A green and simple method for preparation of an efficient palladium adsorbent based on cysteine functionalized 2,3-dialdehyde cellulose

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Abstract A green and efficient adsorbent for adsorption of palladium ions was prepared from 2,3-dialdehyde cellulose (DAC) originating from nanocellulose from the green algae *Cladophora*. The DAC was functionalized with cysteine via reductive amination in a convenient one-pot procedure to provide the adsorbent. The adsorption properties for adsorbing palladium(II) ions, including capacity, adsorption isotherm and kinetics, were studied. The successful reductive amination of cysteine with 2,3-dialdehyde cellulose was confirmed by FT-IR, elemental analysis and XPS. The adsorbent was characterized by SEM, XRD, gas adsorption and TGA. The adsorbent had a high adsorption capacity (130 mg palladium per gram adsorbent) and enabled fast adsorption of palladium(II) ions from solution (80 % of maximum capacity reached in 2 h). Adsorbent materials suitable for both filters (fibrous) and column matrixes (spherical particles) could be obtained in an efficient manner by controlling the degree of oxidation while producing the DAC material.

Keywords 2,3-dialdehyde cellulose · Palladium adsorption · Cellulose beads · Nanocellulose

Introduction

The transition metal palladium is widely used in e.g. electronic-, pharmaceutical- and chemical industry, due to its specific physical and chemical properties. The recovery and extraction of palladium from industrial waste has gained considerable interest due to high demand, low natural abundance (Barakat et al. 2006; Liu et al. 2003) and the heavy-metal toxic effect palladium exerts to animals, plants and humans (Nolan and Lippard 2008). Furthermore, palladium is a frequently used catalyst for the formation of C–C bonds in the production of pharmaceuticals and is allowed only in sub 5 ppm amounts in pharmaceuticals (Products CfPM 2002). Therefore, searching for efficient methods for palladium recovery and extraction is important. Further, palladium can be used as a benchmark transition metal and knowledge gained about palladium recovery could likely be useful for developing recovery methods also for other transition metals, e.g. platinum, rhodium and ruthenium.

Some well-known methods including chemical precipitation (Vincent et al. 2007), ion exchange (Anpilogova et al. 2014), solvent extraction (Paiva et al. 2014), membrane separation (Li et al. 1994) and adsorption (Gupta et al. 2003; Sharma and Rajesh 2014) are employed to recover palladium. Among the above-mentioned methods, adsorption is highly efficient and is frequently used. Several studies have investigated palladium ions adsorption using e.g. thiol-

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functionalized silica (Lim et al. 2011; Qishu et al. 2012), modified chitin or chitosan (Fujiwara et al. 2007; Wasikiewicz et al. 2007) and functionalized polymers or resins (Awual et al. 2013; Jermakowicz-Bartkowiak et al. 2005; Venkatesan et al. 2005). Among the adsorbents, some are not environmentally benign and rely on a petrol feedstock, whereas others are green, e.g. chitin or chitosan, but suffer from lower adsorption capacity. Furthermore, the ease of extracting or desorbing the palladium ions from the adsorbent in order to recycle the precious metal greatly varies between the different materials, where the biopolymers can be simply incinerated at a relatively low temperature to obtain the pure palladium, a procedure that is not convenient for e.g. the silica-based adsorbents.

Several aspects are important to consider when developing an efficient material for adsorption. Besides the obvious advantages of having a large surface area, ample coordination sites, and efficient coordination of the adsorbate, the practical execution of the adsorption is a key aspect e.g. by using filters or columns. For filters, a material with fibrous character is desired as it is beneficial for the strength of filters. A material used as matrix in columns on the other hand should preferably have a spherical morphology to keep backpressure to a minimum.

Cellulose is the most abundant renewable biopolymer in nature and is a promising raw material in terms of cost of production and ease of modification (Klemm et al. 2005). Periodate oxidation of cellulose is a highly specific reaction for converting the 2,3-dihydroxyl groups to 2,3-dialdehyde groups without significant side reactions (Bruneel and Schacht 1993; Maekawa and Koshijima 1984). The resulting aldehyde groups can be further transformed to e.g. carboxyl groups (Maekawa and Koshijima 1984; Takaichi et al. 2014), primary alcohols (Casu et al. 1985), or imines (Schiff bases) with primary amines (Sabzalian et al. 2014), which enables the use of 2,3-dialdehyde cellulose (DAC) as a suitable starting material in a wide range of applications e.g. as an adsorbent of heavy metals (Nada and Hassan 2006), DNA (Su et al. 2007) or dyes (Kitkulnumchai et al. 2008).

Our group has made research efforts towards finding useful applications of *Cladophora* nanocellulose (Carlsson et al. 2014; 2015; Metreveli et al. 2014; Nyholm et al. 2011; Razaq et al. 2012). The use of *Cladophora* nanocellulose is well in line with the concept of sustainable industrial scale processing, as the source of this cellulose is abundant and, in

addition, *Cladophora* algae are typically considered undesirable pollutants, known for forming large, foul-smelling, algal mats and having adverse effects on the aquatic ecosystem as well as harbouring bacterial pathogens (Mihrianyan 2011). Furthermore, no large scale applications for this source of cellulose exists so the use of this source is not in conflict with other applications e.g. food production, fuel production or building materials. Recently, we reported a new and convenient method for producing DAC beads by periodate oxidation of *Cladophora* nanocellulose (Lindh et al. 2014; 2016). The method provides spontaneous bead formation in a one-pot procedure under aqueous conditions at high degrees of oxidation, circumventing the traditional tedious procedure for bead formation typically involving: (1) dissolution of cellulose, (2) shaping of the beads and (3) regeneration of the polysaccharide, where one or more steps typically employ environmentally harmful solvents (Gericke et al. 2013). The periodate oxidation can also be controlled to produce materials with fibrous character by performing less extensive periodate oxidation. Based on our work on periodate oxidation of *Cladophora* cellulose we now introduce a green, renewable and efficient material for adsorption of palladium ions. Different kinds of DAC was prepared by periodate oxidation and were further functionalized via reductive amination with cysteine in a facile one-pot procedure. The obtained materials were used for palladium ion adsorption and were characterized by SEM, XRD, gas adsorption, FTIR, TGA and XPS.

Experimental

Materials

Nanocellulose from *Cladophora* algae was provided by FMC Biopolymer. Sodium metaperiodate (NaIO_4), hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$), 2-picoline-borane ($\text{C}_6\text{H}_7\text{BH}_3$), L-cysteine and other chemicals used were of analytical or reagent grade and were used as received. Deionized water was used throughout the experimental procedures.

Preparation of DAC

The preparation of DAC proceeded according to literature procedure (Lindh et al. 2014). In short,

Cladophora nanocellulose, 20 g in 1.5 L of water was mixed with 134 g of sodium metaperiodate (5 mol per mol of anhydroglucose units) dissolved in the same medium as the cellulose. The periodate-containing reaction mixture was carefully wrapped in aluminum foil to avoid light exposure. The reaction mixture was vigorously stirred at room temperature in the dark for 13 days. Aliquots were withdrawn after 2 and 13 days (750 mL each time) and named 2D-DAC and 13D-DAC, respectively. The withdrawn aliquots were immediately quenched via the addition of ethylene glycol and washed repeatedly with water to provide pure DAC. DAC samples were dried under reduced pressure at 40 °C and used in their dry state for further reactions.

Reductive amination of DAC

Dried DAC (2D-DAC or 13D-DAC), 1 g, was added to a 250 mL round-bottom flask, which contained 100 mL methanol. After vigorous stirring, to make the DAC suspend well, L-cysteine (7.57 g, 10 equiv.) and 2-picoline-borane (2.67 g, 4 equiv.) were added successively. The reaction mixture was stirred at room temperature for 24 h. The products, named 2D-DAC-LC and 13D-DAC-LC, were washed with distilled water followed by ethanol and dried under reduced pressure at 40 °C for further use.

Scanning electron microscopy

Scanning electron micrographs were taken with a LEO1550 field-emission SEM instrument (Zeiss, Germany) operated at 1 kV with an in-lens secondary electron detector. Samples were mounted on aluminum stubs by means of double-sided adhesive carbon tape and sputtered with gold/palladium to avoid charging effects.

X-ray diffraction

X-ray diffraction (XRD) analysis was performed with a diffractometer having Bragg-Bretano geometry (Cu K α radiation; $\lambda = 1.54 \text{ \AA}$) (D5000, Siemens/Bruker, Germany). The crystallinity index of the nanocellulose and its derivatives was calculated using the Segal empirical equation (Segal et al. 1959).

$$CrI = \frac{I_{22.5^\circ} - I_{18^\circ}}{I_{22.5^\circ}} \quad (1)$$

where *CrI* stands for crystallinity index of cellulose. $I_{22.5^\circ}$ represents the peak diffraction intensity corresponding to crystalline cellulose and I_{18° is the peak diffraction intensity corresponding to the amorphous sections at 2-Theta, 22.5° and 18°, respectively.

Nitrogen sorption isotherm analysis

Nitrogen gas adsorption and desorption isotherms of *Cladophora* nanocellulose and its derivatives were performed on an ASAP 2020 instrument (Micromeritics, USA). The specific surface area was calculated based on the BET (Brunauer et al. 1938) method during adsorption with the ASAP 2020 software, while the pore size distribution was determined according to the density functional theory (DFT) method using the model for nitrogen at 77 K.

Fourier transform infrared spectroscopy (FTIR)

FTIR spectra were recorded on a Tensor 27 FTIR spectrometer (Bruker, Germany). The resolution was set to 4 cm⁻¹ with 64 scans over a range of 4000–400 cm⁻¹. Samples were ground with KBr and prepared into pellets for FTIR measurements.

Thermal gravimetric analysis (TGA)

Samples were analyzed with a TGA/SDTA851 instrument (Mettler Toledo, Switzerland), at a temperature range of 25–800 °C with a heating rate of 5 °C per minute under air or nitrogen atmosphere.

X-ray photoelectron spectroscopy (XPS)

High-resolution XPS spectra for C, N, O, S, and Pd were performed with an ESCA instrument (Physical Electronics, U.S.) equipped with an Al K α source (1486.6 eV, 45 W). The analyzer was operated at 23.5 eV pass energy, while electron and Ar⁺ gun neutralization was applied to compensate for surface charging effects. Elemental atomic concentrations and ratios were calculated from the XPS peak areas with the Multipak software (Physical Electronics, U.S.).

Determination of aldehyde content

In order to determine the degree of oxidation (D.O.), elemental analysis was conducted. The DAC samples were transformed to aldoximes via Schiff base reactions with hydroxylamine according to a literature procedure (Lindh et al. 2014) and were analyzed for elemental composition (C, H, and N). To a stirred 100 mL RB-flask was added dried DAC (100 mg), 40 mL of acetate buffer (pH 4.5), and 1.65 mL of hydroxylamine solution (aqueous, 50 wt%). The reaction mixture was stirred at room temperature for 24 h. The product was thoroughly washed with water and dried under reduced pressure prior to elemental analysis. The term “degree of oxidation” (D.O.) represents the ratio of 2,3-alcohols in the anhydroglucose units that has been transformed into their corresponding aldehydes. The highest degree of oxidation, i.e. 100 %, corresponds to all anhydroglucose units being converted to the corresponding non-cyclic 2,3-dialdehyde structures, which would correspond to approximately 12.5 mmol of aldehyde groups per gram of cellulose.

Determination of cysteine content

The degree of functionalization, i.e. the degree of cysteine coupled to the DAC, was determined via elemental analysis (C, H, N and S) of the 2D-DAC-LC and 13D-DAC-LC samples. The term “degree of functionalization” represents the ratio of the original 2,3-alcohols in the anhydroglucose units that has been functionalized with L-cysteine via reductive amination of the periodate induced 2,3-dialdehydes. The highest degree of functionalization, i.e. 100 %, corresponds to all of the original 2,3-dialcohols being functionalized with L-cysteine, which would correspond to approximately 12.5 mmol of cysteine per gram of cellulose.

Adsorption experiments

A series of Pd(OAc)₂ solutions of various initial concentrations (10–600 mg/L of Pd(OAc)₂) were prepared by dissolving given amounts of Pd(OAc)₂ in acetonitrile. 10 mL aliquots were placed in 15 mL plastic vials and a given amount of adsorbent was added to each vial. Each vial was then sealed and fixed on a tube rotator (VWR Tube Rotator) and rotated for 24 h. The vials were centrifuged at 4700 g for 10 min.

An aliquot of the supernatant was then withdrawn and analyzed by UV–vis spectroscopy (Shimadzu, UV-1800, Japan). Blank solutions containing equivalent initial concentration of Pd but without addition of adsorbent were subjected to the same procedure. Adsorption isotherms were carried out at room temperature, 22.5 °C.

The adsorption isotherm data were analyzed by both the Langmuir (2) and Freundlich (3) models, which are expressed in linear form as (Freundlich 1906; Langmuir 1918),

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{1}{q_0} C_e \quad (2)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (3)$$

respectively. Adsorption kinetics for palladium ion adsorption on DAC-based adsorbent was explored in a batch experiment. A number of vials (15 mL) containing the same concentration of Pd(OAc)₂ (100 mg/L) with the same amount of adsorbent (4 mg) were prepared, and after 2, 4, 8, 15, 30, 60, 120, 240, 360, 480, 1440, 1860 and 4320 min, the suspension in the corresponding vial was filtered through a PTFE (Polytetrafluoroethylene) filter. Adsorption amount was calculated by the difference of the concentration of initial solution of Pd(OAc)₂ and the filtrate, both of which were measured with UV–vis spectrophotometer. Blank controls were taken without addition of adsorbent. All the experiments were performed at room temperature (22.5 °C).

Results and discussion

In this study two types of DACs were prepared, differing in the degree of oxidation (D.O.). One type was oxidized to 30 % D.O. by carrying out the oxidation for two days (2D-DAC) and the other had a D.O. of 85 %, which was achieved by performing the oxidation for 13 days (13D-DAC). The 2D-DAC and the 13D-DAC were subjected to reductive amination with L-cysteine using 2-picoline-borane as reducing agent, providing 2D-DAC-LC with a degree of L-cysteine functionalization of 9 % and 13D-DAC-LC with a degree of L-cysteine functionalization of 49 % (Fig. 1). 2-picoline-borane is a non-toxic and efficient reducing agent, which is selective towards imines and

Fig. 1 Reaction scheme for the preparation of cysteine functionalized DAC and a plausible coordination mode for the adsorption of Pd(II) ions

thus allows the direct conversion of carbonyl compounds into amines in a one-pot procedure (Cosenza et al. 2011; Ruhaak et al. 2010; Sato et al. 2004). The functionalized DACs contain plentiful coordination sites, which enable efficient adsorption of palladium. The L-cysteine functionalized DAC materials were then subjected to the adsorption of Pd(II) ions and provided high adsorption capacity. For convenience, the adsorbents 2D-DAC-LC and 13D-DAC-LC loaded with palladium were named 2D-DAC-LC-Pd and 13D-DAC-LC-Pd, respectively.

Adsorption isotherm and kinetics

Equilibrium adsorption time is used to evaluate the effect of the contact time between adsorbent and adsorbate (Awual et al. 2013). The results of the relationship between adsorption amount and contact time are shown in Fig. 2a. The data indicate that the adsorption of Pd(II) ions was fast and 80 % of

maximum adsorption amount could be reached after 2 h. As the adsorption almost reached equilibrium in 24 h, this time was selected in further experimental work for obtaining the adsorption isotherms.

An adsorption isotherm can be used to characterize the relationship between the adsorbent and the adsorbate. This provides a relationship between the concentration of adsorbate in the solution and the amount of adsorbate adsorbed on to solid phase when the two phases are at equilibrium (Sağ 2001). The adsorption isotherms for Pd(II) on 2D-DAC-LC and 13D-DAC-LC are presented in Fig. 2b. The amount of metal ions adsorbed at equilibrium per unit mass (q_e) of the DAC-LC increased first with the increase of the equilibrium concentration of solute (C_e) then almost reached a plateau value, which represents saturation of the active chelation sites on DAC-LC.

The Langmuir plot (C_e/q_e against C_e) was used to obtain Langmuir constants, q_0 and b , related to the adsorption capacity and energy of adsorption,

Fig. 2 **a** Effect of contact time on Pd(II) adsorption and **b** adsorption isotherm for Pd(II) on 2D-DAC-LC and 13D-DAC-LC. Connecting line in **a** and **b** only to serve as guide to the eye

respectively. From the Freundlich model, the n and K_F are provided, which relates to the adsorption intensity and the adsorption capacity, respectively. All the parameters are shown in Table 1. The Langmuir model yielded high correlation coefficient values (R^2) 0.9988 and 0.9985 and the q_0 values were 130.4 mg/g and 60.7 mg/g for Pd(II) adsorbed on 2D-DAC-LC and 13D-DAC-LC, respectively. Values for adsorption capacity of other adsorbents presented in literature are given in Table 2 for comparison. The somewhat surprising higher adsorption capacity for 2D-DAC-LC compared to 13D-DAC-LC, despite the lower content of coordinating cysteine groups, is probably a result of lower accessible surface area of the bead shaped 13D-DAC-LC (see Table 3).

The thermodynamic parameter, the Gibbs free energy (ΔG°) (see Table 1), for 2D-DAC-LC and 13D-DAC-LC was evaluated from the Langmuir constant using the equation (Gupta et al. 2006)

$$\Delta G^\circ = -RT \ln b \quad (4)$$

where b is the equilibrium constant and R is the universal gas constant. The negative values of ΔG° confirm the feasibility of the adsorption process.

In order to investigate the mechanism of adsorption, the kinetic models for pseudo first order (5) (Lagergren 1898) and pseudo second order (6) (Sparks 1986) were applied. The pseudo first order model is expressed by

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (5)$$

where q_e and q_t are the amounts of adsorbed Pd(II) (mg/g) at equilibrium and time t , respectively, and k_1 (min^{-1}) is the rate constant of pseudo-first-order adsorption. The pseudo second order model is given by

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

where k_2 [$\text{g}/(\text{mg min})$] is the rate constant of pseudo-second-order adsorption, q_e is the amount of Pd(II) adsorbed (mg/g) at equilibrium, and q_t is the amount of the adsorption (mg/g) at any time t .

Based on the results in Fig. 3, it is obvious that the adsorption behavior is best described by the pseudo second order model, providing a R^2 value >0.99 for both adsorbents, implying that the adsorption kinetics is largely controlled by chemisorption.

Morphological characterization

SEM micrographs of samples of unmodified *Cladophora* nanocellulose, 2D-DAC, 13D-DAC and the corresponding ligand functionalized derivatives, before and after adsorption of palladium, are shown in Fig. 4. As previously described (Lindh et al. 2014), extensive periodate oxidation, i.e. 13 days oxidation, provided drastic change to the cellulose morphology (producing beads with a relatively smooth surface), while 2 days oxidation induced a more compact cellulose compared to the unmodified *Cladophora* nanocellulose. Furthermore, the reductive amination with L-cysteine on DAC provided materials with less compact and more porous texture. Adsorption experiments provided little or no change to the derivatives morphology, neither for 2D-DAC nor 13D-DAC.

FTIR spectroscopy

Figure 5 illustrates the FTIR spectra of unmodified *Cladophora* nanocellulose and the functionalized derivatives. The signals at 880 (Fig. 5b) and 1734 cm^{-1} (Fig. 5c) are assigned to the hemiacetal and carbonyl groups, respectively (Rowen et al. 1951; Spedding 1960). When studying the spectra of *Cladophora* cellulose, 2D-DAC and 13D-DAC in these two regions, the signals increase as the D.O. increases. Furthermore, after L-cysteine-modification,

Table 1 Adsorption parameters of Pd(II) ions on 2D-DAC-LC and 13D-DAC-LC and Gibbs free energy (ΔG°) for adsorption

Adsorbent	Langmuir			Freundlich			$-\Delta G^\circ$ (kJ/mol)
	q_0 (mg/g)	$b \times 10^4$ (L/mol)	R^2	K_F	n	R^2	
2D-DAC-LC	130.4	3.566	0.9988	82.63	12.17	0.9644	25.75
13D-DAC-LC	60.7	2.496	0.9985	33.20	9.34	0.9722	24.87

Table 2 Comparison of adsorption capacity of different adsorbents

Adsorbent	Adsorption capacity (mg/g)	References
Cellulose-MBT	5	(Sharma and Rajesh 2014)
Native cellulose	1.87	(Sharma and Rajesh 2014)
Radiation cross-linked carboxymethylchitin hydrogels	2.68	(Wasikiewicz et al. 2007)
Chitosan resin modified with L-lysine	109.47	(Fujiwara et al. 2007)
Polystyrene-divinylbenzene functionalized with isothiuronium	20	(Venkatesan et al. 2005)
Carbon black modified with L-Cysteine	84	(Panchompoo et al. 2011)
Mesoporous silica functionalized with 3-(((5-ethoxybenzenethiol)imino)methyl)-salicylic acid ligand	164.2	(Awual et al. 2013)
2D-DAC-LC	130.4	This work
13D-DAC-LC	60.7	This work

Table 3 Pore volume and SSA of cellulose and its derivatives

	Pore volume (cm ³ /g)	SSA (m ² /g)
<i>Cladophora</i> cellulose	0.6	102
2D-DAC	0.4	47
2D-DAC-LC	1	141
13D-DAC	0.003	1
13D-DAC-LC	0.3	47

a more distinct signal at 1734 cm⁻¹ corresponding to carbonyl groups (Spedding 1960) (comparing ii) and iii), or v) and vi)), verified the introduction of L-cysteine on DAC.

X-ray photoelectron spectroscopy (XPS)

The XPS spectra in wide scans of 2D-DAC, 2D-DAC-LC, 2D-DAC-LC-Pd, 13D-DAC, 13D-DAC-LC and 13D-DAC-LC-Pd are presented in Fig. 6. From the spectra of 2D-DAC and 13D-DAC, the characteristic peaks of C 1s (285 eV) and O 1s (531 eV) are shown. For the spectra of 2D-DAC-LC and 13D-DAC-LC, the additional peaks corresponding to N 1s (398 eV) and S 2p (164 eV) peaks can be clearly seen and the spectra of 2D-DAC-LC-Pd and 13D-DAC-LC-Pd reveal the further addition of signals for Pd 3d₅ (335 eV) and Pd 3d₃ (340 eV) (Moulder et al. 1992).

Fig. 3 **a** Pseudo first order kinetics and **b** pseudo second order kinetics for Pd(II) on 2D-DAC-LC and 13D-DAC-LC (the concentration of palladium acetate in acetonitrile was 100 mg/L)

Fig. 4 SEM micrographs of **a** unmodified *Cladophora* nanocellulose, **b** 2D-DAC, **c** 2D-DAC-LC, **d** 2D-DAC-LC-Pd, **e** 13D-DAC, **f** 13D-DAC-LC and **g** 13D-DAC-LC-Pd

Thermal gravimetric analysis (TGA)

Thermal stability of nanocellulose, oxidized nanocellulose and the corresponding derivatives was investigated by TGA and the obtained curves are depicted in Fig. 7. It can be seen that degradation of 2D-DAC and 13D-DAC compared to that of unmodified *Cladophora* nanocellulose is initiated at a lower temperature, both in compressed air and under nitrogen atmosphere. Furthermore, the degradation of 2D-DAC-LC and 13D-DAC-LC commences at a lower temperature than that of 2D-DAC and 13D-DAC, which indicates that the thermal stability of materials deriving from nanocellulose decreases after modification in terms of oxidation and L-cysteine modification. On the other hand, final weight percentages of 2D-DAC-LC-Pd and 13D-DAC-LC-Pd are substantially higher than for the corresponding material before

adsorption of palladium, both in compressed air and nitrogen atmosphere, which confirms the adsorption of palladium ions during the adsorption experiments. These TGA results confirm the XPS results that palladium ions were adsorbed on 2D-DAC-LC and 13D-DAC-LC and also demonstrate that the L-cysteine modification was functional.

Surface area and porosity analysis

Nitrogen sorption isotherms at a temperature of 77 K and pore size distribution for *Cladophora* nanocellulose and its derivatives are given in Fig. 8. The pore volume and specific surface area (SSA) of *Cladophora* nanocellulose and its derivatives are displayed in Table 3. The SSA decreases with increased D.O., two orders of magnitude from 102 to 1 m²/g corresponding to unmodified *Cladophora* nanocellulose and 13D-

Fig. 5 FT-IR spectra of **a** 4000–400 cm^{-1} , **b** 1000–800 cm^{-1} and **c** 1850–1650 cm^{-1} for **i**) unmodified *Cladophora* nanocellulose, **ii**) 2D-DAC, **iii**) 2D-DAC-LC, **iv**) 2D-DAC-LC-Pd, **v**) 13D-DAC, **vi**) 13D-DAC-LC and **vii**) 13D-DAC-LC-Pd

Fig. 6 XPS wide scans of **a** 0–1100 eV, **b** 150–180 eV and **c** 345–405 eV for **i**) 2D-DAC, **ii**) 2D-DAC-LC, **iii**) 2D-DAC-LC-Pd, **iv**) 13D-DAC, **v**) 13D-DAC-LC and **vi**) 13D-DAC-LC-Pd

DAC. Interestingly, after the modification with L-cysteine, the SSA increases significantly, to 141 m^2/g for 2D-DAC-LC and to 47 m^2/g for 13D-DAC-LC, which is supported by the more porous texture observed by SEM (see Fig. 4). In Fig. 8b, the pore size distributions of the samples are shown. All of the samples have a pore size range primarily in the mesoporous region (2–50 nm), except for 2D-DAC-

LC, which has a broader pore size distribution with a mode at 45 nm.

X-ray diffraction (XRD) spectroscopy

XRD curves for *Cladophora* cellulose, 2D-DAC, 2D-DAC-LC, 2D-DAC-LC-Pd, 13D-DAC, 13D-DAC-LC and 13D-DAC-LC-Pd are given in Fig. 9. As

Fig. 7 Thermograms performed in **a** compressed air and **b** nitrogen for dried *Cladophora* nanocellulose, 2D-DAC, 2D-DAC-LC, 2D-DAC-LC-Pd, 13D-DAC, 13D-DAC-LC and 13D-DAC-LC-Pd

Fig. 8 **a** Nitrogen sorption isotherms ($T = 77$ K) and **b** pore size distribution for cellulose and its derivatives

described in Segal's empirical equation (Segal et al. 1959), the intensity of 2-Theta at about 22.5° and 18° corresponds to crystalline and amorphous sections of cellulose, respectively. The intensity of peaks at about 22.5° decreases for 2D-DAC, 2D-DAC-LC and 2D-DAC-LC-Pd compared to unmodified cellulose, which indicates a decrease of crystallinity of the cellulose derivatives after chemical functionalization. Furthermore, the peaks at about 22.5° disappear in the spectra of 13D-DAC, 13D-DAC-LC and 13D-DAC-LC-Pd, which suggest that these samples become completely amorphous.

Conclusions

The novel adsorption materials described herein provide a green and efficient alternative to frequently used adsorbents based on a petrol feedstock. The use of environmentally benign and renewable cellulose from the undesirable polluting green algae *Cladophora*, functionalized with the natural amino acid cysteine, constitutes a green approach to enable recovery of the transition metal palladium. The results from the adsorption study indicate that the adsorption of palladium ions is mainly governed by chemisorption. The

Fig. 9 XRD curves for i) *Cladophora* nanocellulose, ii) 2D-DAC, iii) 2D-DAC-LC, iv) 2D-DAC-LC-Pd, v) 13D-DAC, vi) 13D-DAC-LC and vii) 13D-DAC-LC-Pd

adsorbent has a high adsorption capacity and enables fast adsorption of palladium ions from solution. With our process, materials suitable for both filters (fibrous materials) and for column matrixes (spherical beads) can be obtained. The adsorption materials were extensively characterized using several different methods e.g. FTIR, SEM, XRD, XPS, TGA, elemental analysis and gas adsorption.

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