Oxolane-2,5-dione modified electrospun cellulose nanofibers for heavy metals adsorption

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ABSTRACT

Functionalized cellulose nanofibers have been obtained through electrospinning and modification with oxolane-2,5-dione. The application of the nanofibers for adsorption of cadmium and lead ions from model wastewater samples is presented for the first time. Physical and chemical properties of the nanofibers were characterized. Surface chemistry during preparation and functionalization was monitored using Fourier transform-infrared spectroscopy, scanning electron microscopy, carbon-13 solid state nuclear magnetic resonance spectroscopy and Brunauer Emmett and Teller. Enhanced surface area of $13.68\,m^2\,g^{-1}$ was recorded for the nanofibers as compared to the cellulose fibers with a surface area of $3.22\,m^2\,g^{-1}$. Freundlich isotherm was found to describe the interactions better than Langmuir: $K_f = 1.0$ and $2.91\,mmol\,g^{-1}$ ($r^2 = 0.997$ and 0.988) for lead and cadmium, respectively. Regenerability of the fiber mats was investigated and the results obtained indicate sustainability in adsorption efficacy of the material.

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1. Introduction

There are various ways through which wastewater can be treated, such as, adsorption, precipitation, flocculation, ion exchange, reverse osmosis and filtration. Of all these methods, adsorption is the most effective and versatile method for heavy metal removal given that the alternative methods have high operating cost and generates solid waste which poses disposal challenges [1–4]. The use of biopolymers have been suggested as a possible intervention tool for metal removal as they are safe since there is no generation of solid waste as the adsorbents can be regenerated and they are biodegradable. Cellulose, the most abundant of all biopolymers has been studied intensely in the past two decades for possible application in mopping up of toxic heavy metals from the environment [5,6]. It is not effective in its natural form due to limited adsorption sites and low stability. Functionalization strategies have been employed to improve the surface and stability of this abundantly occurring biopolymer. This has been achieved through

two main routes: (i) introduction of functional groups into the raw cellulose backbone and (ii) modification of the fiber dimensions to increase its surface area and pore volume followed by change of the functional groups on the cellulose surface. The second route which ends up generating fibers with diameters in the nano-scale range through electrospinning has been considered as the way to go in recent years, as is evidenced by the number of publications in this area of research [7].

Previous studies have shown that adsorbents can be modified by chemically bonding groups that cross-link and improve the strength and porosity of the adsorbent or have functional ends that act as chelating agents affording sites for attachment of heavy metal cations. Preparation of nanofibers from cellulose through electrospinning, poses challenges as dissolution of cellulose is limited to a few solvents, long dissolution periods of up to 48 h and some dissolution processes leading to opening of the anhydroglucosidic chain. Frey [8] suggested the use of cellulose derivatives like cellulose acetate, hydroxypropyl cellulose, hydroxypropyl methylcellulose and ethyl-cyanoethyl cellulose. These derivatives are readily soluble in volatile solvents, which are suitable for electrospinning and can later be converted to cellulose through hydrolysis. The fibers obtained are functionalized into powerful adsorbents since they possess large surface area, high pore volume and strength.
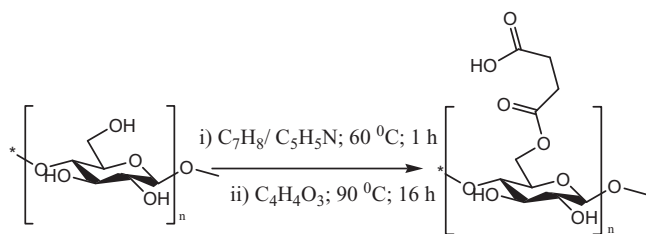
Fig. 1. Reaction scheme for the functionalization of cellulose to cellulose-g-oxolane-2,5-dione.

The objective of this work is to develop an adsorbent which is of low cost, with high regeneration capacity and to investigate its application with simulated heavy metal laden wastewater.

2. Materials and methods

2.1. Materials

Cellulose acetate (M_w = 30,000, % acetyl content = 39.8), N,N-dimethylacetamide (DMAc), acetone, toluene, oxolane-2,5-dione, ethanol all were supplied by Sigma–Aldrich. Metal salts: CH_3COONa, $Pb(NO_3)_2$, $Cd(NO_3)_2$; base (NaOH) and acid (HNO_3) were of analytical grade. All chemicals were used as supplied.

2.2. Electrospinning and deacetylation of cellulose acetate

The electrospinning set-up consisted of the cellulose acetate solution, grounded aluminium foil electrode and a high voltage direct current power supply. The polymer solution was prepared by stirring cellulose acetate, 16% (w/v) in acetone/N,N-dimethylacetamide solvent mixture, $(Me)_2CO$:DMAc, (2:1) for 14 h to ensure solution homogeneity. The grounded aluminium foil collector was placed 14 cm from the tip of a stainless steel needle. A programmable syringe pump (NE-1000 single syringe pump, New Era pump systems®) was used to pump the solution through a 20 gauge (bore diameter = 0.45 mm) stainless steel needle at a flow rate of 0.60 mL h^{-1}. The needle was connected to a high voltage direct current source with a maximum output of 25 kV. The electrospinning voltage for this work was fixed at 15 kV unless otherwise stated. The electrospun fiber mat was heated in an oven at 200 °C for 1 h and peeled off the aluminium foil carefully.
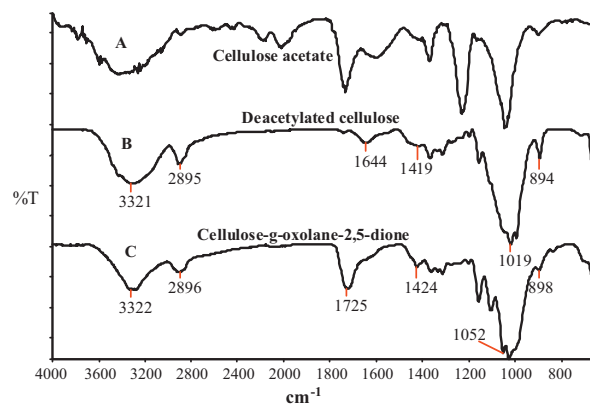

Fig. 2. IR spectra: A, cellulose acetate; B, cellulose; C, cellulose-g-oxolane-2,5-dione.

Deacetylation was performed by soaking the mat in different concentrations of NaOH (0.08–1 M) for optimization and 0.3 M NaOH was chosen as the optimized concentration. The mats were treated with optimized NaOH solution for 8 h followed by washing with double distilled water to obtain neutral pH.

2.3. Synthesis of cellulose-g-oxolane-2,5-dione

The cellulose nanofibers were prepared for functionalization by shaking twice with ethanol followed by toluene to remove water. Cellulose nanofibers (5 g) were added to 90 mL of toluene and 12.5 mL pyridine and heated at 60 °C for 1 h. Oxolane-2,5-dione (15 g) was added and the mixture heated overnight at 90 °C. The mixture was filtered while hot and soxhlet extracted using ethanol to remove unreacted oxolane-2,5-dione, then dried under vacuum at 40 °C, yielding a white fibrous mat. The reaction scheme is shown in Fig. 1.

2.4. Instrumentation

Deacetylation and functionalization were monitored using attenuated total reflectance FT-IR in the 4000–400 cm^{-1} range in four replicate scans. Solid-state cross polarization magic angle spin carbon-13 nuclear magnetic resonance (CP-MAS ^{13}C NMR) spectra of the samples were obtained on a Bruker 600 MHz Avance III Topspin 2.1 spectrometer at room temperature. The measure-
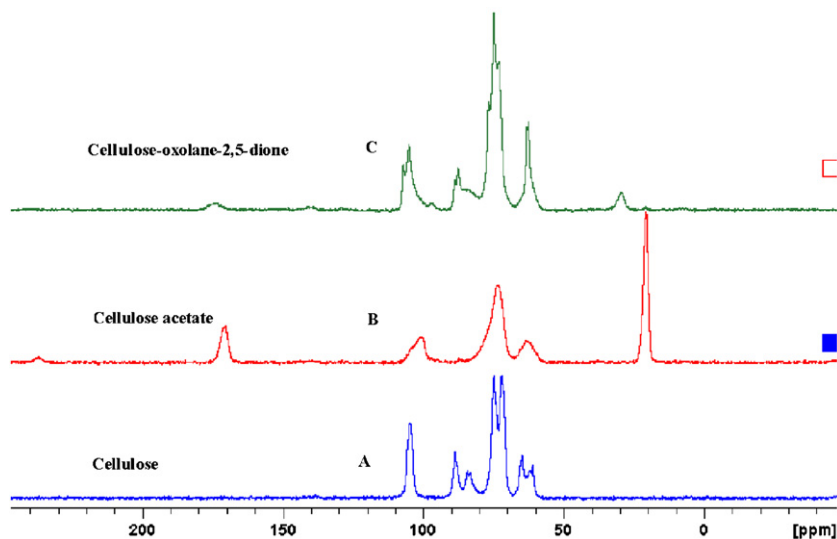

Fig. 3. CP-MAS ^{13}C NMR spectra: A, cellulose; B, cellulose acetate; C, cellulose-g-oxolane-2,5-dione.
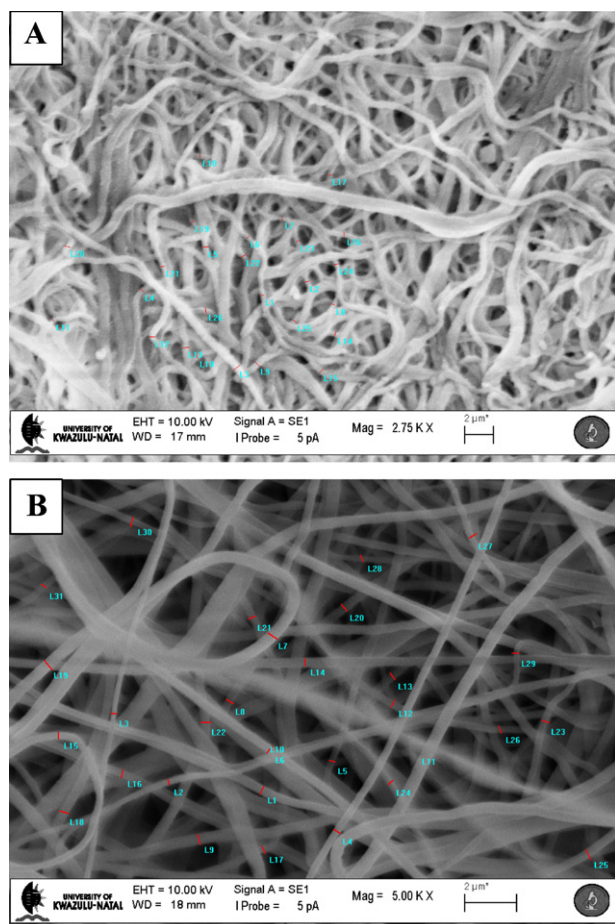
Fig. 4. SEM micrographs: (A) cellulose-g-oxolane-2,5-dione nanofibers and (B) cellulose nanofibers.

ments were obtained at frequencies of 75.47 MHz with a magic angle spinning of 10 kHz. The sample was packed in a 4 mm zirconium rotor. The amount of ligand attached on the cellulose was determined with elemental analysis using a Leco® CHNS-932 elemental analyzer. The morphology of the different types of electrospun cellulose nanofibers: cellulose acetate, deacetylated cellulose acetate and functionalized cellulose fibers, was observed by a Leo 1450 scanning electron microscope, operating at 10 kV and the micrographs generated using SMARTSEM version 5.03.06 software. The samples were prepared by cutting the aluminium foil with the As-spun fibers or spreading the functionalized fibers and adhering them over double faced carbon tape on copper stubs. Each sample was gold coated using a sputtering instrument for observation under scanning electron microscope. The diameters of the electrospun fibers were obtained directly from the SEM images using Image Pro Plus 6 software. Adsorption capacities for the fibers were calculated by monitoring the residual amount of metal ions using ICP-OES (PerkinElmer® ICP-OES optima 2100DV, USA) while pH was monitored using a hand-held combination pH meter (HI 98830) from Hanna Inc. Surface textural properties were determined by Surface Area and Porosity Analyzer (ASAP2020 V3. 00H, Micromeritics Instrument Corporation, Norcross, USA). All the gases used for analysis were instrument grade.

2.5. Adsorption studies

Batch adsorption studies were performed to monitor the removal of heavy metal ions by the adsorbent and obtain the equilibration data. Different pH values, contact time and solution
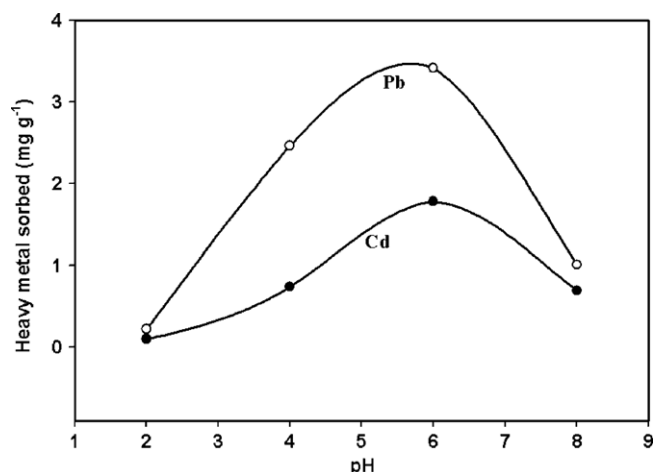

Fig. 5. pH optimization for adsorption of Pb and Cd metal ions from model solutions. Concentration of Pb and Cd, 100 mg L^{-1}, volume used 20 mL, exposure time 8 h.

concentrations were optimized at ambient temperature. Equilibrium isotherms required for design and operation of adsorbent to treat heavy metal bearing wastewaters were obtained. Fixed volume (20 mL of 20–200 mg L^{-1}) of single metal ion solutions were transferred into polyethylene bottles containing the adsorbent (0.04 g) and agitated between 10–600 min on a mechanical shaker. The mixture was then centrifuged at 5000 rpm for 10 min. The supernatant was filtered using a 0.45 μm microfilter and analyzed for residual metal ion concentration. To ensure accuracy, reliability and reproducibility of the data collected, all the batch experiments were performed in duplicate and the mean values of the data sets are presented. The amount of metal ion adsorbed was calculated according to Eq. (1):

$$q = \frac{C_0 - C_f}{M} V \qquad (1)$$

where q is the amount of metal ion adsorbed (mg g^{-1}), C_f and C_0 are final and initial metal ion concentrations (mg L^{-1}), respectively, V is the volume of metal ions used (L), and M is the mass of adsorbent (g).

3. Results and discussion

3.1. Fourier transformation-infrared spectroscopy

The IR spectra representing the conversion of cellulose acetate to cellulose-g-oxolane-2,5-dione is shown in Fig. 2. Cellulose acetate (Fig. 2A), has a peak at 1730 cm^{-1}, representing a CO stretch, which disappears during hydrolysis, leaving the peak at 1644 cm^{-1} [9]. The intensity of the peak at 2895 cm^{-1} due to C–H stretch increased significantly (Fig. 2B). These peaks together with those at 1419–1019 cm^{-1}, suggest the spectrum for cellulose (Fig. 2B). Moreover, the broad peak from 1100–1000 cm^{-1} has a higher intensity than in Fig. 2A due to generation of the C–OH groups which appear in this region [10]. The peaks at 1730 and 1250 cm^{-1} associated with the acetate groups disappear, in deacetylated cellulose, signifying successful deacetylation. The appearance of the peak at 1725 cm^{-1} due to carbonyl group stretch (Fig. 2C) suggests functionalization of cellulose with oxolane-2,5-dione [2].

3.2. Solid state 13-Carbon nuclear magnetic spectroscopic analysis

The NMR studies (Fig. 3) shows the spectra for cellulose (Fig. 3A), cellulose acetate (Fig. 3B) and cellulose-g-oxolane-2,5-
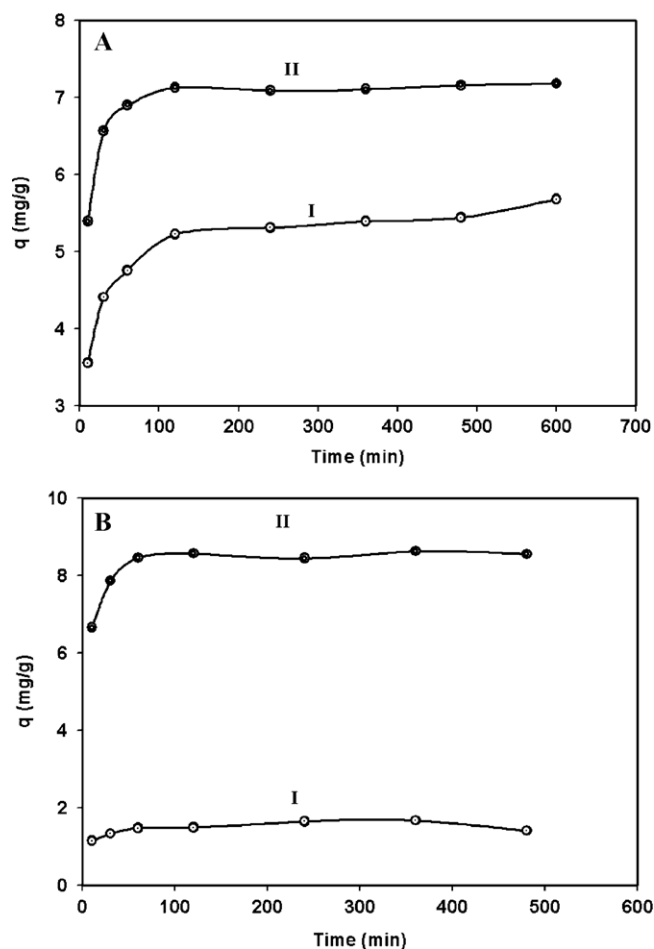
Fig. 6. Effect of contact time on adsorption: (A) Pb and (B) Cd (I: cellulose and II: cellulose-g-oxolane-2,5-dione nanofibers).

dione (Fig. 3C). The downfield signal at δ 170 ppm (Fig. 3B) is due to carbonyl (CO) group while the upfield one at δ 20 ppm confirms presence of methyl carbons present in the acetate chain. The signals between δ 104 and 65 ppm represent the cellulose skeleton [11]. The cellulose spectrum (Fig. 3A) confirms the successful deacetylation of cellulose acetate. Functionalization of cellulose with oxolane-2,5-dione is confirmed by the presence of the car-
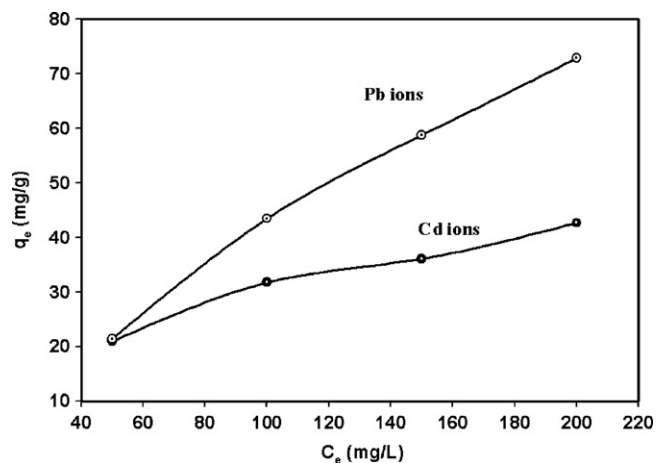

Fig. 7. Adsorption isotherm for Pb and Cd. Contact time 180 and 200 min, respectively, adsorbent concentration 2 g L^{-1}, solution pH 5.8, volume 0.02 L.
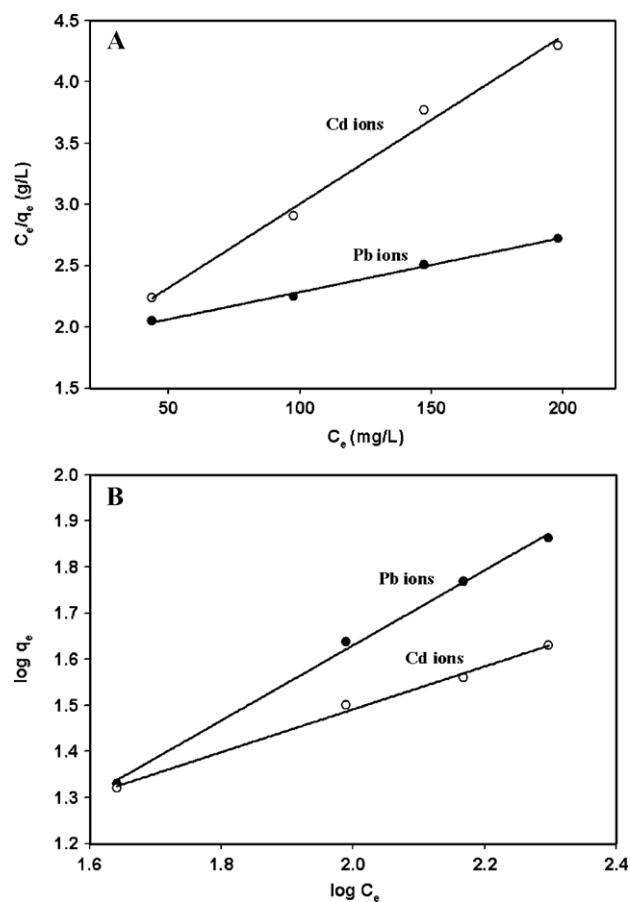

Fig. 8. (A) Langmuir and (B) Freundlich isotherms for Cd and Pb ions adsorption on cellulose-g-oxolane-2,5-dione nanofibers.

bonyl group (CO) signal at δ 173 ppm and methylene carbons (–CH$_2$–) at δ 29.9 ppm (Fig. 3C).

3.3. Morphological investigation using scanning electron microscopy

Morphological studies, Fig. 4, were carried out using scanning electron microscope (SEM). The functionalized cellulose had an average submicron fiber diameter of 384.86 nm was calculated as an average value from 50 measurements using Image Pro Plus 6® software (Fig. 4). The fiber integrity and porosity was maintained during deacetylation and functionalization. The surface area and pore size were obtained as 13.68 m^2 g^{-1} and 115.95 Å. The carbon content of the functionalized cellulose was determined to be 46.53%.

3.4. Optimization of adsorption parameters

The rate of cation removal from a solution is dependent on availability of sites able to donate electrons and/or pore able to trap the target metal ions. Other factors include pH, contact time and concentration. The pH for optimum adsorption was established by subjecting the material to 100 ppm of metal ion solutions at pH 2, 4, 6 and 8. Removal of Cd and Pb was observed to decrease after pH above 6 and 5.8, respectively, as shown in Fig. 5. This is due to the formation of insoluble metal hydroxides and is in agreement with previous results [12]. The metal uptake at pH 2 is negligible, as the energetic and kinetic favours proton attachment on the adsorption sites. This phenomenon offers the possibility for using this low pH effect for metal elution and nanofiber regeneration. In fact, at pH 2,

Table 1
Langmuir and Freundlich isotherm constants for Cd and Pb onto functionalized cellulose, nano and raw fibers.

Metal ion	q_{max} (mmol g^{-1})	Langmuir		Freundlich		
		K_L (L mmol^{-1})	r^2	K_f (mmol g^{-1})	n	r^2
Cd	0.59[a]	0.001	0.989	2.91	1.93	0.988
	0.13[b]	0.02	0.998	0.002	0.39	0.979
Pb	1.21[a]	0.002	0.995	1.0	1.23	0.997
	0.24[b]	0.01	0.986	0.002	0.43	0.942

[a] Cellulose-g-oxolane-2,5-dione nanofibers.
[b] Raw cellulose-g-oxolane-2,5-dione.

the metal ions are leached out of the nanofibers and into solution. The optimized pH (pH 5.8), was used to monitor the adsorption for lead and cadmium ions from simulated solutions.

Contact time is a pertinent parameter in determining the performance of an adsorbent. A high rate of removal of toxic substances from wastewaters is a gauge for quality adsorbent. Adsorption was monitored by exposing 0.04 g of adsorbent material to 20 mL of 20 ppm lead and cadmium solution. Performance of functionalized (II) and unfunctionalized (I) cellulose fibers were investigated based on the amount of metal ions adsorbed as a function of contact time, as shown in Fig. 6A (Pb) and B (Cd). A high uptake rate witnessed for the first 60 min, could be explained by the availability of many adsorption sites in the materials. As the metal ions get attached to these sites with contact time, the amount of adsorbed metal ions gradually reaches a maximum when there is no more significant metal removal taking place. Equilibrium is therefore established.

The equilibrium time for lead and cadmium was 120 and 60 min (Fig. 6A, II and B, II), respectively. This is a marked improvement compared to the equilibration time for the same metals on raw cellulose, results of previous study not included. The functionalized cellulose nanofibers showed improved adsorption compared to the functionalized cellulose bulk fibers. This is explained by the high number of hydroxyl groups exposed for reaction with oxolane-2,5-dione as a result of the increased surface area and pore volume on cellulose nanofibers, thereby increasing the adsorption sites. At equilibrium time, the removal of lead and cadmium was approximately 46.5 and 42.5%, respectively.

3.5. Adsorption isotherms: Langmuir and Freundlich isotherms

Adsorption isotherms are meant to draw relationships between the adsorbate concentration in the bulk and the amount adsorbed at the interface. The assumption often made is that every adsorption site is equivalent and the ability of a particle to bind is independent of whether or not adjacent sites are occupied [13].

Langmuir and Freundlich are the most commonly used solid–liquid phase isotherms, and were used to describe the relationship between the metal ions in solution and the functionalized nanofibers. The Langmuir model is applicable in cases where only one molecular layer (monolayer) of adsorbate is formed at the adsorbent surface while Freundlich isotherm model is widely used for heterogeneous surfaces energies. The linearized form of the two adsorption isotherms models is defined by the following equations: Eqs. (2) and (3) illustrating Langmuir and Freundlich, respectively.

Langmuir adsorption isotherm (Eq. (2))

$$\frac{C_e}{q_e} = \frac{1}{q_{max}}C_e + \frac{1}{q_{max}K_L} \tag{2}$$

where C_e is the equilibrium concentration of adsorbate (mg L^{-1}), q_e is the amount of material adsorbed at equilibrium (mg g^{-1}), q_{max} is the adsorption capacity of adsorbent (mg g^{-1}) and K_L a Langmuir constant related to energy.

Freundlich adsorption isotherm (Eq. (3))

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \tag{3}$$

where q_e and C_e assume the same quantities as in Langmuir while K_f and n are adsorption capacity and adsorption intensity constants, respectively [9].

The adsorption kinetics were studied using different concentration for lead and cadmium: 20, 50, 100, 150 and 200 mg L^{-1} at an adsorbent concentration of 2 g L^{-1}. The adsorption isotherms, Langmuir and Freundlich, are represented by Figs. 7 and 8, respectively.

The order in adsorption behaviour was Cd > Pb. This could be explained by the chelation and entrapment of cadmium on the ligand as well as the pores on the surface of the functionalized cellulose. The maximum adsorption (q_{max}), reported in Table 1 demonstrates the higher capacity of cellulose-g-oxolane-2,5-dione nanofibers for Pb and Cd removal as compared with oxolane-2,5-dione functionalized raw cellulose fibers. The adsorption capacities for functionalized cellulose nanofibers are 1.0 and 2.91 mmol g^{-1} for Pb and Cd, respectively, compared to 0.002 mmol g^{-1} for raw cellulose (Table 1). Moreover, Table 1 shows that the metal uptake data agrees strongly with Freundlich adsorption isotherm model with correlation coefficient (r^2) of 0.99. This supports the theory that the adsorption sites on the surface of cellulose were increased after surface modification to nanofibers followed by functionalization with oxolane-2,5-dione.

Table 2
Summary of Langmuir and Freundlich isotherm constants for Cd and Pb for regenerated cellulose-g-oxolane-2,5-dione nanofibers.

		Langmuir			Freundlich		
		q_{max} (mmol g^{-1})	r^2	K_L (L mmol^{-1})	n	K_f (mmol g^{-1})	r^2
Run 1	Cd	0.59	0.989	0.00983	1.93	2.91	0.988
	Pb	1.21	0.995	0.00217	1.23	1.0	0.997
Run 2	Cd	0.47	0.986	0.0113	1.64	1.56	0.961
	Pb	2.42	0.994	0.00101	15.38	1.7	0.936
Run 3	Cd	0.52	0.992	0.0098	1.52	1.35	0.977
	Pb	1.61	0.878	0.00156	1.08	0.6	0.997

Table 3
A comparison of adsorption capacities ($mmol\,g^{-1}$) of cellulose-g-oxolane-2,5-dione with some commercial adsorbents.

Sorbent	Pb	Cd	Reference
Duolite GT-73	0.59	0.94	[14]
Amberlite 200	1.22	2.0	[14]
Activated carbon	0.002	0.003	[12,15]
Resin (Dowex 50W	2.05	2.4	[16]
Cellulose-g-oxolane-2,5-dione	1.0	2.91	This study

3.6. Regeneration of adsorbent

Cellulose-g-oxolane-2,5-dione nanofibers used for adsorption studies were regenerated by shaking in 3 M HNO₃ solution and filtering, followed by repeatedly rinsing with double distilled water until neutral pH. The material was then vacuum dried for 24 h. Its adsorption capacity was measured as before and the results used to determine reusability of the adsorbent. The adsorption capacities of the regenerated material are summarized in Table 2.

It can be observed, from the values, that the adsorption capacity did not change significantly, confirming that cellulose-g-oxolane-2,5-dione nanofibers are potent adsorbent material. The adsorption capacity of cellulose-g-2,5-dione was compared with commercial adsorbents (Table 3). The results showed that it performed quite well and is feasible in its application on a large scale.

4. Conclusion

In the present study, cellulose nanofibers were regenerated from electrospun cellulose acetate through deacetylation. The regenerated cellulose nanofibers were successfully functionalized as confirmed by spectroscopic analysis. The functionalized adsorbent showed great potential when subjected to heavy metal remediation. The improved surface properties as well as the fast kinetics whereby heavy metals can be adsorbed, makes this biosorbent potentially useful for water purification purposes. It is also worth noting that the material could be recycled without significant drop in its adsorption capacity. Since the preparation of these functionalized materials is cheap and easy, the resulting material is cost effective.

Acknowledgements

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