM sorbents for Cr (VI) ions remediation were (1.035 and 1.036) and (6.32 and 7.78), respectively. These values indicate the improved Cr (VI) ions remediation capability and intensity, respectively.

The maximum Cr (VI) ions remediation efficiency (q_{max}) of the CNM and S-CNM sorbents per unit mass was 60.24 and 156.25 mg g^{-1}, respectively. This displays the adsorbent used have high heavy metal ions remediation ability in general and Cr (VI) ions remediation efficiency in particular. Additionally, the considerable higher remediation ability of the S-CNM sorbent compared to CNM sorbent was because of the augmented amount of functional groups resulted from the addition of succinic anhydride into the CNM. Therefore, from the above all values of adsorption isotherm parameters it is possible to conclude that, the isotherms well fit to describe both Cr (VI) -CNM and Cr (VI) -S-CNM adsorption from wastewater.

\[
\frac{C_e}{Q_e} = \frac{1}{bQ_{max}} \frac{C_e}{Q_{max}}
\]

\[
R_L = \frac{1}{1 + bC_0}
\]

\[
\log q_e = \log k_f + \frac{1}{n} \log C_e
\]

\[
\Delta G^o = -RT \ln K_C
\]

where q_{max} is the maximum eradication capability of heavy metals per unit mass of adsorbent (mg g^{-1}), K_f is the adsorption capability of the CNM and S-CNM sorbents and n is the binding intensity. T is absolute temperature in Kelvin, R is the ideal gas constant (8.314 J mol^{-1}K^{-1}) and K_C is the equilibrium constant calculated by multiplying the sorbate molar weight with Langmuir constant (b).

The thermodynamic study of the Cr (VI) ions remediation process was carried out using standard thermodynamic parameter, such as, Gibbs free energy (\Delta G^o). The Gibbs free energy (\Delta G^o) of the adsorption of Cr (VI) ions on CNM and S-CNM was calculated using equation (7). Table 3 presents the calculated Gibbs free energies for the studied heavy metals. The entire obtained \Delta G^o was negative suggesting spontaneous adsorbing mechanism. Different temperatures (25 °C, 30 °C and 40 °C) were used to determine the thermodynamic parameter and reported at optimized temperature. The value of \Delta G^o change with operational temperature with highest values occurs at optimum temperature of 25 °C suggesting that adsorption efficiency increase by decreasing the temperature and the negative value for \Delta G^o confirms the eradication of Cr (VI) ions was spontaneous and feasible.

### 3.6. Adsorption kinetic

The rates of Cr (VI) ions remediation by CNM and S-CNM sorbents were established using linearized pseudo-first order (equation (8)) and pseudo second order (equation (9)), respectively. The plot of Ce/qe versus Ce and the plot of log qe versus log Ce was given in figures 9(a) and (b), respectively.

\[
\log(qe - qt) = \log qe - \frac{K_f t}{2.303}
\]
The R² determination of the experimental data using pseudo-first order (PFO) kinetics model was too poor both at initial concentration and final eradication processes because the experimental qₑ value was much different than the calculated qₑ value for both sorbents. This specifies that the adsorption kinetics does not follow this model. Therefore, figures 9(a) and (b) indicates a representative fitness of the data corresponding to pseudo second order (PSO) model for Cr (VI) ions adsorption on CNM and S-CNM sorbents. This result was in agreement with the research reported by Priyadarshini et al [60] on kinetics, thermodynamics and isotherm studies on adsorption of eriochrome black-T from aqueous solution using Rutile TiO₂. The kinetics data were found from figures 9(a) and (b) and presented in table 3. The kinetics model delivers maximum correlation coefficient value (R² = 0.987 and 0.992, for PSO) and below satisfactory correlation coefficient value (R² = 0.765 and 0.976, for PFO) in CNM and S-CNM sorbents for Cr(VI) ions remediations, respectively. Therefore, the study indicated that the PSO model better represents the Cr (VI) ions remediation kinetics, suggesting that the remediation processes are chemisorption. This conclusion is because of Langmuir adsorption isotherm models assume the chemisorption occurs between the adsorbent and adsorbate via the formation of an ionic bond. Thus, in this study the chemisorption occurs between the positively charged Cr (VI) ions and the negatively charged CNM adsorbents via the formation of an ionic bond.

### 3.7. Regeneration test

Due to the outstanding binding capability of the sorbent materials S-CNM was selected for regeneration purpose and ready for the desorption experiment and presented in figure 10 for the % heavy metal eradication after the 1st, 4th and 13th cycles. Regeneration assessments were carried out to authenticate the reusability of the material for practical application in real systems. Desorption study of the heavy metals for the adsorbents with HCl

### Table 3. The values of parameters and correlation coefficients of Pseudo second order (PFO) and Pseudo second order (PSO) kinetics.

| Parameters | Kinetics adsorbents | PFO | PSO |
|------------|---------------------|-----|-----|
|             | qₑ. cal. (mg g⁻¹)   | qₑ. exp. (mg g⁻¹) | K₁ | R² | qₑ. cal. (mg g⁻¹) | qₑ. exp. (mg g⁻¹) | K₂ | R² |
| CNM        | 31.09               | 8.25 | 0.534 | 0.765 | 11.83 | 11.78 | 0.898 | 0.992 |
| S-CNM      | 5.69                | 5.54 | 0.273 | 0.976 | 23.23 | 23.20 | 0.387 | 0.987 |

\[
\frac{t}{qₑ} = \frac{1}{K₂qₑ} + \frac{t}{qₑ} \tag{9}
\]
desorption solution was carried out using batch experiments. It is found that the adsorption capability of Cr (VI) ions for S-CNM adsorbents progressively decreases with increasing cycles of reusable trial. The decrease in adsorption capability of the adsorbents with increased reusable times is normally due to the loss of reactive sites on the adsorbents. The pleased reusability with preserving moderately extraordinary binding performance for the selected adsorbent specifies the effective sorbent of S-CNM adsorbents for exploiting in remediation of heavy metal cations and anions or other adsorption systems. Generally, it was found that the binding capability of the S-CNM sorbents did not significantly change after 13th cycle of operation as the % R was yet great. The decreases in %R for the 13 consecutive cycles were no more than 5%. This recommends that this adsorbent can be used for heavy metal removals for long time with an outstanding possibility. This result was in agreement with study conducted by [51] for the removals of heavy metals from wastewater by using HPG-MNP sorbent.

4. Conclusions

Both CNM and S-CNM sorbents were prepared by chemical methods and utilized as low-cost, renewable, high uptake capabilities, have remarkable characteristics and eco-friendly sorbent for the remediation of Cr (VI) ions from real wastewater. The remediation capability of the S-CNM sorbents towards Cr (VI) ions in comparison with the CNM was remarkably improved after succinic anhydride-modification. The proposed mechanisms for the remediation process under optimum condition of S-CNM adsorbent mainly encompass the interaction of ester, carboxyl and hydroxyl groups of cellulose and Cr (VI) ions, lead to the sorbents show the greatest Cr (VI) ions remediation capability for the modified adsorbent than the pristine adsorbent. The Cr (VI) ions-remediation process for both CNM and S-CNM sorbent systems were fitted with both Langmuir and Freundlich isotherm and the rate of the interaction between the Cr (VI) ions and CNM and S-CNM sorbents were described by PSO model. The regeneration experiment results have shown that the used sorbent were re-generable and economically friendly used for successive 13th cycles as adsorbent for contaminant removals. Therefore, in the whole, the obtained results suggested that S-CNM sorbent is considered as an effective sorbent for the removal of Cr (VI) ions in particular and contaminants in general from the wastewater.

Acknowledgments

Authors acknowledge Adama Science and Technology University (ASTU) for funding this work. This work has been funded through Project (ASTU, SoANS/JV-259298/2019), Research and Technology Transfer Office, Adama Science and Technology University.
Conflict of interest

Based on this research work there is no potentially available conflicts of interest, authorship, and/or publication of this article.

ORCID iDs

Hizkeal Tsade Kara ⓒ https://orcid.org/0000-0002-6700-1978
Fedlu Kedir Sabir ⓒ https://orcid.org/0000-0002-6235-1530

References

[1] Mohammed N, Grishkevich N and Tam K C 2018 Environ. Sci. Nano. 5 623–58
[2] Chowdhury S, Mazumder M A J, Al-Attas O and Husain T 2016 Sci. Total Environ. 569–570 476–88
[3] Ayangbenro A S and Babalola O O 2017 Int. J. Environ. Res. Public Health. 14 194
[4] Khadem H, Gabarron M, Abbaspour A, Martinez-Martinez S, Faz A and Acosta J A 2019 chemosphere 11 045
[5] Ali H, Khan E and Ihal I 2019 J. Chem. 199 1–14
[6] Egdawatte S, Datt A, Burns E A and Larsen S C 2015 Langmuir 31 7553–62
[7] Oxlbl M, Aroua M K, Daud W A W and Baroutian S 2009 Water. Air. Soil Pollut. 200 59–77
[8] Shang J, Zong M, Yu Y, Kong X, Du Q and Liao Q 2017 J. Environ. Manage. 197 331–37
[9] Santosh C, Velmurugan V, Jacob G, Jeong S K, Grace A N and Bhattachar J A 2016 Chem. Eng. J. 306 1116–37
[10] Bolisetti S and Mezzenga R 2016 Nat. Nanotechnol. 11 365–71
[11] Hosseini S S, Birjgak E, Tan N R, Ortal I, Ghabramani M, Alaei and Shahmirzadi M A 2016 J. Water Process Eng. 9 78–110
[12] Alipour A, Zarinabadi S, Azimi A and Mirzaei M 2020 International Journal of Biological Macromolecules 151 124–35
[13] Anirudhan T S, Deepa J R and Chirsta J 2016 Journal of Colloid and Interface Science 467 307–20
[14] Chang L, Qingmiao W, Feifei J and Shaoxian S 2019 Journal of Molecular Liquids 292 111390
[15] Bhanjana G, Dilbaghi N, Kim K and Kumar S 2017 Journal of Molecular Liquids 242 966–70
[16] Li J, Zuo K, Wu W, Xu Z, Yi Y, Jing Y and Dai H 2018 Carbohydrate Polymers 196 376–84
[17] Pyrzynska K 2019 Journal of Environmental Chemical Engineering 7 102795
[18] Anirudhan T S and Shainy F 2015 Journal of Colloid and Interface Science 452 22–31
[19] Yu L, Ruan S, Xu X, Zou R and Hu J 2017 Nano Today. 17 79–95
[20] Kamar Z, Hakalabti M, Tammelin T and Mathew A P 2017 RSC Adv. 7 5232–41
[21] De E M, Melo J H and Clark A S 2017 Green Chem. 19 3408–17
[22] Habibi S and Jamshidi M 2020 Mater. Sci. Semicond. Process. 109 104927
[23] Rol F, Belgacem M N, Gandini A and Bras J 2019 Prog. Polym. Sci. 88 241–64
[24] Barbosa R F S, Souza A G, Ferreira F F and Rosa D S 2019 Carbohydr. Polym. 218 208–17
[25] Sebaqui H, Mushil E, Morimune S, Salajok M, Nishino T and Berglund I A 2012 ACS Appl. Mater. Interfaces 4 1043–9
[26] Li C, Ma H, Venkateswaran S and Haos B S 2019 Chem. Eng. J. 389 123458
[27] Zhou H, Zou H, Xue F, He H and Wang S 2020 Chem. Eng. J. 385 123879
[28] Kumar M, Ijose A M, Somasekharita H, Rao A, Fauzi I, Farnood R and Namibti PMG 2020 Chem. Eng. J. 393 124367
[29] Liu P, Borelli P, Biczio M, Kokol V, Oksman K and Mathew 2015 Hazard. Mater. 297 184–175
[30] Zhou Y, Fu S, Zhang L, Zhan H and Levit MV 2014 Carbohydr. Polym. 101 75–82
[31] Adel A, El-Shafei A, Ibrahim A and Al-Shemy M 2018 Industrial Crops & Products 124 155–65
[32] Do Nascimento J H O, Almomani F, Bhosale R, Khraisheh M and Almomani T 2019 Desalination and Water Treatment. 229 101308–10
[33] Barros E C S, Santos L S Jr, Silva M M F, Fonseca M G, Santana S A A and Airoldi C 2013 J. Mater. Sci. Semicond. Process. 16 79–87
[55] Kaprara E, Tziarou N, Kalaitzidou K, Simeonidis K and Balcells L 2017 Sci. Total Environ. 605-606 190–8
[56] Simeonidis K, Kaprara E, Samaras T, Angelakeris M, Pliatsikas N and Vourlias G 2015 Sci. Total Environ. 535 61–8
[57] Elboughdiri N 2020 Cogent Engineering 7 1782623
[58] Mahmood Z, Zahra S, Iqbal M and Aamir M 2017 Appl Water Sci. 7 3469–81
[59] Rangabhashiyam S, Giri M S, Nandagopal Nakkeeran E and Selvaraju N 2016 Environ. Monit. Assess. 188 411
[60] Priyadarshini R et al 2018 IOP Conf. Ser.: Mater. Sci. Eng. 310 012051