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RESEARCH PAPER

Remediation of Contaminated Water with Chromium VI by Sorption in Surface-activated-nanocellulose spheroids

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ABSTRACT

Chromium VI is a frequent pollutant of industrial liquid effluents. It is a substance classified as a carcinogen group I. In this study, a Cr VI sorption mechanism was developed by using nanocellulose spheroids (hydrogel) obtained from ivory nut. Cr VI was detected in water by a colorimetric method, using 1, 5-diphenylcarbazide at λ 540 nm. Then, the sorption capacity of nanocellulose spheroids was tested by varying the solution's pH and temperatures. The outcome of the experiment shows that the most efficient pollutant's adsorption conditions are occur at pH 4 and 25 °C. Removal percentages of Cr VI reached 91.29% (+/-1.36) and 95.33% (+/- 0.86). Additionally, the sorption kinetics showed that the adsorption reaction on the material reaches its equilibrium 20 to 30 minutes after the reaction starts. Finally, an analysis of adsorption isotherms showed a high adjustment with the Langmuir and Freundlinch isotherms. In this frame, this work's results show that nanocellulose beads are an interesting alternative to efficiently reduce Cr VI from industrial and drinking water.

Keywords: hydrogel pH-temperature sorption isotherms

INTRODUCTION

Water quality is considered a big concern since it is the most vital resource on which social, economic, and ecosystem activities depend (Kumar et al., 2020; Westall and Brack, 2018). Its preservation is a priority within a context where water pollution is considered as one of the most significant challenges humanity must overcome (Kardam et al., 2014). Water is said to be polluted when it contains micro- organisms of animal or human origin, industrial or domestic sewage, organic or inorganic substances or poisonous chemical substances (Mitiku, 2020)

Water pollutants can be classified as organic such as hydrocarbons, proteins, fats, oils, esters, pesticides, and aromatic compounds (Wilson and Jones, 1993); whereas the inorganic pollutants as heavy metals are of special concern (Chowdhury et al., 2016). Heavy metals are introduced into the environment naturally due to volcanic activity (Park et al., 2000), rock erosion and forest fires. On the other hand, anthropogenic activities such as mining, agriculture, and industry play a major role in water pollution (Owa, 2013). Metals such as Cu, Zn, Ni, Pb, Cd, and Cr have been found to harm human and animal health (Adimalla, 2020). Chromium's importance must be highlighted over other polluting metals since it is widely used in wood preservation, as well as plastic and pigments production (Oladoja et al., 2013). Cr VI resulting from industrial waste contaminates countless bodies of water worldwide which has severe impacts on human and animal health (Kardam et al., 2014). The

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International Agency for Research on Cancer has classified this element as a group I carcinogen specially affecting lung and gastrointestinal tract (Straif et al., 2009; Zhang et al., 2020).

Due to the high impact of Cr VI in nature and human health, it is of high importance developing decontamination strategies for industrial waters. Among the techniques used to decontaminate Cr VI the most efficient and utilized are: oxidation-reduction (Li et al., 2018; phytoremediation (Rezania et al., 2015); ion exchange (Fu and Wang, 2011); precipitation (Cainglet et al., 2020); capture by biopolymers (Gupta and Diwan, 2017); adsorption (Fu and Wang, 2011); membrane filtration (Owlad et al., 2009); biosorption (Abdolali et al., 2017); and capture by nanoparticles (Qu et al., 2013). The use of nanoparticles, due to its high surface area, are the most promising strategies to remove Cr VI from water (Bhattacharya et al., 2013);

Nanoparticles measure less than 100 nm in at least one of their three physical dimensions. Many of them contain high reactivity and sorption capacity (Klemm et al., 2018). Functionalization of nanoparticles enhances their ionic strength to interact with heavy metals such as Cr VI.

Nanocellulose (NC) as a prominent material for decontamination of Cr VI. It is extracted from the most widespread, renewable and sustainable biopolymer on earth (Dhali et al, 2021). Nanocellulose is obtained when cellulose chains are bundled together generating highly ordered regions that can be isolated (Trache et al, 2020)

Additionally, Nanocellulose fibers (NCF) have properties that stand out for many applications and their extraction from lignocellulosic biomass, especially from agricultural residues, has been extensively studied (Tshikovhi et al., 2020). In the production of cellulose nanoparticles, non-cellulosic materials such as lignin and hemicellulose are removed by a pretreatment (Phanthong et al., 2018). The separation of lignin and other molecules interact with cellulose in lignocellulosic materials requires intensive energy input and, frequently, the use of polluting chemicals (Portero et al., 2020).

NC retains several cellulose properties, such as its hydrophobicity, crystallinity, and ability to be modified (Klemm et al., 2018). Three types of these particles can be found: nanocellulose crystals (CNC), cellulose nanofibrils (CNF), and bacterial nano cellulose (BNC). They differ from each other in their origin and in the obtainment methods, functionalization, shape, particle size, size dispersity, and mechanical characteristics (De France et al., 2017).

In this framework, the use of non-lignocellulosic feedstocks such as seeds may facilitate NC's extraction. Seeds lack of lignin and offer opportunities as novel feedstocks for nanomaterial production (Haafiz et al., 2013).

Moreover, NC has been widely used for its mechanical and chemical properties. The hydroxyl groups present on its surface allow a relatively easy chemical modification (He et al., 2014). The modifications lead to an increase in the range of applications of these nanoparticles. Esterification of positive or negative chemical groups to the primary or secondary hydroxyl groups of glucose monomers is the most employed strategy for surface modification of cellulose nanoparticles (Gan et al., 2020). Modified NC can bind charged molecules via ionic linkages.

This study reports the use of tagua NC spheroids for the remediation of Cr VI contaminated water. Through the use of specially tailored hydrogel spheroids masked with quaternary ammonium. It is proved to be a promising technique as it has been possible to remove up to between 91.29-95.33% of Cr VI in an aqueous solution.

MATERIALS AND METHODS

The nanocellulose fibers were prepared through hydrolysis using sulfuric acid. Then, 20 g of tagua pulp was chopped in a blender. Next, 175 mL of sulfuric acid was added at a concentration of 64% w/w preheated at 45 °C. The reaction continued for 60 minutes maintaining stable temperature. Subsequently, the reaction is stopped by adding diH_2O. Then, it was centrifuged and washed using dialysis membranes until the pH was neutral (Menon et al., 2017). Finally, it was sonicated with a Vibra-Cell sonicator (Sonics & Materials Inc., Newtown, CT, USA) for 30 minutes at 25ºC (Qua et al., 2009). The hydrogel was prepared with ultra-pure water and sonicated at 130 W and 20 kHz for 3-5 minutes until a consistent, homogeneous and transparent hydrogel was obtained.

Moreover, the shape and approximate size of the NC particles were measured by using a Brucker — model dimension icon AFM. This allowed to characterize nanoparticles in width, depth, and length. A series of dilution factors were tested to obtain individual fiber nanoparticles.

Additionally, a solution was prepared with 1.46 g of quaternary ammonium in one liter of water (Bingol et al., 2004). The sol-to-gel transition of the aqueous solution of nanocellulose (1% w/v), was attained by dripping 10 mL of nanocellulose suspension (1% w/v) onto 25 mL of a quaternary ammonium solution preheated at different temperatures (50, 60, 70 and 80 ° C).

To detect Cr VI in the solutions 1.5 g of 1,5-diphenylcarbazide (complexing agent) were dissolved in 50 mL of acetone (Huang et al., 2020). Then, a mix of 10 µL of H_2SO_4 50% v/v solution, and 20 µL of the complexing agent were dissolved in 1 mL of a solution with $K_2Cr_2O_7$. Finally, a spectrophotometer (Helyos β, Thermospectronic) was used to detect the presence of Cr VI at 540 nm (Mohamad et al., 2013).

Meanwhile, a stock solution (1,000 mg Cr (VI)/L) was prepared by dissolving 2.829 g of $K_2Cr_2O_7$ (CAS 7778-50-9; ≥99.0%; Sigma–Aldrich) in 1 L of deionized distilled water. For nanocellulose spheroids sorption experiments, diluted solutions were prepared with concentrations ranging from 10 to 100 mg Cr (VI)/L (Campaña et al., 2019). Subsequently, a calibration curve type $y = mx + b$ was used by assaying concentrations within the range 0.01 to 1 mg/L, to obtain a linear equation. This equation was used to calculate the concentration of Cr VI in water.

In order to achieve the study aim, a series of Cr VI solutions of 10 and 100 mg/L were adjusted at pH 4, 6 and, 8, respectively. The solutions were tested at temperatures of 15, 20, and 25 (°C). Nanocellulose spheroids were added to each Cr VI solution in a ratio of 1:2. Then, they were stirred for 3 hours at the temperatures mentioned above. The experiments were performed by triplicate. Additionally, the concentration of the solution exposed to the NC was calculated. The percentage of metal removal (% MR) was obtained with equation 1:

$$\% RM = \frac{Ci - Ce}{Ci} * 100 \quad (1)$$

Where: *Ci* is the initial Concentration, and *Ce* is the final Concentration of Cr VI (Zhu et al., 2014)

As part of the statistical analysis, an angular transformation was made on the % MR in order to normalize the data expressed in terms of percentage for statistical analysis. Consequently, ANOVA calculated the significance, and a Tukey test was established to determine the optimal Cr VI sorption conditions (Lee & Lee, 2018).

Once optimum pH and temperature were established, a series of solutions of Cr VI at concentrations 10, 25, 50, 75, 100 (mg/L), were added to nanocellulose gel spheroids at a 2:1 volume rate. The tests were carried out by triplicate at 10, 15, 20, 30, 90, 120, and 180 minutes.

Subsequently, the % MR and the Concentration of Cr VI removed were plotted as a function of time.

Where: q_e is the amount of metal adsorbed at equilibrium (mg/g); c_i is the initial and equilibrium Concentration (mg/L); c_e is the equilibrium concentration (mg/L); v is the volume of solution (L); and w is the amount of biosorbent (g) (Zhu et al., 2014).

Two isotherms were evaluated, the Langmuir's and Freundlich's isotherms. Equations 2 and 3 were used for this purpose:

$$q_e = \frac{q_m * b * c_e}{1 + b * c_e} \tag{2}$$

$$q_e = k_f * c_e^{\frac{1}{n_f}} \tag{3}$$

Where q_e is the amount of metal adsorbed in equilibrium (mg/g); q_m is the maximum amount of adsorbate adsorbed (mg/g); c_e is the final Concentration of the metal (mg/L); b is the Langmuir constant (L/mg); n_f is the affinity constant between adsorbate and adsorbent; and k_f is the Freundlich constant (Yao et al. 2016).

Finally, A column of 26 cm length, 1 cm diameter, and 20 mL capacity was packed with NC spheroids. Then it was filled with Cr VI solutions at concentrations of 10, 100 mg/L. After that, the samples were injected under pressure. These experiments were carried out at 25 °C for 20 and 30 minutes.

RESULTS AND DISCUSSION

Acid extraction was primarily the strategy to dissolve hemicellulose, hydrolyze cellulose bundles, and functionalize cellulose fibrils. Before gelation, the extracted nanocellulose presents a massive ultrastructure, where single bundles or fibrils are almost impossible to distinguish. Nanocellulose particles get homogeneously dispersed in water as a stable colloid system. This outcome results of the esterification of hydroxyl group by sulfate ions (Phanthong et al., 2018). Ultrasound helps the dispersion of nanoparticles to get stable suspensions (Li et al., 2013).

According to Meier, 1958 ivory nut contains 6% of NC. Moreover, it is important to highlight the absence of lignin on ivory nut NC, according to Phanthong et al., 2018 lignocellulosic sources contain about 10- 25% by weight dry like raw banana fiber containing 5.7% of lignin, jute fiber 10.7% (Abraham et al., 2011; Krishnamoorthy, 2021).

Moreover, individual fibrils are visible after a series of dilutions with water. The most appropriate dilution was 2 x 10^{-3} (Fig. 1). Also, the elongated fibrils vary in terms of dimensions within a range of 3-5 nm in width. Remarkably, these fibers present longitudinal folding that generates angles. Thus, this characteristic contributes to the entanglement of gels (Chaabouni & Boufi, 2017). Compared to other studies fibrils dimensions can vary according to the source as nanocellulose obtained from banana rachis 10-60 nm, pineapple 20-80 nm, leaf 50-150 and coir 40- 90 nm (Deepa et al., 2015).

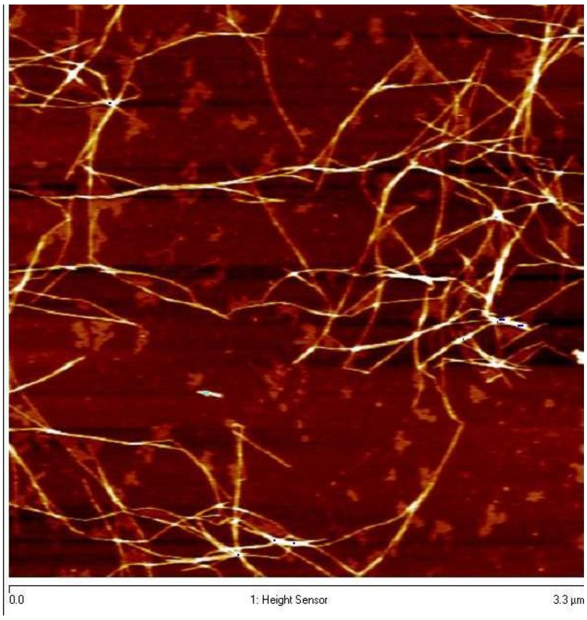

Fig 1. An image of NC fibers in AFM 3.3 um bar scale.

Our analysis showed that he optimum formation of gel spheroids (in terms of their consistency and shape) was attained at 70 °C. The spheroids were formed with an average diameter of 2 mm (Fig. 2). Heat enhances the interaction between cationic surfactants and negative charges of nanocellulose, consequently, the resultant spheroids' consistency and shape are a direct function of crosslinking (Bora and Dutta, 2014).

Fig 2. Nanocellulose spheres treated with quaternary ammonium.

In this study, the nanocellulose produced was obtained from the fractionation of the endosperm of tagua (*Phytelephas aequatorialis*). As a product it acquires a surface charge, given by the esterification of OH groups in glucose with SO_3^- groups. According to previous analyzes (unpublished data), it is known that this nanocellulose contains 0.128 mmol- SO_3^- /

g. As well, the concentration of SO_3^- groups esterified to OH groups in glucose, depends on the acid hydrolysis conditions. For example, Harris & McNeil, 2020 found 0 - 1.9 mmol SO_3^- / g.

On the other hand, quaternary ammonium is a cationic surfactant that has been used on clays and zeolites since it improves the affinity with non-ionic and hydrophobic organic compounds (Li & Bowman, 1998). It has also been used to modify the surface of nanocellulose (He et al., 2014). For example; Li et al., (2018) used quaternary ammonium to promote antibacterial activity in nanocellulose-based materials (Chen et al., 2017) used ammonium-modified nanocellulose to degrade methyl orange dye.

Moreover, quaternary ammonium is a cation with an NR_4^+; where R represents the alkyl/aryl group structure that can easily interact with the SO_3^- functional group of nanocellulose fibrils (Gerba, 2015). When nanocellulose was dripped on dissolved quaternary ammonium, crosslinking occurred with additional surface charge change. This charged surface interacts with Cr VI in aqueous solution (Li et al., 2018).

Additionally, the ANOVA analysis did not show statistically significant differences regarding the different temperature treatments. The pH is the only factor that affects the % MR significantly. Additionally, Tukey's test showed the higher Cr VI removal at pH 4.0. In several studies, the influence of pH for the sorption of Cr VI was evaluated. These have shown that this factor (pH) has a significant impact on the percentage of removal (Tovar et al., 2014). It is also known that Cr VI can be present in many forms such as H_2CrO_4, $HCrO_4^-$, CrO_3^{-2} and $Cr_2O_7^{-2}$; depending on pH and its Concentration (Jiang et al., 2014). Thus, when the pH is between 1 and 4, the predominant form is $HCrO_4$. It interacts with the monovalent anion NR_4^+. Next, when the pH increases, the most common forms of Cr VI are $Cr_2O_7^{-2}$ and $Cr_2O_4^{-2}$. So that two anions of NR_4^+ interact with those forms of Cr VI. Consequently, with a higher pH the MR % decreases (Karthikeyan et al., 2005).

The results of this research coincide with those obtained in a study carried out by He et al., 2014 which reported that the highest Cr VI sorption values were between pH 3 to 4. Moreover, an acidic pH is favorable because of protons (H^+) increase on the nanocellulose surface. Giving rise to a strong electrostatic attraction between the positively charged surface and the chromate ions (Fijałkowska et al., 2020). Additionally, Haroon et al., 2020 used activated carbon and found that at a pH of 3 the highest sorption values were obtained. According to the ANOVA results, the temperature variation in the experiments did not show a statistical significance. Nevertheless, a slight enhancement of Cr VI sorption at higher temperatures would be associated with the reaction's endothermic nature. This phenomenon can be explained by the increase of the intraparticular diffusion rate of Cr VI ions, into the nanocellulose spheroids' pores (Zhang et al., 2014). Moreover, the final Concentration of Cr VI decreases until the matrix is saturated. In Table 1, it can be observed that the concentration decreases progressively until it reaches 20 to 30 minutes. Since the % MR increased as time passed; all the samples were exposed for 180 min (3 h). However, it can be seen that the majority of the samples reached their maximum % MR in the vicinity of 20 to 30 minutes (Table 2). While in the study done by, He et al., 2014 it took around 50 minutes to obtain an efficiency of almost 100%. In the research of Jiang et al., 2014, sorption equilibrium was obtained at 120 min. This because HA-Fe_3O_4 was used to adsorb Cr VI; resulting in a % MR of 80 to 90%. On the other hand, Zhu et al., 2014 study obtained a 80% efficiency in 10 minutes.

Table 1. Variation on the final Concentration of solutions of Cr VI after being exposed to the sorption matrix during different timeslots.

Time (min)	**Initial Concentration mg/L**				
0	10	25	50	75	100
10	2.04 ± 0.03*	4.27 ± 0.38	43.09 ± 0.95	44.60 ± 0.92	27.71 ± 0.96
15	1,22 ± 0.06	2.83 ± 0.19	6.91 ± 0.67	7.37 ± 0.68	26.51 ± 1.21
20	0,68 ± 0.02	2.17 ± 0.20	6.59 ± 0.96	6.21 ± 0.43	10.93 ± 1.04
30	0,69 ± 0.001	2.17 ± 0.34	2.96 ± 0.35	3.49 ± 0.64	8.15 ± 0.66

* Standard deviation

Table 2. Variation of% RM in solutions of Cr VI after being exposed to the sorption matrix for different timeslots.

Time (min)	**Initial Concentration mg/L**				
0	10	25	50	75	100
10	79.34 ± 0.96 *	82.91 ± 1.53	13.81 ± 1.91	40.53 ± 1.23	72.28 ± 0.96
15	87.66 ± 1.216	88.67 ± 0.78	86.17 ± 1.35	90.17 ± 0.91	73.48 ± 1.21
20	93.18 ± 1.04	91.29 ± 0.80	86.81 ± 1.92	91,71 ± 0.58	89.06 ± 1.04
30	93.08 ± 0.66	91.29 ± 1.36	94.07 ± 0.7	95.33 ± 0.86	91.84 ± 0.66

* Standard deviation

Water remediation must include an isotherm analysis to determine its effectiveness (Lombardo and Thielemans, 2019). Additionally, it is essential to establish an equal saturation time to increase its productivity. The isotherms analysis relates the amount of solute adsorbed in equilibrium per weight of adsorbent (Romero et al., 2005).

Two adsorption isotherms were evaluated: Langmuir and Freundlich. For the Langmuir isotherm, a linear graph was constructed as a function of the final metal concentration (mg/L) (*ce*); and the amount of metal adsorbed at equilibrium (mg/g) (*qe*). As a result, an R^2 of 0.979 was obtained out of the linear regression. Additionally, values for *Qm* and *b* were obtained, 588.232 mg/g and 4.25 $x10^{-5}$

For the Freundlich isotherm, another linear regression was obtained, whose R^2 was 0.966. In addition, the value of the heterogeneity factor (*n*) was calculated, and the Freundlich constant (k_f) which is associated with the adsorption capacity. The values obtained were 0.8917 and 1.31025 (mg / g)] respectively.

The results obtained were adjusted to Langmuir's isotherm, meaning that the surface of the adsorbent and all the sorption sites are homogeneously distributed. Besides, each cation can interact with a single molecule of Cr VI, forming a monolayer as a consequence (Giles et al.,1974). It also suggests that uptake occurs on a homogeneous surface and assumes uniform energies of adsorption onto the surface, followed by a transmigration of the adsorbate (Romero et al., 2005). However, results also show a high adjustment to the Freundlich isotherm, which means that multilayer adsorption also occurs (Yao, 2016), this model proposes a monolayer with heterogeneous energetic distribution of active sites, describing also an interaction between the absorbed molecules (Romero et al., 2005).

The adsorption method showed higher efficiency compared to other published works. A comparison is shown in Table 3.

As can be evidenced in Table 3 *Qm* stands out comparing the value with other studies. This parameter enhances the absorbate absorbed by the matrix, we suggest that the porosity of the material promotes the affinity that was evidenced on our results. Additionally, *b* value corresponds to the constant representing the affinity, the lower the value, the higher the affinity. Remarkably, the surface modification given to the nanocellulose spheroids promotes the affinity due to ionic bonds between Cr VI and the modified matrix.

Table 3. Adsorption isotherms data reported in the literature and contrasted with the present study.

Methodology	*Qm*	b	*n*	Reference
Surface-activated-nanocellulose	588.235	4.25 x10^{-5}	0.8917	Current work
Quaternary ammonium-functionalized aerogels	17.66	2.24	-	He et al (2014)
Polyaniline impregnated nanocellulose composite	48.92	2.16	-	Jain et al (2017)
Modified cellulose	22.20	0.214	-	Kalidhasan. et al (2012)
Chitosan	153.850	5.978 x10^{-3}	0.7353	Baran et al. (2007)
Chitin	70.422	9.670x10-3	1.76603	Baran et al. (2007)
Agave lechuguilla biomass		2.95 x10^{-4}	10.22	Romero et al. (2005)
Surfactant–modified serpentine for fluoride	57.33	2.188		Mobarak et al. (2019)

In practical terms, the water treatments are performed in columns that save space; improve the surface contact with the water pollutants; and allow cleaning and or replacement of the adsorbent matrix (Leupin et al., 2005).

Complimentary experiments carried on in columns (data not shown) yielded very similar results when compared to the experiments in beakers herein reported, where MR% were ranged between 91.29% (+/-1.36) and 95.33% (+/- 0.86) of the total Cr VI. Columns ensure the distribution of the contaminated bed homogeneously in the adsorbent (Ali, 2014). A notable advantage of columns is that the NC matrix can undergo a desorption process after saturation. Thus, they can be reutilized (Figueira et al., 2004).

CONCLUSIONS

To summarize, the use of a nanocellulose hydrogel as a bio sorbent to remediate water contaminated with Cr VI was shown to be an efficient method (% removal of the metal between 91.29- 95.33%) (He et al. 2014). The pH produced an increase in the sorption capacity of this material. On the other hand, in the sorption kinetics, a sorption equilibrium was obtained at 20-30 min depending on the metal’s initial concentration. Additionally, this experiment fitted the Langmuir adsorption isotherm better than the Freundlich isotherm. High affinity was shown between the adsorbent and the adsorbate.

Finally, the column's use to capture Cr VI showed an efficiency similar to the tests carried out previously tests where different concentrations, pH, and temperature was considered. Therefore, nanocellulose spheroids masked with quaternary ammonium (a porous hydrogel matrix masked by a strong cation) represent a suitable combination to remediate water contaminated with Cr VI. Lastly, nanocellulose spheroids can also be reutilized after regeneration cycles. The applied methodology seems to be an efficient method to remediate water contaminated with Cr VI (Fig. 3)

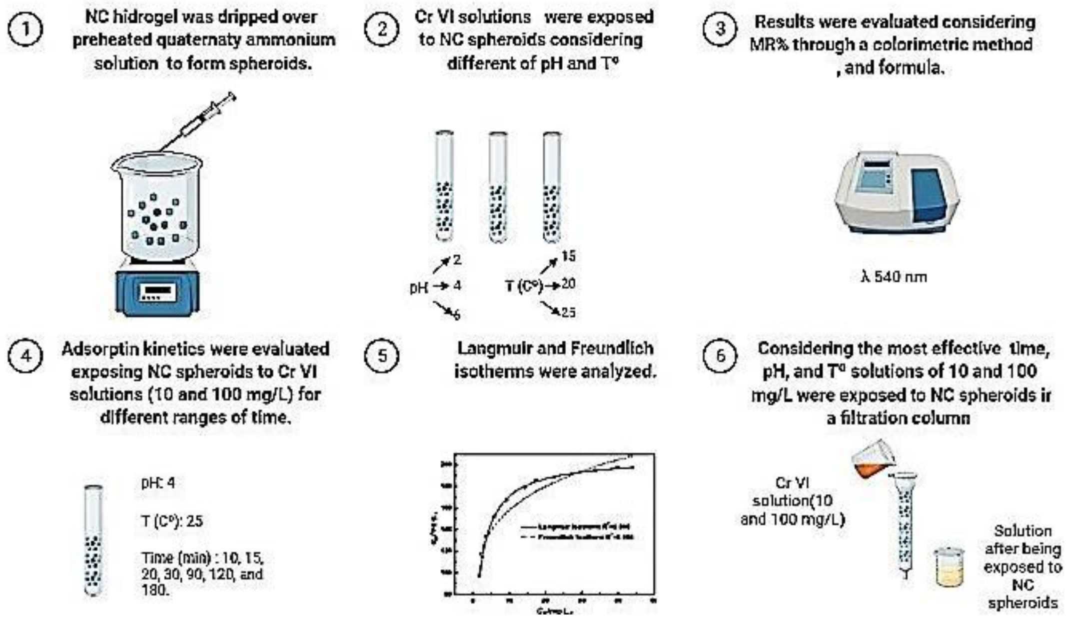

Fig 3. Cr VI remotion process employing nanocellulose spheroids

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CONFLICT OF INTEREST

The authors declare there is no conflicts of interest in this study.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research

REFERENCES

Abdolali, A., Ngo, H., Guo, W., Zhou, L., Zhang, J., Liang, S. and Liu, Y. (2017). Application of a breakthrough biosorbent for removing heavy metals from synthetic and real wastewaters in a lab-scale continuous fixed-bed column. Bioresour. Technol., 229;78-87.

Abraham, E., Deepa, B., Pothan, L. A., Jacob, M., Thomas, S., Cvelbar, U. and Anandjiwala, R. (2011). Extraction of nanocellulose fibrils from lignocellulosic fibres: A novel approach. Carbohydr. Polym., 86(4); 1468-1475.

Adimalla, N. (2020). Heavy Metals Pollution Assessment and Its Associated Human Health Risk Evaluation of Urban Soils from Indian Cities: A Review. Environ. Geochem. Health,42 (1); 173–90.

Ali, I. (2014). Water treatment by adsorption columns: evaluation at ground level". Sep. Purif. Rev., 43 (3); 175-205.

Baran, A., Bıçak, E., Baysal, Ş. H. and Önal, S. (2007). Comparative studies on the adsorption of Cr(VI) ions on to various sorbents. Bioresour. Technol., 98(3); 661–665.

Bhattacharya, S., Saha, I., Mukhopadhyay, A., Chattopadhyay, D. and Chand, U. (2013). Role of nanotechnology in water treatment and purification: potential applications and implications. Int J Chem Sci Technol., 3(3); 59-64.

Bingol, A., Ucun, H., Bayhan, Y. K., Karagunduz, A., Cakici, A. and Keskinler, B. (2004). Removal of Chromate Anions from Aqueous Stream by a Cationic Surfactant-Modified Yeast. Bioresour. Technol. 94 (3); 245–49.

Bora, T. and Dutta, J. (2014). Applications of nanotechnology in wastewater treatment — a review. J. Nanosci. Nanotechnol., 14 (1); 613-626.

Cainglet, A., Tesfamariam, A. and Heiderscheidt, E. (2020). Organic Polyelectrolytes as the Sole Precipitation Agent in Municipal Wastewater Treatment. J. Environ. Manage. 271; 111002.

Campaña-Pérez, J. F., Barahona, P. P., Martín-Ramos, P. and Barriga, E. J. C. (2019). Ecuadorian yeast species as microbial particles for Cr (VI) biosorption. Environ. Sci. Pollut. Res., 26(27); 28162-28172.

Chaabouni, O. and Boufi, S. (2017). Cellulose nanofibrils/polyvinyl acetate nanocomposite adhesives with improved mechanical properties. Carbohydr. Polym., 156; 64-70.

Chen, Y., Liu, H., Geng, B., Ru, J., Cheng, C., Zhao, Y. and Wang, L. 2017. A reusable surface-quaternized nanocellulose-based hybrid cryogel loaded with N-doped TiO_2 for self-integrated adsorption / photo-degradation of methyl orange dye. RSC Adv., 7 (28); 17279-17288.

Chowdhury, S., Mazumder, M. J., Al-Attas, O. and Husain, T. (2016). Heavy Metals in Drinking Water: Occurrences, Implications, and Future Needs in Developing Countries. Sci. Total Environ. 569; 476–488.

De France, K. , Hoare, T. and Cranston, E. (2017). Review of hydrogels and aerogels containing nanocellulose. Chem. Mater., 29(11);4609-4631.

Deepa, B., Abraham, E., Cordeiro, N., Mozetic, M., Mathew, A. P., Oksman, K. and Pothan, L. (2015). Utilization of various lignocellulosic biomass for the production of nanocellulose: a comparative study. Cellulose, 22(2); 1075–1090.

Dhali, K., Ghasemlou, M., Daver, F., Cass, P. and Adhikari, B. (2021). A review of nanocellulose as a new material towards environmental sustainability. Sci. Total Environ., 15; 145871.

Figueira, G. M., Park, K. J., Brod, F. P. R. and Honorio, S. L. (2004). Evaluation of desorption isotherms, drying rates and inulin concentration of chicory roots (Cichorium intybus L.) with and without enzymatic inactivation. J. Food Eng., 63(3); 273-280.

Fijałkowska, G., Wiśniewska, M. and Szewczuk-Karpisz, K. (2020). Adsorption and electrokinetic studies in kaolinite/anionic polyacrylamide/chromate ions system. Colloids Surf., A, 603; 125232.

Fu, F. and Wang, Q. (2011). Removal of heavy metal ions from wastewaters: a review. Journal of environmental management, 92(3); 407-418.

Gan, P. G., Sam, S. T., Abdullah, M. F. B. and Omar, M. F. (2020). Thermal Properties of Nanocellulose-Reinforced Composites: A Review. J. Appl. Polym. Sci. 137 (11); 48544.

Gerba, C. (2015). Quaternary ammonium biocides: efficacy in application. Appl. Environ. Microbiol., 81 (2); 464-469.

Giles, C. H., Smith, D. and Huitson, A. (1974). A general treatment and classification of the solute adsorption isotherm. I. Theoretical. J. Colloid Interface Sci., 47 (3); 755-765.

Gupta, P. and Batul, D. (2017). Bacterial Exopolysaccharide Mediated Heavy Metal Removal: A Review on Biosynthesis, Mechanism and Remediation Strategies. Appl. Biotechnol. Rep. 13; 58-71.

Haafiz, M. M., Eichhorn, S. J., Hassan, A. and Jawaid, M. (2013). Isolation and characterization of microcrystalline cellulose from oil palm biomass residue. Carbohydr. Polym., 93(2); 628-634.

Haroon, H., Shah, J. A., Khan, M. S., Alam, T., Khan, R., Asad, S. Arif, M., Farooq, G., Iqbal, M. and Bilal, M. (2020). Activated carbon from a specific plant precursor biomass for hazardous Cr (VI) adsorption and recovery studies in batch and column reactors: Isotherm and kinetic modeling. J. Water Process. Eng., 38; 101577.

Harris, J. T. and McNeil, A. J. (2020). Localized hydrogels based on cellulose nanofibers and wood pulp for rapid removal of methylene blue. J. Polym. Sci., 58(21); 3042-3049.

He, X., Cheng, L., Wang, Y., Zhao, J., Zhang, W. and Lu, C. (2014). Aerogels from quaternary ammonium-functionalized cellulose nanofibers for rapid removal of Cr (VI) from toilet. Carbohydr. Polym., 111; 683-687.

Huang, Y., Zeng, Q., Hu, L., Xiong, D., Zhong, H. and He, Z. (2020). Column study of enhanced Cr (Ⅵ) removal and removal mechanisms by *Sporosarcina saromensis* W5 assisted bio-permeable reactive barrier. J. Hazard. Mater., 405; 24115.

Jain, P., Varshney, S., Srivastava, S. (2017). Site-specific functionalization for chemical speciation of Cr (III) and Cr (VI) using polyaniline impregnated nanocellulose composite: equilibrium, kinetic, and thermodynamic modeling. Appl. Water Sci., 7(4); 1827-1839.

Jiang, W., Cai, Q., Xu, W., Yang, M., Cai, Y., Dionysiou, D., O'Shea, K. (2014). Cr (VI) Adsorption and Reduction by Humic Acid Coated on Magnetite. Environ. Sci. Technol., 48 (14); 8078–8085.

Kalidhasan, S., Gupta, P. A., Cholleti, V. R., Kumar, A. S. K., Rajesh, V. and Rajesh, N. (2012). Microwave assisted solvent free green preparation and physicochemical characterization of surfactant-anchored cellulose and its relevance toward the effective adsorption of chromium. J. Colloid Interface Sci., 372 (1); 88-98.

Kardam, A., Raj, K. R., Srivastava, S. and Srivastava, M. M. (2014). Nanocellulose Fibers for Biosorption of Cadmium, Nickel, and Lead Ions from Aqueous Solution. Clean Technol. Environ. Policy 16 (2); 385–93.

Karthikeyan, T., Rajgopal, S., Miranda, L. (2005). Chromium (VI) adsorption from aqueous solution by Hevea Brasilinesis sawdust activated carbon. J. Hazard. Mater., 124 (1-3); 192-199.

Klemm, D., Cranston, E. D., Fischer, D., Gama, M., Kedzior, S. A., Kralisch, D., Rauchfuss, F. (2018). Nanocellulose as a natural source for groundbreaking applications in materials science: Today’s state. Mater. Today, 21(7); 720-748.

Kumar, V., Sharma, A., Kumar, R., Bhardwaj, R., Kumar Thukral, A. and Rodrigo-Comino, J. (2020). Assessment of heavy-metal pollution in three different Indian water bodies by combination of multivariate analysis and water pollution indices. HERA, 26(1), 1-16.

Krishnamoorthy, K. (Ed.). (2021). Novel Nanomaterials: Energy storage and harvesting applications of nanomaterials.

Lee, S. and Lee, D. K. (2018). What is the proper way to apply the multiple comparison test?. Korean J. Anesthesiol., 71 (5); 353.

Leupin, O. X., Hug, S. J. and Badruzzaman, A. B. M. (2005). Arsenic Removal from Bangladesh Tube Well Water with Filter Columns Containing Zerovalent Iron Filings and Sand. Environ. Sci. Technol., 39(20); 8032–8037.

Li, M., Liu, X., Liu, N., Guo, Z., Singh, PK, & Fu, S. (2018). Effect of surface wettability on the antibacterial activity of nanocellulose-based material with quaternary ammonium groups. Colloids Surf., A, 554; 122-128.

Li, Y., Li, G., Zou, Y., Zhou, Q. and Lian, X. (2013). Preparation and characterization of cellulose nanofibers from partly mercerized cotton by mixed acid hydrolysis. Cellulose, 21(1); 301–309.

Li, Z., Bowman, R. 1998. Sorption of perchlorethylene by surfactant-modified zeolite as controlled by surfactant loading. Environ. Sci. Technol., 32 (15); 2278-2282.

Lombardo, S. and Thielemans, W. (2019). Thermodynamics of Adsorption on Nanocellulose Surfaces. Cellulose 26 (1); 249–79.

Meier, Hans. 1958. On the Structure of Cell Walls and Cell Wall Mannans from Ivory Nuts and from Dates. BBA, 28; 229–40.

Menon, M. P., Selvakumar, R. and Ramakrishna, S. (2017). Extraction and modification of cellulose nanofibers derived from biomass for environmental application. RSC Adv., 7(68); 42750-42773.

Mitiku, A. A. (2020). A review on water pollution: causes, effects and treatment methods. Int. J. Pharm. Sci. Rev. Res., 60(2); 94-101.

Mobarak, M., Mohamed, E. A., Selim, A. Q., Sellaoui, L., Lamine, A. B., Erto, A. and Seliem, M. K. (2019). Surfactant–modified serpentine for fluoride and Cr (VI) adsorption in single and binary systems: Experimental studies and theoretical modeling. Chem. Eng. J., 369; 333-343.

Mohamad, S., Mohd Yusof, N. H. and Asman, S. (2013). Effect of Bifunctional Isocyanate Linker on Adsorption of Chromium (VI) Diphenylcarbazide Complex onto b-Cyclodextrin." Chem. Asian J. 25 (4); 2213–20.

Oladoja, N. A., Ololade, I. A., Alimi, O. A., Akinnifesi, T. A. and Olaremu, G. A. (2013). Iron incorporated rice husk silica as a sorbent for hexavalent chromium attenuation in aqueous system. Chem. Eng. Res. Des., 91(12); 2691-2702.

Owa, F. D. (2013). Water Pollution: Sources, Effects, Control and Management. Mediterr. J. Soc. Sci. 4 (8); 65.

Owlad, M., Aroua, M., Daud, W. and Baroutian, S. (2009). Removal of hexavalent chromium-contaminated water and wastewater: a review. Water, Air, Soil Pollut., 200 (1-4); 59-77.

Park, C. H., Keyhan, M., Wielinga, B., Fendorf, S. and Matin, A. (2000). Purification to Homogeneity and Characterization of a Novel Pseudomonas Putida Chromate Reductase. Appl. Environ. Microbiol. 66 (5); 1788–95.

Phanthong, P., Reubroycharoen, P., Hao, X., Xu, G., Abudula, A. and Guan, G. (2018). Nanocellulose: Extraction and application. Carbon Resour. Convers., 1(1); 32-43.

Portero Barahona, P., Bastridas, B., Gil, J., Ramos, P. and Carvajar, J. (2020). Cellulosic Ethanol: Improving Cost Efficiency by Coupling Semi-Continuous Fermentation and Simultaneous Saccharification Strategies. Processes 8(11); 1459.

Qu, X., Alvarez, P. J. and Li, Q. (2013). Applications of Nanotechnology in Water and Wastewater Treatment. Water Res. 47 (12); 3931–46.

Qua, E. H., Hornsby, P. R., Sharma, H. S., Lyons, G. and McCall, R. D. (2009). Preparation and characterization of poly (vinyl alcohol) nanocomposites made from cellulose nanofibers. J. Appl. Polym. Sci., 113(4); 2238-2247.

Rezania, Shahabaldin , Ponwaj, M., Talaiekhozani, A., Mohammad, S., Fadhil, M., Mar, S., Sabbaghm, F. and Sairan, F. (2015). Perspectives of Phytoremediation Using Water Hyacinth for Removal of Heavy Metals, Organic and Inorganic Pollutants in Wastewater. J. Environ. Manage. 163; 125–33.

Romero-González, J., Peralta-Videa, J. R., Rodrıguez, E., Ramirez, S. L. and Gardea-Torresdey, J. L. (2005). Determination of thermodynamic parameters of Cr(VI) adsorption from aqueous solution onto Agave lechuguilla biomass. J. Chem. Thermodyn., 37(4); 343–347.

Straif, K., Benbrahim-Tallaa, L., Baan, R., Grosse, Y., Secretan, B., El Ghissassi, F. and Cogliano, V. (2009). A review of human carcinogens—part C: metals, arsenic, dusts, and fibres. Lancet Oncol., 10(5); 453-454.

Tovar, C., Ortiz, A., Paternina, E. (2014). Removal of Pb (II), Ni (II) and Cr (VI) in aqueous solutions using chemically modified matrices. Prospectiva, 12 (2); 7-17.

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. Front. Chem., 8, 392.

Tshikovhi, A., Mishra, S. B. and Mishra, A. K. (2020). Nanocellulose-based composites for the removal of contaminants from wastewater. Int. J. Biol. Macromol., 152; 616-632.

Westall, F. and André, B. (2018). The Importance of Water for Life. Space Sci. Rev. 214 (2); 50.

Wilson, C. and Jones., C. (1993). Bioremediation of Soil Contaminated with Polynuclear Aromatic Hydrocarbons (PAHs): A Review. Environ. Pollut. 81 (3); 229–49.

Yao, C., Wang, F., Cai, Z. and Wang, X. (2016). Aldehyde-functionalized porous nanocellulose for effective removal of heavy metal ions from aqueous solutions. RSC Adv., 6 (95); 92648–92654.

Zhang, Z., Cao, H., Song, N., Zhang, L., Cao, Y. and Tai, J. (2020). Long-Term Hexavalent Chromium Exposure Facilitates Colorectal Cancer in Mice Associated with Changes in Gut Microbiota Composition. Food Chem. Toxicol. 138; 111237.

Zhang, Z. Q., Liao, M. C., Zeng, H. Y., Xu, S., Liu, X. J., Du, J. Z., ... and Huang, Q. J. (2014). Temperature effect on chromium (VI) removal by Mg / Al mixed metal oxides as adsorbents. Appl. Clay Sci., 102; 246-253.

Zhu, J., Gu, H., Guo, J., Chen, M., Wei, H., Luo, Z. and Wei, S. (2014). Mesoporous magnetic carbon nanocomposite fabrics for highly efficient Cr (vi) removal . J. Mater. Chem. A, 2 (7); 2256-2265.