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# A fully bio-sourced adsorbent of heavy metals in water fabricated by immobilization of quinine on cellulose paper

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## ABSTRACT

The fabrication of a fully bio-sourced adsorbent of Cd(II) by covalent immobilization of quinine on cellulose paper is described. The double bond of commercially available quinine was converted to a terminal alkyne function which was reacted with cellulose paper, chemically modified with azide functions, through a 1,3-dipolar cycloaddition, leading to Cell-Quin. The adsorption efficiency of Cell-Quin was investigated to determine the optimal pH, contact time and dose of adsorbent, ultimately leading to high levels of removal. The mechanism of adsorption of Cell-Quin was deeply rationalized through kinetic experiments and isotherm modeling. We also showed that Cell-Quin could adsorb other heavy metals such as Cu(II), Pb(II), Ni(II) and Zn (II).

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## Introduction

Access to safe water sources is a critical problem in developing countries where deficient water supply networks associated with polluted water resources are major public health concerns as the most vulnerable populations face a constant threat of cholera and dysentery. Although both the nature and the origin of pollution observed in water resources are variable from one region to another, anthropogenic activities are the main responsible and recurrent pollution profiles are observed worldwide. The World Health Organization identified 10 chemicals of major public health concerns found in many places all over the world. This list of hazardous chemicals includes four heavy metals, i.e., mercury, lead, cadmium and arsenic, which are major contaminants of

water resources. Both political and societal pressures have been driving forces to identify enabling technologies and develop innovative solutions for addressing the problem of water contamination by heavy metals.

A large variety of methods has been proposed and the most relevant ones include flocculation, adsorption, ion-exchange, nanofiltration, precipitation and electrolysis (Barakat, 2011; Fu and Wang, 2011). Recently, bio-adsorption has emerged as a very attractive strategy for the development of cost-effective and sustainable technologies. Bio-adsorption combines the capabilities and operational simplicity of adsorption with the biocompatibility, low cost and biodegradability of bio-sourced materials (Bailey et al., 1999; Bilal et al., 2013; Demirbas, 2008; Hegazi, 2013; Nguyen et al., 2013; Sud et al., 2008; Wan Ngah and Hanafiah, 2008; Wang et al., 2016).

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Chitosan, a linear polysaccharide of  $\beta$ -(1,4)-linked D-glucosamine residues, and its chemically modified analogs have aroused a great interest due to its inherent coordinating properties with metals through C2-amino groups (Aliabadi et al., 2014, 2013; Li and Bai, 2005; Li et al., 2019; Sahebamee et al., 2019; Zhou et al., 2005, 2004). Chitosan is industrially prepared by deacetylation of chitin which is a biopolymer extracted from the exoskeleton of shrimps. Although the use of chitosan-based adsorbents gave outstanding results for the remediation of heavy metals in aqueous environment, it suffers from several drawbacks. Chitosan is (1) partially soluble in water and acidic organic solutions, (2) commercially available with purity of ca. 80% only, (3) expensive with regard to its prospective use on large tonnage, especially for developing countries. Moreover, the impact on the biodiversity of crustaceans upon large industrial demands could be a major concern deserving a precautionary consideration.

Cellulose, a natural linear polysaccharide of  $\beta$ -(1,4)-linked D-glucose residues, is the most abundant biopolymer on earth with an estimated annual bioproduction of ca.  $1.5 \times 10^{12}$  tons (Hon, 1994; Kim et al., 2015; Klemm et al., 2005). Cellulose addresses most of the issues associated with the use of chitosan, as it is (1) highly hydrophilic but not soluble in water, (2) commercially available with high purities, and (3) at least 10 times less expensive than chitosan. However, by contrast with chitosan, cellulose has poor coordinating properties with heavy metal and its use as adsorbent requires chemical transformations (Hokkanen et al., 2016; Kumar et al., 2017; O'Connell et al., 2008). Several strategies involving graft copolymerization on the cellulose backbone (Güçlü et al., 2003; O'Connell et al., 2006; Roy et al., 2009; Tian et al., 2011; Yu et al., 2013b; Zheng et al., 2011), fabrication of cellulose-based composites (Choi and Jeong, 2008; Yang et al., 2014; Zhang et al., 2019) or chemical functionalization of the cellulose chains (Hokkanen et al., 2013; Li et al., 2015; Yu et al., 2013a), have been successfully explored on either wood pulp, micro- or nanocellulose, while the use of cellulose paper has been mostly overlooked.

We recently underlined the assets of chemically modified cellulose papers which can be used either as an adsorbent in static liquids or as a filtration membrane for liquid streams (d'Halluin et al., 2017). We initially developed a virtually universal device for the removal of heavy metals from aqueous solutions by the simple grafting of ethylenediaminetetraacetic acid (EDTA) moieties to cellulose filter paper (Cell-EDTA) through esterification. While Cell-EDTA displays a high level of metal removal efficiency (>90%), EDTA is a persistent and toxic organic pollutant compromising the biodegradability of the device. We addressed this major concern, with the development of a second generation of cellulose paper-based adsorbent by grafting spermine, a natural polyamine, on the cellulose backbone (Cell-Sperm), (Nongbe et al., 2018b). Cell-Sperm is a fully bio-sourced and biodegradable device which displays a similar level of heavy metal removal than Cell-EDTA, including Cd(II) and Pb(II). Unfortunately, Cell-Sperm still suffers from the high cost of commercially available spermine which compromises further industrial developments, especially in developing countries. With the aim of developing a fully bio-sourced and affordable metal remediation device for domestic uses, especially for people living in developing countries where public water supply networks are

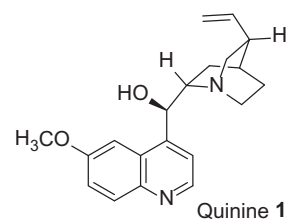


Fig. 1 – Structure of quinine 1.

often missing or damaged, we established the following requirements. The decontamination device must (1) be based on cellulose which is the cheapest biopolymer, (2) use affordable bio-sourced chelating moieties grafted on the cellulose backbone, (3) be producible by developing countries using local manpower and endemic natural resources.

While cellulose can be found everywhere on Earth, the main challenge at the beginning of this research project was to find a natural product-based chelating moiety, forming stable complexes with heavy metals, which could be found in several continents and ideally in many developing countries. After an extensive literature search, we reasoned that quinine 1 could be the ideal candidate (Fig. 1) (Hubel et al., 1999; Rey et al., 2006). Quinine is an alkaloid isolated from the bark of cinchona trees with a worldwide recognition for its use as a medication to treat malaria and babesiosis. Originally, cinchona plants are endemic to Andean forest of Western South America. However, due to the large worldwide demand for quinine 1 as anti-malaria drug during the 19th and first half of 20th centuries, cinchona plants were naturalized in Southwest Pacific, Central America, and Africa. In other words, cinchona plants are currently distributed in many regions on earth and especially in developing countries. From a chemical point of view, quinine 1 has three donor sites (one hydroxyl group and two nitrogen atoms) which can be involved in different coordination modes with metals and one site (olefin) for anchoring onto cellulose. The importance of cinchona alkaloids as ligand for metal species has been revealed with the development of the asymmetric Sharpless dihydroxylation of olefins.

In the frame of our long-standing interest for the development of paper-based technologies for pollutant sensing (Rull-Barrull et al., 2016a; Rull-Barrull et al., 2016b) and heavy metal removal from water (d'Halluin et al., 2017; Nongbe et al., 2018b; Rull-Barrull et al., 2016c), we describe herein a fully bio-sourced device fabricated from cellulose paper and quinine (Cell-Quin) for the removal of cadmium from water. Because Cell-Quin can operate without any dedicated equipment and specific training, we believe it could be well-suited for domestic applications in developing countries.

## 1. Materials and methods

### 1.1. General remark

All commercial solvents and reagents were used as received from Sigma-Aldrich, Fischer Scientific Ltd., Alfa Aesar. Quinine was purchased from Acros with 99% purity and used

without purification. Whatman grade 6 filter paper (42.5 mm  $\phi$ ) with a grammage of ca. 100 g/m<sup>2</sup> was used as cellulose source. FT-IR spectra were recorded on a Bruker Tensor 27 spectrometer with ATR technic. Scanning electron microscopy (SEM) images were recorded with a JEOL 7600F. X-ray photoelectron spectroscopy was performed on a Thermo Fisher Scientific K-ALPHA spectrometer which was used for disk surface analysis with a monochromatized Al K $\alpha$  source ( $h\nu = 1486.6$  eV) and a 200  $\mu$ m spot size. A pressure of  $10^{-7}$  Pa was maintained in the chamber during analysis. The full spectra (0–1150 eV) were obtained at a constant pass energy of 200 eV, and high resolution spectra at a constant pass energy of 40 eV. Charge neutralization was required for all insulating samples. High resolution spectra were fitted and quantified using the AVANTAGE software provided by Thermo Fisher Scientific. Atomic absorption spectroscopy analyses were carried out on a Thermo Scientific ICE 3300. Elemental analyses were performed on a Thermo Fisher Scientific Flash 2000 CHNS organic elemental analyzer. All samples were shaken on an orbital agitator at a speed of 100 rpm; increasing the speed damages the cellulose paper.

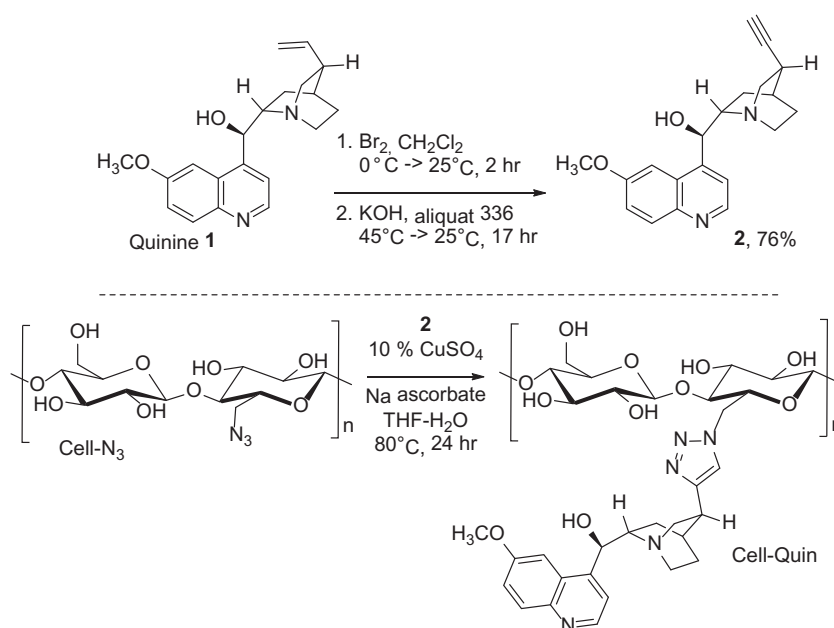
### 1.2. Preparation of the cellulose paper-grafted quinine

We recently described the straightforward preparation of cellulose paper azide (Cell-N<sub>3</sub>) which results from the azidation of C6-alcohol functions of glucose residues (Nongbe et al., 2018a). Cell-N<sub>3</sub> is obtained in two steps from pristine cellulose with degree of substitution (DS) of ca. 40% which means that an average of four azide moieties are incorporated every 10 glucose residues. Cell-N<sub>3</sub> is a powerful molecular platform which can be further functionalized through 1,3-dipolar cycloaddition with alkynes. The covalent immobilization of the quinine skeleton on Cell-N<sub>3</sub> through click ligation required the transformation of the terminal

olefin group of quinine 1 to the corresponding alkyne 2. The formal oxidation of the terminal double bond to the corresponding alkyne was achieved in two steps through a bromination–elimination sequence following a modified published procedure (Scheme 1) (Porta et al., 2015). The copper-catalyzed cycloaddition of Cell-N<sub>3</sub> with 2 was carried out in a mixture of THF and water for 24 hr at 80°C. The resulting Cell-Quin material was thoroughly washed with 10% aqueous EDTA solution to remove any trace of copper residues. The robust linkage of quinine to cellulose paper prevents any further leaching in water during the use of Cell-Quin.

### 1.3. Synthesis of quinine-alkyne 2

To a solution of quinine 1 (1 g, 3.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) at 0°C was added dropwise a solution of Br<sub>2</sub> (320  $\mu$ L, 6.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) in the course of 15 min. The resulting mixture was stirred for 1 hr at 0°C and 2 hr at 25°C. The expected dibrominated quinine derivative was precipitated in petroleum ether (60 mL), filtered and washed with petroleum ether (20 mL) and dried under vacuum to give a yellow solid which was used in the next step without further purification. Starks' catalyst (Aliquat 336, 0.6 mmol) was added to a solution of the di-brominated quinine derivative in THF (30 mL) and the resulting mixture was stirred for 5 min. Then, powdered KOH (1.05 g, 1.55 mmol) was added and the resulting suspension was stirred for 1 hr at 45°C. Another portion of powdered KOH (1.05 g, 1.55 mmol) was added again and the resulting mixture was further stirred for 1 hr at 45°C and 16 hr at 25°C. The solid was removed by filtration and thoroughly washed with THF. The filtrate was concentrated under vacuum and the crude solid was purified by flash chromatography (10% MeOH-CH<sub>2</sub>Cl<sub>2</sub>) to give a compound 2 (755 mg, 76%) as a yellow solid. IR (ATR)  $\nu$  3300, 3137, 2932, 2857, 2108, 1621, 1507, 1235, 1027/cm. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  8.57 (d, 1H,  $J = 4.6$  Hz),



Scheme 1 – Chemical modification of quinine 2 and function of Cell-N<sub>3</sub> to give Cell-Quin.

7.90 (d, 1H,  $J = 9.2$  Hz), 7.48 (d, 1H,  $J = 4.6$  Hz), 7.90 (dd, 1H,  $J = 2.6, 9.2$  Hz), 7.21 (d, 1H,  $J = 2.6$  Hz), 5.60 (br d, 1H,  $J = 4.1$  Hz), 3.84 (s, 3H), 3.49–3.56 (m, 1H), 3.33 (dt, 1H,  $J = 4.1, 8.8$  Hz), 3.16 (dd, 1H,  $J = 10.3, 13.5$  Hz), 2.87 (dm, 1H,  $J = 13.3$  Hz), 2.58–2.65 (m, 1H), 2.50–2.53 (m, 1H), 1.98–2.02 (m, 1H), 1.92 (d, 1H,  $J = 2.5$  Hz), 1.77–1.81 (m, 2H), 1.40–1.44 (m, 1H), 1.24–1.28 (m, 1H), 0.87 (app t, 1H,  $J = 5.7$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  157.9, 147.5 ( $\times 2$ ), 144.2, 131.4, 126.7, 121.7, 118.7, 101.4, 87.3, 71.2, 69.1, 59.6, 57.7, 55.9, 42.8, 27.5, 27.2, 25.8, 21.9. HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{20}\text{H}_{23}\text{N}_2\text{O}_2$  323.1760; Found 323.1748.

#### 1.4. Procedure for the pretreatment of cellulose paper

Whatman grade 6 filter paper (42.5 mm  $\varnothing$ , ca. 150 mg) were immersed in 10% ( $w/w$ ) NaOH aqueous solution (250 mL). After being stirred for 20 hr at 25°C on an orbital agitator, the piece of paper was washed six times with EtOH (50 mL) and stored in EtOH.

#### 1.5. Preparation of the azidated cellulose paper (Cell- $\text{N}_3$ )

Activated cellulose paper (145 mg, 0.81 mmol) was immersed in pyridine (10 mL) and treated with *p*-toluenesulfonyl chloride (464 mg, 2.44 mmol). After being stirred for 20 hr at 40°C on an orbital agitator, the piece of paper was removed from the solution and sonicated three times in DMF (20 mL). Elemental analysis provided a degree of substitution of ca. 0.45. The piece of tosylated cellulose paper was immediately immersed in DMF (10 mL) and treated with  $\text{NaN}_3$  (526 mg, 8.10 mmol). After being stirred for 40 hr at 60°C on an orbital agitator, Cell- $\text{N}_3$  was successively sonicated with 20 mL of  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{COCH}_3$ , EtOH and  $\text{CH}_2\text{Cl}_2$  and dried under vacuum ( $\text{DS} = 0.40$ ).

#### 1.6. General procedure for determining the effect of pH

Freshly prepared solutions of metal salts  $[\text{M}(\text{OAc})_2]$ , 100 pm] in Milli-Q water (2 mL) were stirred on an orbital agitator (100 r/min) with Cell-Quin (10 mg, 5 g/L) for 90 min at 25°C with pH ranging from 3 to 9. The pH of the solution were adjusted by addition of aqueous HCl and/or NaOH (1 mol/L). After 90 min of stirring, Cell-Quin was removed and the concentration of metals remaining in solution was analyzed by atomic absorption spectroscopy (AAS). The samples were diluted 20 times in order to reach the linearity of the calibration curves.

#### 1.7. General procedure for determining the effect of contact time

Freshly prepared solutions of metal salts  $[\text{M}(\text{OAc})_2]$ , 100 mg/L] in Milli-Q water (2 mL) were stirred on an orbital agitator (100 r/min) with Cell-Quin (10 mg, 5 g/L) at 25°C and at the optimal pH (see text). The concentration of metals remaining in solution was measured by AAS after 0.5, 1.5, 2, 2.5, 3, 4, 5, 6 and 12 hr. The samples were diluted 20 times in order to reach the linearity of the calibration curves.

#### 1.8. General procedure for determining adsorption isotherms

Freshly prepared solutions of  $\text{Cd}(\text{OAc})_2$  in Milli-Q water (2 mL) were stirred on an orbital agitator (100 r/min) with Cell-Quin (10 mg, 5 g/L) for 6 hr at 25°C and pH 8. The initial

concentration of  $[\text{M}(\text{OAc})_2]$  was varied from 5 to 1000 mg/L (5, 25, 50, 75, 100, 200, 300, 400, 500 and 1000 mg/L). The concentration of Cd(II) remaining in solution was determined by AAS. The samples were diluted 20 times in order to reach the linearity of the calibration curves.

## 2. Results and discussion

The grafting was easily followed by FTIR spectroscopy with the complete disappearance of the vibration band  $\nu_{as}(\text{N}_3)$  at 2110/cm and the concomitant formation of a strong band at 1618/cm attributed to vibration bands  $\nu(\text{C}=\text{C})$  and  $\nu(\text{C}=\text{N})$  (Fig. 2).

The chemical changes of surface nitrogen element upon immobilization of **2** onto Cell- $\text{N}_3$ , were conveniently followed by X-ray photoelectron spectroscopy (XPS). The high resolution C1s spectrum of Cell-Quin showed a significant increase of the component corresponding to C–C bonds at 284.9 eV (Fig. 3b and e). The N1s peak envelopes for Cell- $\text{N}_3$  and Cell-Quin are shown in Fig. 3c and Fig. 3f. Deconvolution of the N1s photoemission curves of Cell- $\text{N}_3$  reveals three components at 399.9, 401.2 and to 404.3 eV (Fig. 3c) while the N1s peak envelop of Cell-Quin (Fig. 3f) reveals the disappearance of the component at ca. 404–405 eV, attributed to electron-deficient nitrogen atoms of azide groups, which confirms the formation of the 1,2,3-triazole cycle.

The fiber network of cellulose paper was not significantly affected by the successive chemical steps as the average diameter of fibers determined on SEM images was in the range of 5–25  $\mu\text{m}$  for the pristine paper, Cell- $\text{N}_3$  and Cell-Quin (Fig. 4).

### 2.1. Adsorption studies

We initiated this project to address the dramatic pollution of drinking water resources in Côte d'Ivoire (formerly Ivory Coast), by heavy metals and especially cadmium which

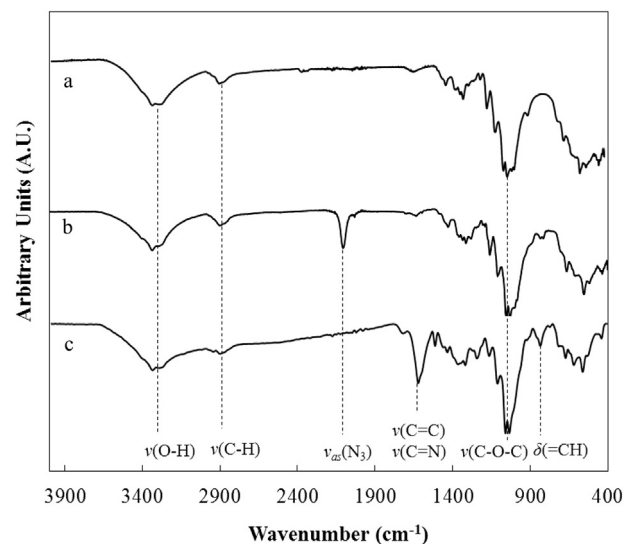


Fig. 2 – FT-IR spectra of (a) pristine cellulose paper, (b) Cell- $\text{N}_3$  and (c) Cell-Quin.



contaminate ground water (Tohouri et al., 2017). The rapid demographic growth of Côte d'Ivoire combined with the increase of industrial activities resulted in a severe pollution as most domestic and industrial sewage water are often discharged without treatment. While we selected Cd(II) as benchmark metal in our optimization studies for the reasons discussed above, the methodology and results provided in this contribution are far beyond the case of Côte d'Ivoire.

## 2.2. Effect of the pH and contact time

We initially investigated the efficiency of the adsorption of Cd(II) on Cell-Quin as a function of the pH value of aqueous solutions. The pH value significantly affects the efficiency of adsorption processes as it affects both the surface charge of the adsorbent and the metal speciation in the solution (Berber-Mendoza et al., 2006). In aqueous solution, Cd(II) mainly exists as free  $\text{Cd}^{2+}$  at pH values ranging from 3 to 8. At higher pH values,  $\text{CdOH}^+$  (pH 9–10) and  $\text{Cd}(\text{OH})_2$  (pH 11) become the predominant species (Berber-Mendoza et al., 2006). We determined the level of adsorption of Cd(II) species onto Cell-Quin over a range of pH values from 3 to 9. Each measurement were conducted for 90 min at 25°C with aqueous solutions containing 100 mg/L of Cd(II) and 5 g/L of Cell-Quin. After removal of Cell-Quin, the residual concentration of Cd(II) in solution was analyzed by atomic absorption emission (AAS). The graph depicted in Fig. 5a, shows the evolution of the percentage of metal adsorbed on Cell-Quin as a function of the pH value. There is no clear tendency as the percentage of metal adsorbed varies non-linearly from 45% to

65%. This behavior evolution likely results from the modification of the coordination mode of  $\text{Cd}^{2+}$  to quinine as under acidic condition (pH < 7) different nitrogen atoms can be protonated according to their basicity. The highest level of adsorption (65%) was located at ca. pH 8, a value which is in the range of the recommended values for drinking water ( $6.5 < \text{pH} < 8.5$ ). These results mean that Cell-Quin could be used for the purification of drinking water. The decrease of the adsorption capacity at pH > 8 could be related to the formation of  $\text{CdOH}^+$  species which likely have a lower affinity for quinine.

Having determined the best pH conditions for the adsorption of Cd(II) species on Cell-Quin, we then examined the contact time-adsorption efficiency relationship. As depicted in Fig. 5b, the rate of adsorption is faster in the first 90 min reaching 65% of Cd(II) adsorbed. The adsorption rate significantly decreased upon prolonged contact time, but the level of Cd(II) adsorbed continuously increased until reaching a plateau at 93% after 6 hr.

The dose of Cell-Quin was also investigated under these optimal conditions. At a dose of 1 and 2.5 g/L a modest removal of 28% and 45%, respectively was obtained versus 93% at 5 g/L. Increasing the dose to 10 g/L does not significantly improved the removal efficiency (95%). Therefore, we used 5 g/L of Cell-Quin for all subsequent studies.

In order to confirm the coordination properties of quinine in the adsorption process and determine whether the triazole linker plays a role in the coordination properties of Cell-Quin, we compared the level of removal of Cell-Quin with pristine cellulose paper (Cell) and the adsorbent lacking the quinine moieties

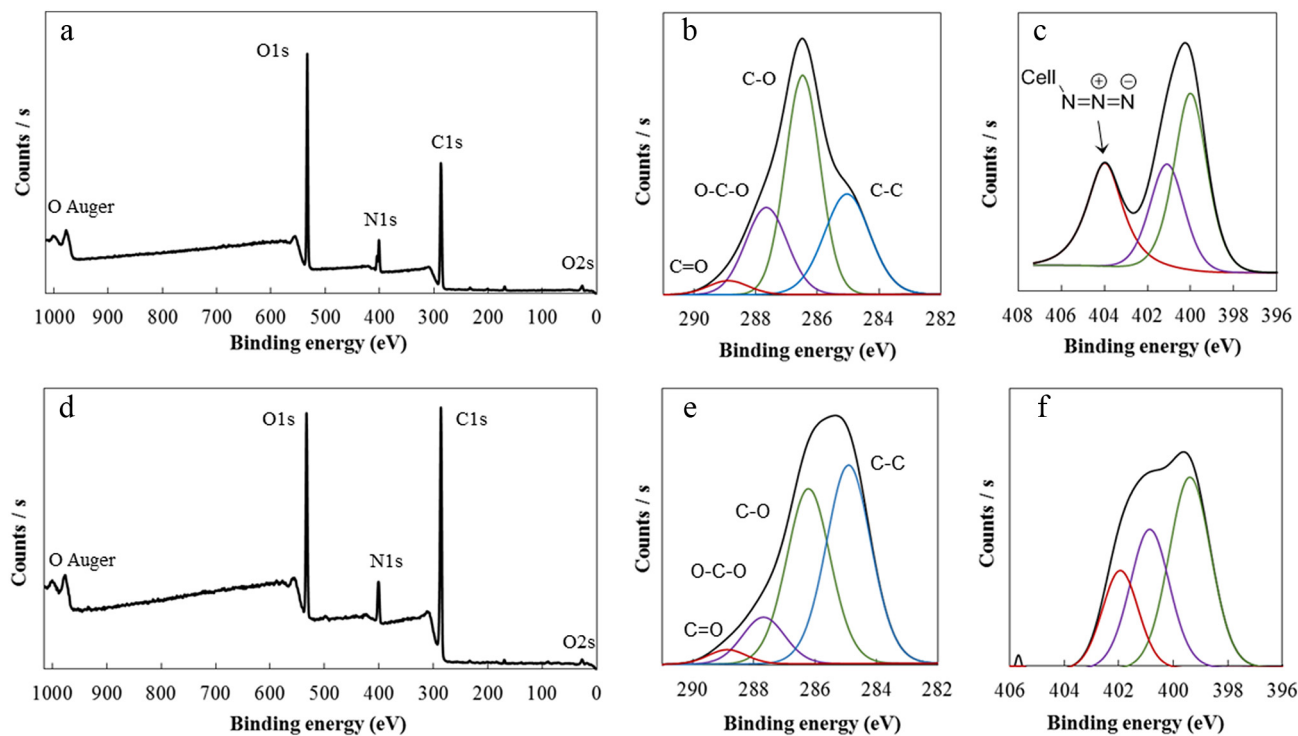


Fig. 3 – Survey scan spectra of (a) Cell- $\text{N}_3$  and (d) Cell-Quin. High resolution  $\text{C}1\text{s}$  spectrum of (b) Cell- $\text{N}_3$  and (e) Cell-Quin. High resolution  $\text{N}1\text{s}$  spectrum of (c) Cell- $\text{N}_3$  and (f) Cell-Quin.

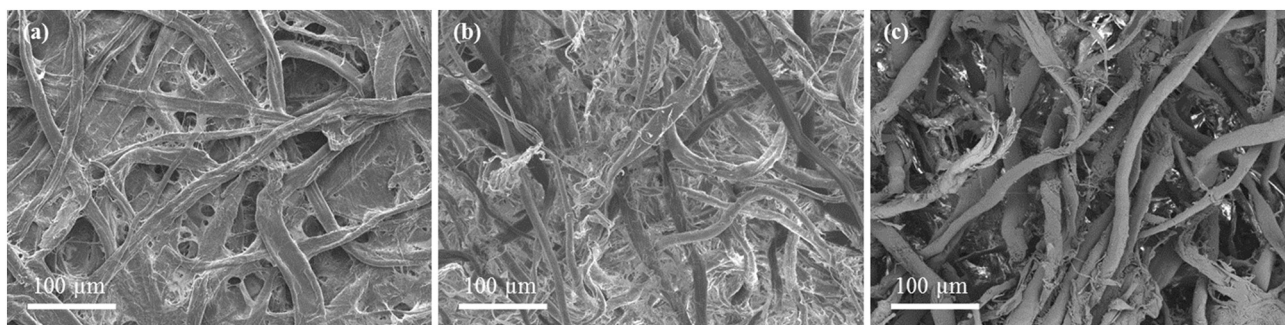


Fig. 4 – SEM images of (a) pristine cellulose paper, (b) Cell-N<sub>3</sub> and (c) Cell-Quin.

prepared through the ligation of phenylacetylene with Cell-N<sub>3</sub> (Cell-Ph). Under the optimal conditions (pH 8, 6 hr, 25°C, 5 g/L), only 5% Cd(II) species were adsorbed on Cell and 17% on Cell-Ph (versus 93% for Cell-Quin). These results suggest that quinine has a predominant role in the high level of removal recorded with Cell-Quin, presumably through the formation of multidentate complexes (Hubel et al., 1999; Rey et al., 2006). The formation of multidentate complexes on Cell-Ph would require a spatial proximity of at least two triazole moieties. As the degree of substitution is lower than 50%, less than one on two glucose units are statistically grafted, reducing the probability to have spatially close triazole moieties. The coordination of Cd species to nitrogen atom of Cell-Quin was also clearly evidenced by XPS analysis of the N1s region where a significant modification of the intensities of the three components at 399.4, 400.8 and to 401.6 eV was observed (Fig. 6b).

We also evaluated the reusability of Cell-Quin under the optimal conditions (pH 8, 6 hr, 25°C, 5 g/L) through successive adsorption–desorption processes of Cd(II) ions. The desorption stage was carried out in acidic conditions (0.5 mol/L HCl, 25°C, 30 min). We observed a gradual decrease in the level of Cd(II) adsorbed upon successive reuses with 93%, 85% and 70%

for the first, second and third uses, respectively. However, the decrease was not ascribed to an alteration of the material but rather to the difficulty to desorb Cd(II) species in 0.5 mol/L HCl, before a next reuse.

A deeper insight into the mechanism of adsorption was assessed through kinetic models (Ho and McKay, 1998). The pseudo-first-order kinetic model which has essentially been used to model the adsorption of organic pollutants such as methylene blue and malachite green (Hameed and El-Khaiary, 2008a; Hameed and El-Khaiary, 2008b; Tan et al., 2008) can be expressed in linear form as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (1)$$

where  $q_e$  (mg/g) and  $q_t$  (mg/g) define the amounts of Cd(II) adsorbed at equilibrium and time (hr), respectively, and  $k_1$  (hr<sup>-1</sup>) is the pseudo-first-order rate constant which describe the mass transfer. This model fails to properly describe the adsorption of Cd(II) on Cell-Quin as the linear plot of  $\log(q_e - q_t)$  versus  $t$  (Fig. 7a) give an unsatisfactory correlation coefficient ( $R^2 = 0.81$ ).

The pseudo-second-order kinetic model was initially described by Ho to model the adsorption of divalent metals

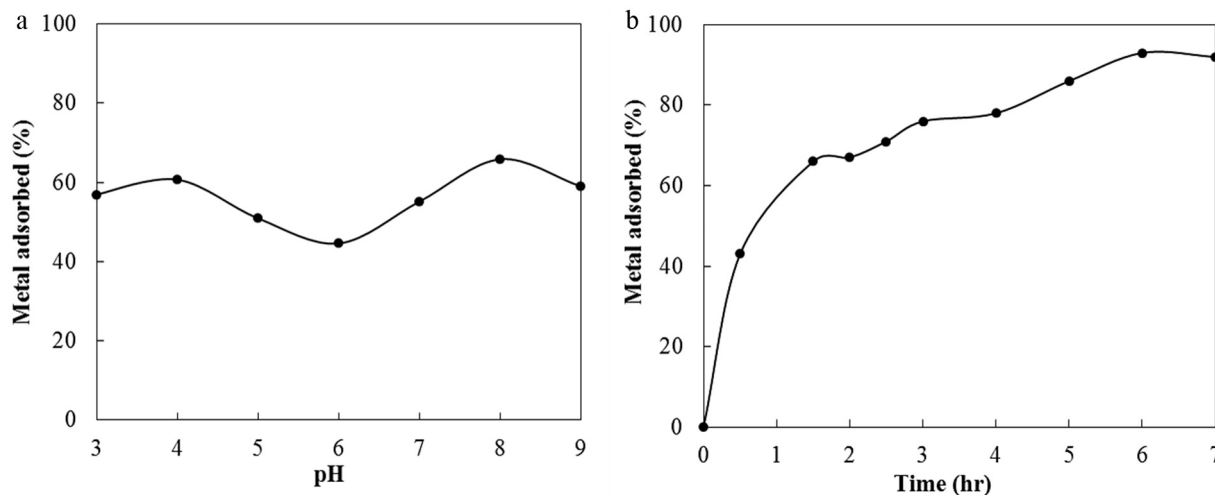


Fig. 5 – (a) Effect of the pH value on the adsorption efficiency of Cd(II) on Cell-Quin for 90 min. (b) Effect of contact time on the adsorption efficiency of Cd(II) on Cell-Quin for 90 min at pH 8. Initial concentration of metal ions = 100 mg/L, adsorbent dose = 5 g/L, 25°C.

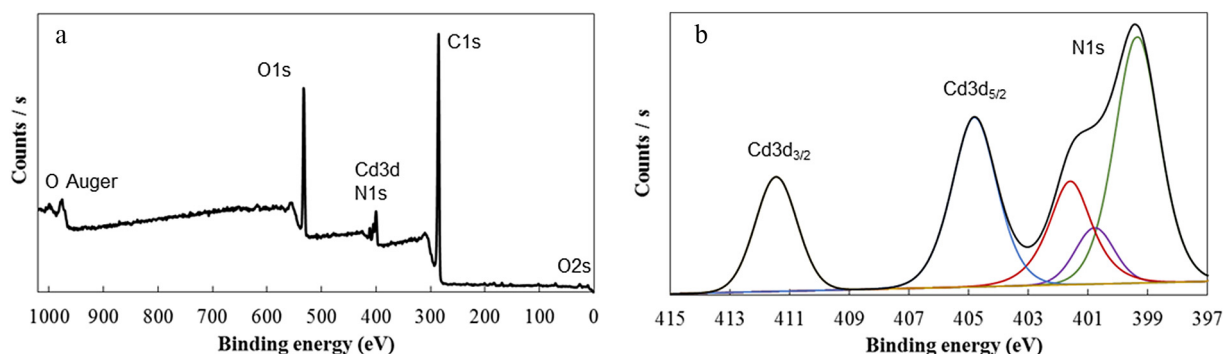


Fig. 6 – (a) Survey scan spectrum and (b) High resolution Cd3d and N1 s spectra of Cell-Quin upon coordination with Cd(II).

onto peat (Ho, 2006) can be expressed in linear form as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

where  $q_e$  (mg/g) and  $q_t$  (mg/g) define the amounts of Cd(II) adsorbed at equilibrium and time  $t$  (hr), respectively, and  $k_2$  (g/(mg·hr)) is the pseudo-second-order rate constant of adsorption. The linear plot of  $\frac{t}{q_t}$  versus  $t$  give a straight line with an excellent correlation coefficient ( $R^2 = 0.98$ ) suggesting the rate of adsorption (1) mainly depends of chemisorption processes and (2) is poorly affected by mass transfer in solution (Fig. 7b).

The kinetic parameters extracted from the pseudo-first-order and pseudo-second-order models are depicted in Table 1. The results confirms the good correlation of the pseudo-second-order model with the adsorption of Cd(II) on Cell-Quin as the calculated  $q_e$  correlates with the experimental value.

### 2.3. Adsorption isotherms

The nature of the interaction between the adsorbent and the adsorbate at the equilibrium can be better understood through isotherm equations. The Langmuir, Temkin and Freundlich adsorption isotherms are the most representative models which cover most mechanisms of adsorptions frequently encountered.

Adsorption processes leading to the formation of a monolayer of adsorbate on a homogeneous surface of adsorbent are accurately described by the Langmuir isotherm. This model also assumes that there is a finite number of energetically equivalent and isolated binding sites which are not affected by chemical interactions. The following linear equation describes the Langmuir isotherm:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{b q_m} \quad (3)$$

where  $q_e$  (mg/g) and  $q_m$  (mg/g) represent the amount of adsorbed at the equilibrium and for a complete coverage, respectively,  $C_e$  (mg/L) is the equilibrium concentration of Cd (II) and  $b$  (L/mg) is the Langmuir constant.

On the contrary, the Freundlich isotherm is more adapted if the adsorption process favors to the formation of a several layers of adsorbate on a heterogeneous surface of adsorbent. It can be expressed with the following linear equation:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (4)$$

where the capacity and intensity of adsorption are described by the Freundlich constants  $K_f$  (L/mg) and  $1/n$ , respectively.

The Temkin isotherm assumes a linear decrease of the heat of adsorption rather than a logarithmic evolution as expressed in the Freundlich model. The Temkin isotherm take

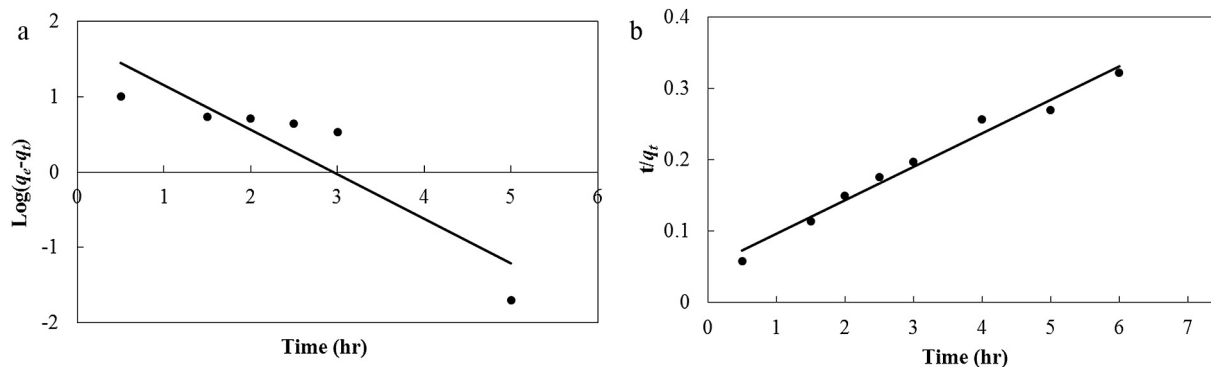


Fig. 7 – (a) Pseudo-first-order plot for Cd(II) adsorption on Cell-Quin. (b) Pseudo-second-order plot for Cd(II) adsorption on Cell-Quin. Initial concentration of metal ions = 100 mg/L, adsorbent dose = 5 g/L, pH = 8, t = 6 hr, 25°C.

**Table 1 – Kinetic parameters from the pseudo-first-order and pseudo-second-order models.**

Parameter	Pseudo-first-order model	Pseudo-second-order model
$q_{e,exp}$ (mg/g)	18.6	18.6
$q_{e,calc}$ (mg/g)	55.9	21.3
$k_1$ (hr <sup>-1</sup> )	1.36	–
$k_2$ (g/(mg·hr))	–	$4.49 \times 10^{-2}$
$R^2$	0.81	0.98

**Table 2 – Adsorption of heavy metals with Cell-Quin. Initial concentration of metal ions = 100 mg/L, adsorbent dose = 5 g/L, 25 °C.**

Metal	Optimal pH	Optimal contact time (hr)	Metal removed
Pb(II)	4	12	86%
Cu(II)	4	6	85%
Zn(II)	4	12	83%
Ni(II)	9	12	77%

into account the effects of adsorbate/adsorbate interactions and the following Eq. (5) implies a uniform distribution of binding energy:

$$q_e = \left(\frac{RT}{b}\right) \ln(A_T) + \left(\frac{RT}{b}\right) \ln(C_e) \tag{5}$$

where  $b$  (J/mol) is a constant related to the heat of adsorption,  $K_T$  (L/g) is the Temkin isotherm constant,  $R$  (8.314 J/mol/K) is the universal gas constant and  $T$  (K) is the absolute temperature.

The linear regression curves representing the three adsorption isotherms are depicted in Fig. 8. The adsorption process is not satisfactorily described by the Langmuir and Temkin isotherms as both models gave modest correlation coefficients  $R^2$  (0.78 for both models). By contrast, the Freundlich model adequately fits to describe the adsorption of Cd(II) on Cell-Quin as the calculated correlation coefficient  $R^2$  reaches 0.99. The value of the  $n$  parameter (1.51) which was extracted from the equation of the linear regression curve of the Freundlich isotherm refers to a favorable adsorption process. From these models we can interpret that the adsorption occurs on a heterogeneous surface through the formation of multiple layers of adsorbate with a non-uniform distribution of binding energy. The porous and heterogeneous framework of cellulose paper likely explain the interpretation of results provided by the Freundlich isotherm.

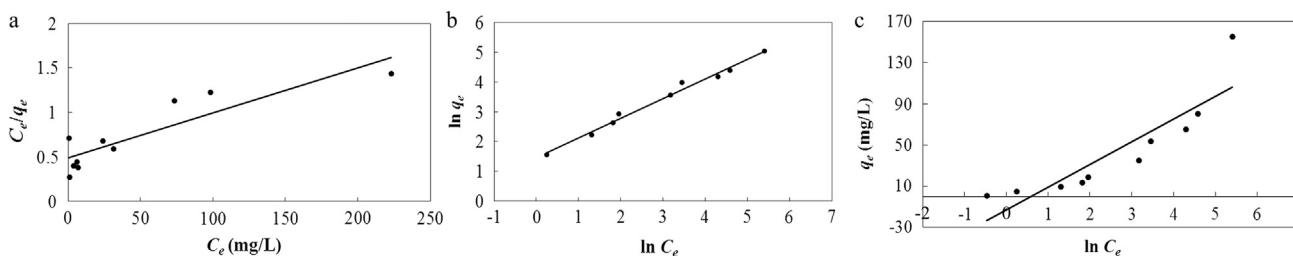
**2.4. Adsorption of other metals**

While we initially focused on the removal of Cd(II) species from aqueous solution, the capacity of Cell-Quin to adsorb Pb(II), Cu(II), Zn(II) and Ni(II) species, which are prevalent

metallic pollutants of water sources, was also assessed. For each metal, we determined the optimal pH and contact time of adsorption. The results, depicted in Table 2, show that Cell-Quin adsorb Pb(II), Cu(II), Zn(II) and Ni(II) from aqueous solutions with a good efficiency. However, the optimal pH of adsorption is out of the of the recommended values for drinking water ( $6.5 < \text{pH} < 8.5$ ) and therefore the use of Cell-Quin to remove Pb(II), Cu(II), Zn(II) and Ni(II) from drinking water is not well adapted.

**3. Conclusion**

In summary, we have developed a fully bio-sourced adsorbent for the removal of Cd(II) in water. The adsorption device was fabricated by chemical functionalization of cellulose paper with quinine moieties, furnishing Cell-Quin. The removal efficiency of Cd(II) in aqueous samples by Cell-Quin was optimized and the mechanism of adsorption was assessed through the study of the Langmuir, Freundlich and Temkin adsorption isotherms. While out of the scope of this study, we also showed that the use of Cell-Quin is not limited to the removal of Cd(II) as Pb(II), Ni(II), Zn(II) and Cu(II) can be adsorbed with a good efficiency. The prototype we developed in this study features many assets for a domestic use as it (1) can be used without equipment and extensive training, (2) adsorbs Cd(II) at pH compatible with the pH of drinking water and (3) is fabricated from bio-sourced materials found in many places on earth and especially in developing countries. While this technology is still in its infancy and certainly requires further toxicological studied, we believe that it may find applications for the foreseeable future.



**Fig. 8 – (a) Langmuir, (b) Freundlich and (c) Temkin isotherms describing the adsorption of Cd(II) on Cell-Quin. Initial concentration of metal ions = 100 mg/L, adsorbent dose = 5 g/L, pH = 8, t = 6 hr, 25°C.**



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