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Magnetic/non-magnetic argan press cake nanocellulose for the selective extraction of sudan dyes in food samples prior to the determination by capillary liquid chromatograpy

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ABSTRACT

Two methods for the determination of Sudan dyes (Sudan I, Sudan II, Sudan III and Sudan IV) in food samples, by solid phase extraction - capillary liquid chromatography, are proposed. Both methods use nanocellulose (NC) extracted from bleached argan press cake (APC), as a nano-adsorbent recycled from an agricultural waste material. One of the methods involves the dispersion of NC in food sample extracts, along with the waste and eluents being separated by centrifugation. In the other method, NC was modified by magnetic iron nanoparticles before using it in the extraction of Sudan dyes. The use of a magnetic component in the extraction process allows magnetic separation to replace the centrifugation step in a convenient and economical way. The two proposed methods allows the determination of Sudan dye amounts at the 0.25–2.00 μg L^{-1} concentration range. The limit of detections, limit of quantifications and standard deviations achieved were lower than 0.1 μg L^{-1}, 0.20 μg L^{-1} and 3.46% respectively, when using NC as a nano-adsorbent, and lower than 0.07 μg L^{-1} 0.23 μg L^{-1} and 2.62%, respectively, with the magnetic nanocellulose (MNC) was used. Both methods were applied to the determination of Sudan dyes in barbeque and ketchup sauce samples, obtaining recoveries between 93.4% and 109.6%.

1. Introduction

The production of novel nanomaterials from renewable and abundant biomass, such as nanocellulose (NC) obtained from native cellulose, has been drawing growing attention in the last decade since it offers unique physiochemical properties with little effect on the environment [1]. Cellulose is one of the main components of argan press cake (APC), a waste agricultural material that remained after the argan oil extraction [2]. Therefore, transforming APC into valuable products, such as cellulose, is a worthy concern. NC, having at least one dimension in the nanometer range can be produced by different methods based on the strong acid hydrolysis, under strictly controlled temperature, agitation, and time. This will cleave the cellulose fibers transversely [3]. They can be divided into two main categories having different morphology: cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs) [1], and have a wide range of exploitation in analytical chemistry [4–6]. Their versatile properties enable the development of nanostructure-based tools offering extremely promising improvements in the analytical basic properties of sensitivity, selectivity and reliability, with respect to previous non nanostructured designs [4–8]. The exploitation of their physical and chemical properties at different analytical steps includes: sample treatment (extraction/clean-up, and preconcentration), chromatographic and CE techniques, and detection. This exploitations contributes to the development of innovative analytical strategies or the improvement of the conventional ones, in order to achieve the required analytical properties (accuracy, precision, sensitivity, selectivity, speed and cost) [4–8]. NC is considered an effective choice for extraction/clean-up, and preconcentration techniques, by virtue of its excellent sorbent properties, due to the hydrophilicity of their surfaces favoring the formation of strong intermolecular and intramolecular hydrogen bonds [6]. NC, prepared from cotton cellulose by sulfuric hydrolysis, provides stable colloid suspensions containing isolated cellulose whiskers thanks to the negatively charged surface resulting from

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esterification of hydroxyl groups by sulfate ions [9,10]. It was demonstrated that modified and non-modified nanocellulose have excellent sorbent capabilities toward Co^{2+} [5], Cu^{2+} [11], danofloxacin [12], haemoglobin [13], rhodamine dyes [14] and silver nanoparticles (AgNPs) [6] in SPE. Magnetic cellulosic materials have also been utilized in SPE processes [15]. Typically, they are prepared by incorporating iron oxides, cobalt ferrites or nickel into the NC matrix [16]. Nanocellulose-based magnetite nanocomposites have been widely applied in biological fields, such as bioseparation [17], catalysis [18] and electrochemical biosensing [19], also recently being used as SPE sorbents in environmental sample pretreatment [20,21]. Nata et al. [20] have applied magnetic NC (MNC) modified by 1.6-hexanediamine for adsorption arsenate ions. A tetraethylenepentamine–functionalized magnetic cellulose composite was also used for the sample treatment (extraction/clean-up, and preconcentration) of metal ions in contaminated waters [21]. When tested on battery waste–contaminated samples containing Al^{3+}, Cu^{2+}, $Ni^{2+,}$ Zn^{2+} and Cr^{3+}, the composite exhibited sorption efficiency of 65–100% [21]. Polymeric ionic liquid prepared by the reaction of Fe_3O_4-cellulose nanohybrid, epichlorohydrin and 1-methylimidazole was used as sorbent for efficient biosorption of Congo red dye [22].

Food quality is closely associated with color and the use of food colorants has been an age-old practice, enhancing the aesthetical appeal of foods. As a class of azo dyes, Sudan dyes (Sudan I, II, III and IV) are widely used in the chemical industry as coloring materials, oils, hydrocarbon solvents, floor polishes, fats, plastics, shoe and printing inks [23]. Due to their intense red color and low price, these compounds have illegally been used as food dye, mainly in chili, curry and paprika powders, as well as palm oil, in order to intensify the color [24–26]. Although the use of Sudan compounds, as food dyes, has been banned by the European Community [27], these compounds are still a public health problem considering the large number of studies showing the presence of these dyes in food all over the world.

For the determination of Sudan I-IV, many techniques have been reported: liquid chromatography [28–31], electrochemical detection [32–34], mass spectrometry detection [35–37] and capillary electrophoresis using UV diode array [38,39]. To perform the extraction of samples, these cleaning procedures are needed in order to remove most of the interferences and to pre-concentrate the analytes of interest. These procedures include solid phase extraction (SPE) [40–42] and supercritical fluid extraction (SFE) [43].

In this work, we used NC extracted from bleached APC and hybrid nanoparticles based on magnetic nanoparticles and NC for clean-up of food samples and the preconcentration of Sudan dyes, prior to their determination by capillary liquid chromatography (CLC). Although the adsorption efficiency of NC is good using centrifugation separation strategy, it might suffer from the inconvenience of tedious recycling processes. Therefore, magnetic separation is a rapid and effective technology for separation, making magnetic nanocellulose (MNC) a good alternative. In fact, this technology is capable of treating large amounts of food samples within a short time. Finally, no research on the application of NC extracted from bleached argan press cake (APC), for the extraction of Sudan dyes as an SPE format in food analysis has been reported. The prepared NC and MNC were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). In the SPE studies, several parameters affecting the extraction efficiency of Sudan dyes were investigated and optimized to possibly be used and considered as a national standard control.

2. Experimental

2.1. Reagents, materials and sample preparation

Sudan I (1-phenylazonaphth-2-ol), Sudan II (1-(2,4-dimethylphenyl) azonapthalen-2-ol), Sudan III (1-(4 (phenyldiazenyl) phenyl) azonaphthalen-2-ol), Sudan IV (1-(2-methyl-4-(2-methylphenyldiazenyl) phenyl) azonapthalen-2-ol, methanol (HPLC grade), ethyl acetate, sodium hydroxide, sodium sulphide, sodium hypochlorite, magnesium sulfate heptahydrate, hydrogen peroxide and sulfuric acid were purchased from Sigma-Aldrich. All stock solutions were prepared in methanol and preserved in the dark. Stock solutions of the different Sudan dyes were prepared at 10 mgL^{-1} and the working standard solutions were obtained by dilution with Milli-Q water (Millipore, Bedford, MA, USA) to the desired concentrations.

Barbecue and ketchup sauces were purchased from a local supermarket (Ciudad Real, Spain). One hundred grams of each sauce sample were weighed and a volume of stock solutions of the Sudan dyes analytes was slowly added in a dropwise manner. The solution was spread over the sample and allowed to stand for 24 h to allow the methanol to evaporate. Afterwards, 1 g of the spiked sample were dispersed into 100 mL of 0.01 mol L^{-1} hydrochloric acid in an ultrasonic water bath at room temperature for 1 h.

2.2. Instrumentation and working conditions

All determination was carried out using an Agilent 1200 capillary liquid chromatography system. It was equipped with a vacuum degasser, a capillary LC pump, a micro well-plate auto sampler (5 µL injection loop), a thermostatted column compartment and a Diode-Array Detector. The data was processed using the Agilent ChemStation. Reversed-phase C18 analytical column Sorbax-C18 column (4.6 mm×150 mm, particle size 5 µm) was used for the separation of the four extracted Sudan dyes.

Fourier transform infrared spectroscopy (FTIR) spectra of CNFs were recorded using a 400 (PerkinElmer, USA) equipped with attenuated total reflectance (ATR). All spectra were obtained under ambient conditions from 32 scans at resolutions of 4 cm^{-1} within the region 4000–650 cm^{-1}. Morphological analysis was carried out by scanning electron microscopy (SEM) (Hitachi SU8030) operating at an acceleration voltage of 5 kV.

X-ray diffraction analysis of the samples was conducted using Philips X´Pert MPD X-ray diffractometer (Philips Co., Netherland) equipped with Ni-filtered Cu Kα radiation generated at 40 kV and 40 mA. The data was collected at an angular range of 5–60° with a scan rate of 4 °/min.

2.3. Preparation of nano-adsorbents used in the extraction of sudan dyes

2.3.1. Preparation of nanocellulose

The nanocellulose was prepared from cellulose which was extracted from argan press cake (APC). A 1 kg of APC was treated with an aqueous 3% (w/w) NaOH and 6% (w/w) Na_2S solution for 2 h at 80 °C, and then washed until neutral solution was obtained. Subsequently the insoluble residue was further bleached with 1% sodium hypochlorite at 45 °C for 1 h and washed with fresh water until NaOCl was completely removed and then treated with 2% H_2O_2, 0.5% $MgSO_4{\cdot}7H_2O$, and 3% NaOH solution for 1 h at 60 °C. After the sample was treated with 1% NaOCl, the reaction was conducted in a water bath at 45 °C for 2 h then treated with 0.5% H_2O_2 and 3% NaOH. The cellulose pulp was washed thoroughly to remove chemicals and then dried in the oven at 60 °C.

1.0g of the extracted cellulose was added in a test tube and a 9g of 10% sulfuric acid was added. The mixture was sonicated at 40 °C for 1 h and diluted to a 20 mL with water and centrifuged at 10,000 rpm for 30 min. The liquid was decanted and the solid was washed several times with distilled water and then centrifuged. This operation was repeated until the pH of the solution was about 6. The obtained nanocelluse (NC) was dried under the vacuum at 60 °C.

2.3.2. Preparation of magnetic nanocellulose

The preparation of magnetic nanocellulose (MNCs) was carried out using other previously techniques [44]. In brief, a 20 mg of the

prepared NC were immersed in 200 mL of freshly prepared aqueous solution of $FeSO_4$ and $CoCl_2$ with a molar ratio of [Fe]/[Co]=2. In this case, the NC were swelled for 15 min to ensure that a homogenous distribution was obtained. Three different solutions of $FeSO_4/CoCl_2$ salts were prepared: C_1: 0.03; C_2 =0.09 and C_3 =0.15 mol. L^{-1}. The system was heated to 90 °C for at least 3 h to enhance the transformation of soluble initial iron/cobalt hydroxides to insoluble iron/cobalt oxyhydroxide complexes. The particle – modified magnetic NC network was then washed thoroughly and then immersed in liquid nitrogen freezed to generate the ferromagnetic aerogel nanoparticles.

2.4. Extraction procedure

When using non-magnetic NC in the SPE, 50-mL of the sample extract or standard solution was mixed with 0.100g of NC, sonicated for 5 min at room temperature and transferred to a 50 mL screw cap. After that, the mixture stood for 10 min and was centrifuged at 8000 rpm for 15 min to complete the phase separation. The Sudan dyes were retained in the NC and the waste solution was discarded. Then, 2 mL of methanol (the minimum amount necessary to completely elute the target analytes from NC) was added to NC. The mixture was sonicated for 5 min and centrifuged for 15 min. The eluent was collected and analyzed using CLC-DAD.

In the case of magnetic SPE, an amount of 50 mg of MNC was put into a 50 mL vial. The first step was conditioning the samples with 2 mL of methanol and then deionized water. After that, 50 mL of Sudan dyes (standard or sample extract) were added to the vial. The mixture was mixed at room temperature for 5 min in order to form a homogenous dispersion solution. After the sample stood for 5 min, magnetic nanomaterials containing the adsorbed Sudan dyes were rapidly removed from the solution under a strong external magnetic field. After discarding the supernatant solution, Sudan dyes were eluted from the magnetic nanomaterials with 2×1.0 mL of methanol. This solution (5 µL) was injected into the CLC-DAD system.

3. Results and discussion

3.1. Characterization of nanocellulose

The FTIR spectra of APC and NC are shown in Fig. 1. The spectrum of NC shows that impurities such as proteins and lipids were removed because their peaks at 1744 and 1628 cm^{-1} are greatly decreased or have completely disappeared. The typical peaks at 1380 and 1056 cm^{-1} associated with cellulosic molecules indicated the enhanced presence of sugar components. The bleaching sequences containing a series of bleaching operations with hypochlorite (NaOCl), hydrogen peroxide (H_2O_2) in basic medium followed by extraction with sodium hydroxide (NaOH) in the presence of low concentration of H_2O_2 and sulfuric acid hydrolysis demonstrates the merit of producing NC from APC.

The X-ray diffraction patterns of APC and NC are shown in Fig. 2 where NC clearly shows three peaks at approximately 15°, 18.5° and 22.8° corresponding to planes associated with Miller indices. XRD results suggest that the nanocellulose extracted from APC via Kraft pulping, bleaching and acid hydrolysis operations exhibits a crystalline morphology of nanocellulose [44].

The SEM images of a dilute suspension of cellulose and nanocellulose are shown in Fig. 3. It is evident that sulfuric acid hydrolysis treatment by hydrolyzed micron nanocelluloses into nanometer scale cellulose is indeed effective. The agglomeration of larger fibrils of cellulose was likely composed of elementary fibril bundles linked together through strong hydrogen bonding of the cellulose fiber, and lead to re-bonding of the inter fibril hydroxyl groups. This was also observed for the extraction of nanocrystalline cellulose from the cotton linter [45].

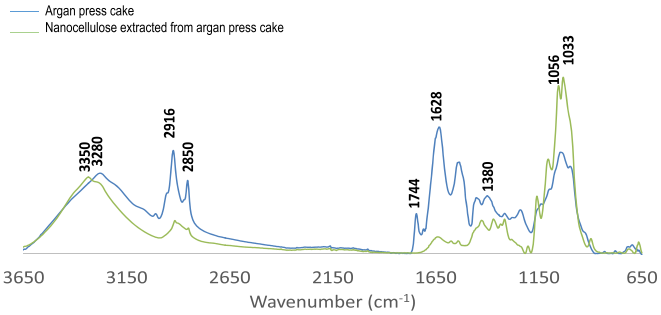

Fig. 1. FTIR spectra of argan press cake (APC) and nanocellulose (NC) extracted from bleached APC.

3.2. Optimization of the extraction conditions

The extraction conditions were optimized in both methods by analyzing a standard solution (1 µg L^{-1}) of a mixture of Sudan dyes compounds. The parameters affecting the performance of the extraction, such as pH, adsorption time, sorbent amount, elution solvent and recycling time of sorbent, were investigated. When one parameter was changed, the other parameters were fixed at their optimal values. NC and MNC with negative adsorbent surfaces [9,10] are used in the SPE of sudan dyes. Taking into account the experimental data obtained by Zhang et al. [46], sudan dyes are weak acids with a pK_a value of about 11.65. However, the azo group in the 1-position that acts as a hydrogen bond acceptor leads to formation of an intramolecular hydrogen bond with the phenolic OH. The absorption of sudan dyes into NC and MNC can be explained by the electrostatic force and charge transfer between the hydroxyl groups of sudan dyes and a negative adsorbent surfaces of NC and MNC. Thus, the influence of solution pH on the recoveries of the four Sudan dyes by SPE with NC and MNC was studied in the range 1.0–12.0. In booth case, good recoveries were obtained for the four sudan dyes when the pH of the sample solution ranged from 1.0 to 9.0. The adsorption of the four Sudan dyes onto the cellulosic sorbents peaked near pH 3.0. When the pH of the solution changed from 9.0 to 12, the retention efficiency of the four sudan dyes onto NC and MNC obviously decreased. This is probably because sudan dyes are weak acids with a pK_a value of about 11.65. Sudan dyes exist as neutral molecules under pH < 11.65, therefore their adsorptions are not affected by the charges on the surface of the adsorbents. However, Sudan dyes may become anion species at a pH above 11, resulting in electrostatic repulsion between analytes and NC and MNC with a negative charge surfaces. Considering that the retention for all analytes peaked at pH of 3.0, the optimal pH of 3.0 was selected for further studies. Next, the effect of the sample contact time with the NC and MNC sorbents was studied within 2–40 min. The results indicated an increase of retention efficiency with the increase of contact time. Therefore, 15 min for NC (method I) and 10 min for MNC (method

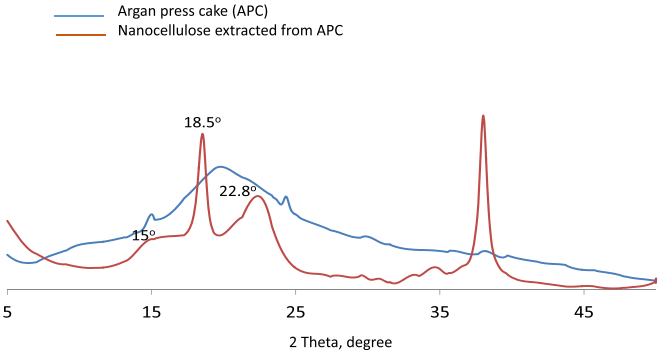

Fig. 2. XRD patterns of argan press cake (APC) and nanocellulose (NC) extracted from APC.

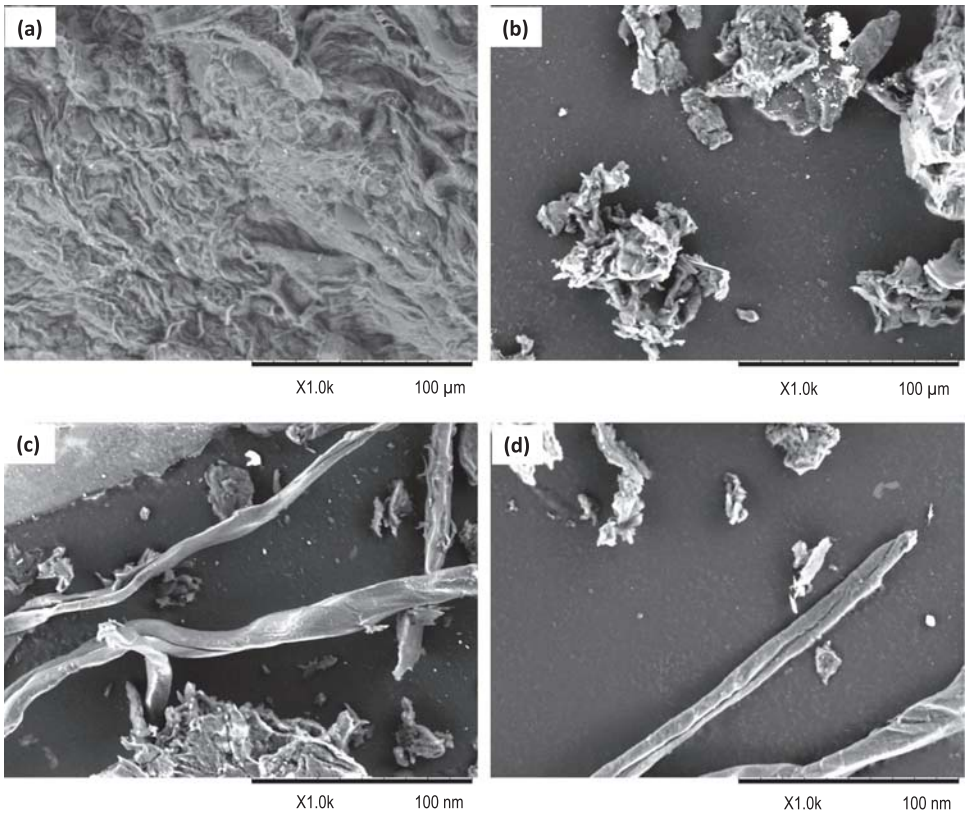

Fig. 3. SEM image of (a), (b) cellulose extracted from argan press cake (APC) and (c), (d) nanocellulose.

II) were selected for further experiments. The optimal amount of NC and MNC used to quantitatively extract Sudan dyes were optimized. For this purpose, different amounts of NC and MNC, ranging from 30 to 300 mg and 10–100 mg, respectively, were tried to extract Sudan dyes from the standard solution (1 µg L^{-1}) at a pH of 3. As observed in Fig. 4, recovery increased when the amount of NC and MNC was increased from 30 to 100 mg and from 10 to 50 mg respectively. When the amount was higher than 100 mg of NC and 50 mg of MNC, any significant recovery improvements were obtained.

Therefore, the optimal amount of NC and MNC sorbents were fixed at 100 mg and 50 mg respectively. On the other hand, desorption conditions were also optimized. Different organic solvents including methanol, ethanol and acetone, were firstly optimized. Experiments were carried out using 100 mg of NC or 50 mg of MNC and 50 mL of Sudan dyes mixture standard solution (1 µg L^{-1}at pH 3). The experimental results indicated that all three organic solvents could elute Sudan dyes. However, desorption ability of the methanol was found to be superior to that of ethanol and acetone. Therefore, methanol was selected for subsequent experiments. Then, the minimum elution solvent volume needed to efficiently elute the adsorbed Sudan dyes was optimized. Different volumes, ranging from 1.0 to 5.0 mL, were tested. The best results were obtained when 2.0 mL was used. Thus, 2×1.0 mL methanol under 5 min of agitation and 15 min of centrifugation was the optimal condition selected for the desorption stage with NC, along with 5 min of agitation with MNC.

After each extraction, sorbent was easily recovered by rinsing it with methanol. Sorbent recycling was then studied, and the results showed that the sorbents can be used at least two times in the case of NC and three times in the case of MNC with the same extraction efficiency.

3.3. Analytical performance and application of the determination of Sudan dyes in food sample

Under optimum conditions, 100 mg of NC (method I) and 50 mg MNC (method II) were evaluated under the adsorption-elution conditions using spiked sauce samples. External calibration curves were constructed by plotting the corresponding peak areas measured by the injection of 6 concentrations of Sudan dyes solutions at 0.25–2 µg L^{-1} after being preconcentrated using the NC and MNC. At least three replicates were performed at each concentration level. Each solution

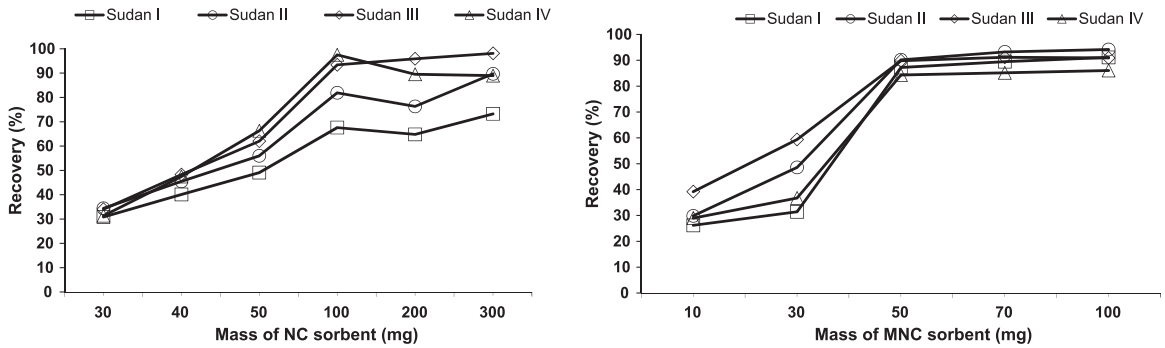

Fig. 4. Effect of nanocelluse (NC) amount (A) and magnetic nanocellulose (MNC) amount (B) in the extraction of sudan dyes.

Table 1
Calibration data and validation parameters for the NC and MNC methods.

Method	Compounds	Linear range (μg L^{-1})	A=(a ± S_a) C +(b ± S_b)	R^2	LOD (μg L^{-1})	LOQ (μg L^{-1})	RSD (%)
Extraction by NC	SD I	0.25–2	A=(323.0 ± 5.2)C+(28.9 ± 6.0)	0.9990	0.06	0.19	1.37
	SD II	0.25–2	A=(267.1 ± 4.2)C+(36.6 ± 4.8)	0.9990	0.10	0.20	1.41
	SD III	0.25–2	A=(397.9 ± 5.5)C-(7.0 ± 6.4)	0.9992	0.05	0.16	2.13
	SD IV	0.25–2	A=(160.7 ± 2.3)C-(1.4 ± 2.6)	0.9992	0.05	0.15	3.46
Extraction by MNC	SD I	0.25–2	A=(512.5 ± 9.8)C-(91.3 ± 10.6)	0.9989	0.06	0.21	2.14
	SD II	0.25–2	A=(435.9 ± 6.0)C-(24.9 ± 6.5)	0.9994	0.05	0.15	1.54
	SD III	0.25–2	A=(575.3 ± 12.0)C-(96.6 ± 13.0)	0.9987	0.07	0.23	1.79
	SD IV	0.25–2	A=(293.3 ± 4.5)C-(18.4 ± 4.9)	0.9993	0.05	0.17	2.62

aSlope; S_a: Standard deviation of slope; b: intercept; Sb: Standard deviation of the intercept; A: peak area; C: Concentration; R: regression coefficient; LOD: limit of detection; LOQ: limit of quantification; RSD: Relative standard deviation (n=11)

Table 2
Determination of Sudan I, Sudan II, Sudan III and Sudan IV in barbeque and ketchup sauces.

Method	Compounds	LOD	Added in the sample	Barbeque sauce		Ketchup sauce	
		(ng g^{-1})	(ng g^{-1})	Found in the sample (ng g^{-1})*	Recovery (%)	Found in the sample (ng g^{-1})[a]	Recovery (%)
Extraction by NC	SD I	16.0	25.0	24 ± 2	97.2	24 ± 2	98.8
			50.0	55 ± 3	111.4	48 ± 2	97.8
			75.0	74 ± 3	98.8	74 ± 2	98.5
			100.0	98 ± 2	98.0	102 ± 2	102.5
	SD II	18.0	25.0	24 ± 2	95.2	24 ± 2	97.2
			50.0	50 ± 2	99.6	49 ± 2	98.2
			75.0	72 ± 3	96.7	77 ± 2	102.9
			100.0	93 ± 3	93.3	93 ± 3	93.4
	SD III	20.0	25.0	27 ± 2	110.8	26 ± 2	103.6
			50.0	55 ± 2	109.2	51 ± 2	102.0
			75.0	81 ± 1	108.7	72 ± 2	95.9
			100.0	101 ± 1	101.0	102 ± 2	102.2
	SD IV	21.0	25.0	24 ± 2	98.0	25 ± 2	98.4
			50.0	55 ± 3	110.2	49 ± 2	97.4
			75.0	74 ± 2	99.3	74 ± 2	98.0
			100.0	99 ± 2	98.7	102 ± 3	102.1
Extraction by MNC	SD I	23.0	25.0	27 ± 2	108.0	27 ± 2	108.8
			50.0	51 ± 2	101.8	51 ± 2	101.6
			75.0	79 ± 2	105.3	74 ± 2	98.5
			100.0	108 ± 2	108.1	106 ± 3	106.0
	SD II	15.0	25.0	24 ± 2	94.0	24 ± 3	95.2
			50.0	49 ± 2	97.6	48 ± 2	95.8
			75.0	71 ± 2	94.5	72 ± 2	95.9
			100.0	95 ± 2	94.8	96 ± 2	95.8
	SD III	19.0	25,0	26 ± 2	104.8	26 ± 2	104.4
			50,0	54 ± 2	108.0	55 ± 2	109.6
			75,0	80 ± 3	106.8	73 ± 2	97.2
			100,0	109 ± 3	109.3	98 ± 2	97.8
	SD IV	15.0	25.0	26 ± 2	105.2	25 ± 2	98.8
			50.0	53 ± 2	105.4	54 ± 3	109.0
			75.0	73 ± 2	97.1	83 ± 3	110.5
			100.0	109 ± 3	109.1	108 ± 2	107.8

[a] Medium values ± SD (n =5).

contained the 4 Sudan dye standards used in this work. The figures of merit of the method are summarized in Table 1. The precision of booth method, expressed as RSD, were obtained by injecting a 1 μg L^{-1} standard solution eleven times during one working day. In all cases, precision RSD values for the responses ranged between 1.37–3.46% for NC and 1.54–2.62% for MNC.

The limits of detection (LODs) and limits of quantification (LOQs) were estimated for signal-to-noise ratios of 3 and 10, respectively. The LODs and LOQs for Sudan dyes are in the range of 0.05–0.10 and 0.15–0.20 μg L^{-1}, respectively for NC and in the range of 0.05–0.07 and 0.15–0.23 μg L^{-1}, respectively for MNC.

The applicability and efficiency of the proposed methods (I and II) were evaluated in the analysis of Sudan dyes from barbeque sauce and ketchup sauce samples (Table 2). Thus, food samples were spiked with the four Sudan dyes at different levels. The concentration of Sudan dyes in the spiked samples was calculated from the calibration equations. The typical chromatograms of the blank and fortified barbeque sauce samples with MNC are shown in Fig. 5. The results obtained are summarized in Table 2. As it is observed in this table, the two methods provide very good recoveries (93.4%–109.6%). Moreover, practical LODs of sudan dyes in barbeque and ketchup sauces, expressed in ng g^{-1} and defined as the minimum level at which a sudan dye can be detected in the samples with acceptable accuracy (> 80%) and precision (< 10%), were 16.0, 18.0, 20.0 and 21.0 with NC and 23.0, 15.0, 19.0 and 15.0 ng g^{-1} with MNC for sudan I-IV, respectively, which were much lower than the LODs of 500–1000 ng g^{-1} recommended by the European Commission before there use were banned [47,48]. These values are also much lower than the reported LODs of 20–50 and 400–1100 ng g^{-1} with liquid extraction (LE) pretreatment and LC–MS [49,50].

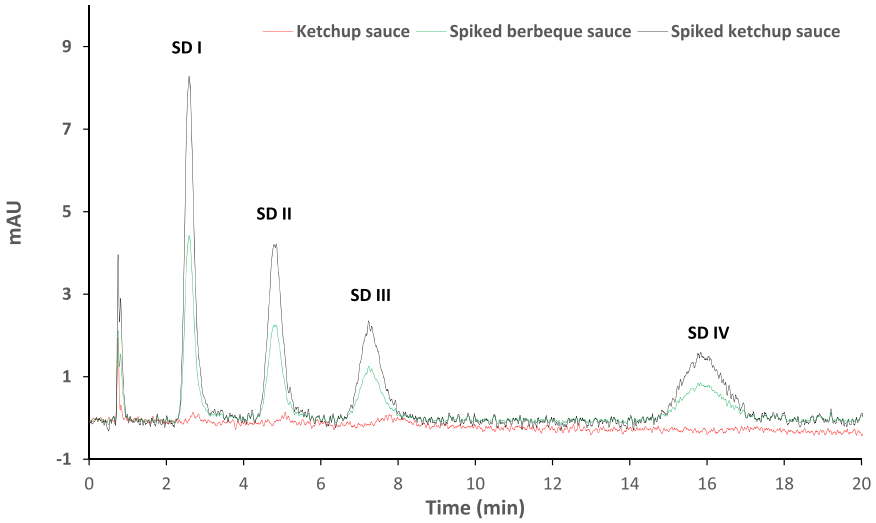

Fig. 5. Chromatograms of blank ketchup sauce and fortified barbeque and ketchup sauces after extraction by magnetic nanocelluse (MNC).

4. Conclusion

It was demonstrated that it is possible to obtain nanocellulose (NC), through argan press cake (APC), by refining, bleaching and sulfuric acid hydrolysis. Therefore, it can be concluded that NC production from APC can be a promising alternative for the reuse of these agricultural residues. Incorporation of magnetism to NC is easy and effective. The participation of a magnetic component in extraction processes allows magnetic separation to replace the centrifugation step in a convenient and economical way. Non-magnetic and magnetic NC were applied for the extraction of Sudan dyes from barbeque and ketchup sauce samples. The use on non-magnetic NC in SPE is time consuming owing to the need for centrifugation for the separation of waste and eluent from the NC sorbent. When magnetic material was incorporated in NC, the sample treatment presented several advantages when compared with using NC without magnetism in the SPE of Sudan dyes. The use of MNC is important in SPE techniques, because the application of magnetic separation technology simplifies sample treatment. The separation phase can be carried out easily by applying an external magnetic field, and the MNC showed great stability, which can allow for the reusability of the nanomaterials three times.

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