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Preparation of an efficient sorbent by washing then pyrolysis of olive wood for simultaneous solid phase extraction of chloro-phenols and nitro-phenols from water

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ABSTRACT

Simultaneous preconcentration of phenol, 2-chlorophenol, 3-chlorophenol, 4-chlorophenol, 2-nitrophenol, 4-nitrophenol, and 2,4-dinitrophenol was improved by using olive wood (OW) washed with ethanol then pyrolyzed at 200 °C as preconcentrating sorbent. Various OW sorbents were prepared by either washing OW (with ethanol, ether, dichloromethane, tetrahydrofuran or n-hexane); or by pyrolysis (at 100, 150, 200, 250 or 300 °C); or by combined pyrolysis/washing. The adsorbents were characterized by elemental analysis, total acidity/basicity, methylene blue relative surface area, point of zero charge, distribution coefficients of the phenols, and sample loading flow rate. It seems that washing and pyrolysis have removed compounds covering the OW pores, which improved the OW porosity and exposed more acidic groups on the OW surface. The pores and the surface acidic groups seem to play major role in phenols sorption. Ethanol-washed OW then pyrolyzed at 200 °C gave the best preconcentration performance towards phenols (300 mg sorbent, 150 mL of the sample (pH 7), and elution with 3 mL of acetonitrile). The method was linear up to 100 $\mu g\,L^{-1}$; limit of quantification: 0.20–0.48 $\mu g\,L^{-1}$. The method could detect phenol and 2,4-dinitrophenol in industrial wastewater with spiked recovery range from 80.2% to 91.4% (±1.1 to 5.5%RSD) for all the phenols.

1. Introduction

Phenolic compounds are discharged into environmental waters causing unpleasant taste and odor [1]. They have a half-life time between 2 and 72 days. They are used extensively in the manufacture of fungicides, herbicides, insecticides, pharmaceuticals, preservatives, glue, paint, fibers, leather, and as intermediates in chemical synthesis. Most of these compounds are toxic carcinogens. Their degradation generates phenol derivatives in the environment [2]. Phenols also exist in wastewaters disposed from petrochemical industry, coking, synthetic rubber, plastics, paper, oil refineries, as well as phenolic resin industries [3]. The Environmental Protection Agency (EPA) calls for lowering phenol content in the wastewater to less than 1 $mg\,mL^{-1}$ [4].

Some analytical instruments, such as HPLC, cannot determine phenols at the prescribed levels. This is a major problem associated with analysis of phenols besides other problems such as matrix interferences. For this reason, it is important to develop a simple and efficient method for accurate determination of these pollutants in water. In this case, sample preconcentration is essential to achieve these limits. Solid phase extraction (SPE) is a technique that is used for preconcentration of analytes in environmental waters [5]. The choice of adsorbent is the most important factor to obtain higher enrichment efficiency of analytes. Various sorbents have been used in the literature for SPE and preconcentration of phenols [6–12].

Due to the widespread cultivation of olives and a large amount of wood from pruning generated every year, olive tree wood constitutes an important agricultural waste-product. Many uses were reported for olive wood, such as: an energy source, a sugar source for bioethanol production, and for production of cellulose kraft pulp and activated carbon [13]. Olive waste materials have been used by many authors for uptake of metal ions from aqueous solutions [14–16]. El-Sheikh et al. [17] used olive pomace for solid phase extraction and preconcentration of Cu(II), Cd(II), Zn(II) and Pb(II) from water. Bio-sorption of phenols using other biomass sorbents was reported by many authors [18–20]. Biosorption of chlorophenols was reviewed by Mathialagan and Viraraghavan [21]. Bio-sorbents of metals were reviewed by Veglio and Beolchini [22], Igwe and Abia [23], and by Miretzky and Cirelli [24].

It is aimed in this work to prepare an efficient, porous olive wood-based sorbent for preconcentration of low level multi-residue phenolic compounds in environmental water. The combined effect of washing olive wood (with various solvents)

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and pyrolysis (at various temperatures) on the preconcentration, recovery and on the flow rate of the water sample through the prepared sorbents were investigated. Four categories of OW-based sorbents were prepared: pyrolyzed only sorbents; washed only sorbent; pyrolyzed then washed sorbents; and washed then pyrolyzed sorbents. Sorbents will be characterized by various techniques.

2. Materials and methods

2.1. Chemicals and materials

Chemicals were purchased from the following sources: 3-chlorophenol (3-CP), 2,4-dinitrophenol (2,4-DNP) from ACROS (Belgium); phenol (Ph) from POCH (Poland); 2-chlorophenol (2-CP), 4-chlorophenol (4-CP) from Fluka (Italy); 2-nitrophenol (2-NP) from Aldrich (Germany); 4-nitrophenol (4-NP) and methanol from Merck (Germany); acetonitrile (ACN), tetrahydrofuran (THF), and dichloromethane (DCM) from TEDIA (USA). All solvents were of HPLC grade.

Olive wood was obtained from olive trees grown in The District of Tareq, a suburb of Amman, during 2008. Olive wood branches and stems were cut into small pieces, ground with a domestic blender, passed through a 1.0 mm sieve, homogenized and labeled as "OW" sorbent. The raw sorbent was used to prepare other treated sorbents. The prepared sorbents were divided into 4 categories: (1) pyrolyzed only sorbents, (2) washed only sorbents, (3) pyrolyzed then washed sorbents, and (4) washed then pyrolyzed sorbents. Sorbents abbreviation and nomenclature are given in Table 1.

Pyrolysis: Pyrolysis was conducted by placing 10.0 g sample of OW inside a furnace under N_2 gas flow at 8.0 L min^{-1} at various temperatures: 100, 150, 200, 250, 300 and 400 °C. Pyrolysis was done by flowing N_2 gas for 15 min, and then the furnace was turned on and adjusted to the desired temperature. The temperature was maintained for one hour after which the furnace was switched-off and N_2 gas flow was maintained until furnace temperature reached room temperature. The obtained sorbents were labeled OW-100, OW-150, OW-200, OW-250 and OW-300, respectively, where the number indicates the pyrolysis temperature.

Washing: Washing the OW-based sorbents was conducted by agitating 10 g OW-based sorbent with 50 mL of the desired solvent for 2 h. The UV–VIS spectrum of the wash was recorded and the process was repeated several times until absorption spectrum was identical with that of the pure washing solvent.

Labeling the sorbents: Sorbents labeling and abbreviation is shown in Table 1. The abbreviation of each sorbent shows the pyrolysis temperature (if any) and the washing solvent (if any) involved in the preparation of each sorbent.

2.2. Characterization of the sorbents

The chemical composition of OW was estimated following the methods described by Doree [25], Browning [26] and Sjostrom [27]. The determination of total acidity and total basicity of the sorbents was determined by following similar procedure as described by Boehm [28]. Elemental micro-analysis of prepared sorbents (C and H) was carried out using Euro-vector model E.A.3000 instrument (Italy) using copper sample tubes. Relative surface area of the sorbents was studied by using methylene blue adsorption method [29–31]. The use of organic dyes for relative surface area estimation was previously reported [29–31], in which similar procedure was followed. It gives a relative estimate of surface area. It is believed that adsorption from solution has the advantage over gas adsorption such that it provides a simple and a more realistic indicator of adsorption when dealing with water pollution [30]. Point of zero charge was estimated as follows: A 100-mg sample of the sorbent was mixed with 10 mL of freshly degassed distilled water and agitated at room temperature for five minutes and pH value was measured. Then another small amount of olive wood-based sorbent (100 mg) was added and the mixture was agitated for another 5 min and the pH was recorded. This cycle was repeated until the pH of the slurry reached a steady value. As the concentration of sorbent in aqueous slurry increases, the pH of the slurry approaches a constant value. This value is taken to be equivalent to the point of zero charge (pH_{PZC}). Permeability of the raw and the treated sorbents (loading flow rate of solution or percolation rate) was estimated by loading 150 mL of water sample through 500 mg sorbent packed and preconditioned in the cartridge (as described in Section 2.4). The total time (in min) required for all the 150 mL to pass through the cartridge was measured from which the flow rate of water sample (mL min^{-1}) was calculated.

Distribution coefficients (K_D) of the phenols towards OW-based sorbents were estimated for each phenol in separate experiments at pH 7. 50 mL solutions of 10 mg L^{-1} of the phenolic compound were mixed with 25 mg sorbent and shaken for three days to reach equilibrium. The equilibrium concentration (C_e) was estimated spectrometrically, from which the adsorbed concentration (q_e) was then calculated using the formula [$q_e = (C_o - C_e)V/m$], where C_o is the initial phenolic compound concentration (mg L^{-1}); C_e is the equilibrium phenolic compound concentration (mg L^{-1}); and q_e is the surface adsorbed concentration of the phenolic compound (mg g^{-1}). K_D is calculated using the formula $K_D = q_e/C_e$.

2.3. Apparatus

The analysis of phenols was carried out using Shimadzu HPLC instrument. The instrument consists of SPD-20A UV/VIS detector, LC-20AD pump, 20 μL sample loop, communication bus module CBM-20A communicator and LC solution software. Separation was performed using ODS hypersil column (150 mm × 4.6 mm, 5 μm) from Thermo scientific.

The following parameters were set for quantitative determination of phenolic compounds in the eluates: The detector wavelength was 280 nm; 20 μL of the eluate was injected into the instrument; the mobile phase was (25MeOH:74H_2O:1acetic acid) at flow rate of 1.5 mL min^{-1}.

Solid phase extraction (SPE) of phenolic compounds was performed using a visiprep-12-port vacuum manifold from Supelco, Germany. The effect of flow rate was studied using gravity, suction and pumping. The outlet tip of the manifold was connected to a vacuum pump (KNF NEUBERGER D-7800, Germany) or to a suction tap. Sorbent materials were packed in cartridges by placing specific mass of the adsorbent in an empty 6 mL polypropylene SPE-tube "filtration tube" (Supelco, USA). Polyethylene frits were used to hold the adsorbent packing in cartridge. All pH measurements of water samples were made using a Weilheim pH meter (Germany) with a combined glass electrode (InoLab, Germany). BARNSTEAD/Thermolyne furnace with temperature range of (room temperature—1200 °C) (Dubuque, IOWA) was used for pyrolysis of OP sorbents under nitrogen atmosphere. A heavy duty blender (Waring commercial, Blender 38BL60, Model 24CB10, 50–60 Hz, 7.5 Amps, USA) was used for grinding the raw olive waste sorbents, then a Moulinex mill (type code 719 211, France) was used for fine grinding of the sorbents. Two test sieves (Frame malt ST steel, Matest, Italy), 50 and 200 μm pore size, were used for particle size control of sorbent.

2.4. General SPE procedure

Cartridge was prepared by placing 300 mg of OW-ethanol-200 in an empty 6-mL polypropylene SPE-tube (Supelco, USA). Polyethylene frits of 20 μm porosity (Supelco) were used to hold

Table 1
Labeling and characterization of prepared OW-based SPE sorbents.

	Sorbent label	Total acidity ($mmol\,g^{-1}$)	Total basicity ($mmol\,g^{-1}$)	MB relative surface area ($m^2\,g^{-1}$)	pH_{pzc}	Mass loss (%)	C (%)	H (%)
Effect of washing								
No washing	OW	0.045	0.150	200	5.98	–	49.0	7.0
Ethanol	OW-ethanol	0.100	0.035	78	5.95	8.4 ± 0.3	42.5	5.8
THF	OW-THF	0.100	0.055	103	5.63	6.7 ± 0.1	45.7	6.1
Ether	OW-ether	0.110	0.050	135	6.04	2.3 ± 0.3	47.7	6.5
DCM	OW-DCM	0.110	0.060	123	6.12	4.3 ± 0.1	41.8	5.7
n-Hexane	OW-hexane	0.110	0.050	106	6.18	7.0 ± 0.2	45.5	6.1
Effect of pyrolysis								
100 °C	OW-100	0.055	0.030	110	6.15	5.5 ± 0.0	47.1	6.6
150 °C	OW-150	0.055	0.045	9	6.05	5.6 ± 0.0	48.8	6.9
200 °C	OW-200	0.065	0.020	176	5.87	18.1 ± 0.1	50.4	6.6
250 °C	OW-250	0.075	0.055	26	7.86	40.1 ± 0.7	64.9	5.3
300 °C	OW-300	0.070	0.050	18	7.29	63.6 ± 0.8	71.3	4.2
Washing then pyrolysis at 200 °C								
Ethanol	OW-ethanol-200	0.060	0.040	106	6.27	15.9 ± 0.5	47.1	6.3
THF	OW-THF-200	0.045	0.020	124	5.69	12.3 ± 0.5	48.5	6.3
Ether	OW-ether-200	0.070	0.025	133	5.95	5.4 ± 0.2	47.9	6.1
DCM	OW-DCM-200	0.055	0.020	120	5.93	7.7 ± 0.5	48.8	6.4
n-Hexane	OW-hexane-200	0.065	0.030	114	5.68	11.5 ± 0.5	48.0	6.1
Pyrolysis at 200 °C then washing								
Ethanol	OW-200-ethanol	0.070	0.050	129	5.93	16.5 ± 0.2	45.0	5.3
THF	OW-200-THF	0.055	0.025	193	5.35	11.6 ± 0.1	49.2	6.9
Ether	OW-200-ether	0.050	0.015	161	5.34	6.4 ± 0.2	48.5	6.8
DCM	OW-200-DCM	0.060	0.035	139	5.58	8.3 ± 0.2	46.9	7.0
n-Hexane	OW-200-hexane	0.070	0.040	147	5.81	12.5 ± 0.5	48.6	6.8
Washing with ethanol then pyrolysis								
100 °C	OW-ethanol-100	0.095	0.070	134	6.07	7.5 ± 0.5	45.6	6.3
150 °C	OW-ethanol-150	0.115	0.060	95	5.86	10.7 ± 0.6	48.2	6.4
250 °C	OW-ethanol-250	0.075	0.035	69	6.81	28.5 ± 0.4	58.9	4.3
300 °C	OW-ethanol-300	0.060	0.045	25	6.98	46.1 ± 0.5	66.4	3.7
Pyrolysis then washing with ethanol								
100 °C	OW-100-ethanol	0.105	0.085	237	6.52	7.8 ± 0.2	47.1	6.1
150 °C	OW-150-ethanol	0.105	0.045	123	6.29	11.1 ± 0.3	46.8	6.2
250 °C	OW-250-ethanol	0.070	0.055	65	7.04	28.8 ± 0.8	58.1	5.5
300 °C	OW-300-ethanol	0.050	0.060	48	7.27	46.7 ± 0.2	68.9	3.2

the adsorbent packing in the cartridge. Cartridge was preconditioned by washing with 5 mL of ACN, then with 5 mL of distilled water, ahead of the preconcentration/speciation procedure. The SPE procedure was executed as follows: 150 mL of water sample, containing the phenolic compounds (at pH 7), is passed under the force of gravity through the sorbent. The retained phenolic compounds were eluted with 3 mL of ACN, which were determined by chromatography (see Section 2.3).

2.5. Sampling and sample preparation

Industrial wastewater samples were collected from the discharge site of Jordan Petroleum Refinery Company. Before use, all the collected samples were filtered through 0.45 μm micro pore glass fiber membranes (Whatman, Germany) and stored in polyethylene bottles at 4 °C.

3. Results and discussion

Olive wood, as any other wood, contains huge number of chemical constituents that may affect its behavior. For example, some antioxidants were isolated from olive wood, such as: hydroxytyrosol, tyrosol, cycloolivil, 7-deoxyloganic acid, oleuropein and ligustroside were isolated [32]. This study highlights the effect of washing and/or pyrolysis of OW on simultaneous SPE and preconcentration of various phenolic compounds from water prior to their HPLC determination. Solvents of various polarities (polarity index *P*[1]: ethanol: 4.3, DCM: 3.1, THF: 4.0, ether: 2.8, hexane: 0.1, n-hexane: 0.1) were used for OW washing, in which extraction of various components from the OW is expected to produce sorbents of various extraction abilities towards phenols. The effect of pyrolysis of OW at various temperatures (100, 150, 200, 250 or 300 °C) was also studied since pyrolysis is also expected to change the chemistry, morphology and porosity of the OW surface and thus affect the SPE of phenols. The effect of combined washing and pyrolysis of OW on SPE of phenols was also studied; in which sorbents of various properties are expected to be produced.

Proximate analysis (chemical composition) of the raw OW showed that it contains 6.9% moisture; 1.8% hemicelluloses; 42.0% (-cellulose; 44.0% lignin; 1.4% ash content. Other characteristics of the raw and the treated sorbents namely, point of zero charge, methylene blue relative surface area and Boehm titrations, and elemental analysis are shown in Table 1. Distribution coefficients (K_D) of the phenolic compounds and the loading flow rate of the water sample through the sorbent under the force of gravity are shown in Table 2. The results of SPE are shown in Tables 2 and 3 and in Figs. 1 and 2.

3.1. Effect of OW washing

From Table 1, it is generally noted that washing OW with various organic solvents caused a mass loss that is proportional to the polarity of the solvents. Washing with n-hexane is exceptional; it caused a relatively high mass loss (7.0%) in spite of its low polarity. In the case of polar solvents, it is expected that polar compounds were leached while n-hexane washed-off non-polar materials. However, in all cases, total acidity of OW-based sorbents have increased (2–2.5-fold) after washing while total basicity have decreased to one-third. This may indicate that the washed-off compounds were of basic nature and they were filling up (or covering) the pores

Table 2
Effect of washing and pyrolysis of OW on sample flow rate, recovery range of the phenols from water and distribution coefficients of phenols (K_D).

	Recovery range (±RSD range) (%)	Flow rate (mL min^{-1})	K_D (L g^{-1})						
			Ph	2-CP	3-CP	4-CP	2-NP	4-NP	2,4-DNP
Effect of washing									
OW	24.5–82.1 (±0.7–9.5)	1.0 ± 0.0	0.44	1.16	1.87	2.0	0.26	1.03	0.24
OW-ethanol	67.4–83.5 (±0.9–2.0)	3.0 ± 0.1	1.09	6.54	7.69	9.09	0.64	2.25	0.57
OW-THF	12.5–84.1 (±2.1–9.8)	2.0 ± 0.1	1.11	6.85	10.42	11.36	0.67	2.31	0.63
OW-ether	16.5–81.2 (±1.6–9.7)	2.1 ± 0.1	1.05	7.194	9.71	10.87	0.62	2.36	0.57
OW-DCM	32.6–52.7 (±0.2–4.5)	2.2 ± 0.1	1.10	7.30	9.90	11.36	0.66	2.46	0.62
OW-hexane	27.7–68.4 (±2.0–4.0)	2.0 ± 0.1	1.05	7.09	9.26	10.64	0.63	2.40	0.59
Effect of pyrolysis									
OW-100	12.5–86.6 (±0.7–5.7)	1.1 ± 0.0	0.80	4.51	5.00	5.53	0.49	2.46	0.47
OW-150	12.2–76.7 (±0.7–9.5)	1.4 ± 0.0	0.78	4.05	4.93	5.38	0.48	2.38	0.45
OW-200	46.6–76.4 (±1.0–2.4)	2.6 ± 0.1	0.72	3.34	4.00	4.44	0.46	2.16	0.44
OW-250	21.8–74.5 (±1.6–7.6)	2.5 ± 0.0	0.76	3.66	4.35	4.76	0.48	2.34	0.45
OW-300	12.9–54.6 (±1.1–5.7)	2.0 ± 0.1	0.72	3.66	4.41	4.88	0.46	2.28	0.43
Washing then pyrolysis at 200 °C									
OW-ethanol-200	76.7–92.2 (±0.3–1.3)	4.7 ± 0.2	0.58	1.01	1.09	1.13	0.25	0.97	0.25
OW-THF-200	42.9–85.4 (±0.8–4.0)	3.5 ± 0.1	0.75	4.00	5.00	5.38	0.45	2.19	0.43
OW-ether-200	40.9–76.7 (±0.7–2.8)	3.4 ± 0.2	0.74	4.65	5.68	4.44	0.45	2.20	0.43
OW-DCM-200	44.9–61.4 (±1.4–3.2)	3.2 ± 0.1	0.83	5.13	6.54	5.68	0.48	2.79	0.46
OW-hexane-200	49.1–83.2 (±1.5–3.5)	3.8 ± 0.1	0.71	3.60	4.00	4.22	0.44	2.12	0.42
Pyrolysis at 200 °C then washing									
OW-200-ethanol	70.9–88.8 (±0.5–2.3)	4.4 ± 0.3	0.60	1.04	1.11	1.17	0.27	0.98	0.27
OW-200-THF	46.0–84.3 (±0.9–3.1)	3.5 ± 0.2	1.00	4.88	5.53	5.99	0.41	1.86	0.40
OW-200-ether	48.8–83.3 (±0.8–3.4)	3.9 ± 0.1	0.99	4.00	4.44	5.00	0.40	1.71	0.40
OW-200-DCM	48.4–65.4 (±0.8–2.7)	2.9 ± 0.1	0.99	4.93	5.68	6.17	0.41	1.94	0.41
OW-200-hexane	44.3–86.8 (±1.0–2.5)	3.7 ± 0.2	0.94	3.47	4.00	4.44	0.39	1.65	0.40
Washing with ethanol then pyrolysis									
OW-ethanol-100	40.6–66.4 (±1.6–4.0)	2.6 ± 0.1	0.65	1.17	1.22	1.32	0.28	1.11	0.27
OW-ethanol-150	27.4–88.8 (±1.3–5.1)	2.9 ± 0.1	0.64	1.14	1.24	1.30	0.28	1.08	0.27
OW-ethanol-250	45.8–89.4 (±0.9–4.0)	4.1 ± 0.1	0.62	1.04	1.11	1.20	0.27	1.05	0.26
OW-ethanol-300	37.4–87.9 (±0.4–4.8)	3.3 ± 0.2	0.65	1.07	1.18	1.27	0.29	1.09	0.27
Pyrolysis then washing with ethanol									
OW-100-ethanol	37.6–59.4 (±0.6–3.4)	2.8 ± 0.1	0.67	1.22	1.27	1.36	0.29	1.13	0.30
OW-150-ethanol	36.3–82.9 (±0.5–5.5)	3.0 ± 0.1	0.67	1.20	1.26	1.33	0.29	1.10	0.28
OW-250-ethanol	44.0–82.8 (±0.3–3.7)	4.0 ± 0.2	0.64	1.11	1.16	1.21	0.28	1.06	0.28
OW-300-ethanol	37.8–67.9 (±0.5–3.4)	3.5 ± 0.2	0.67	1.17	1.21	1.28	0.28	1.12	0.28

Table 3
Optimization of other SPE parameters using *OW-ethanol-200* as the sorbent (spiking 100 μg L^{-1} of each phenol simultaneously into water sample at pH 7.0).

Parameter	Recovery ± RSD (%)						
	Ph	2-CP	3-CP	4-CP	2-NP	4-NP	2,4-DNP
Mass of sorbent (mg)[a]							
100	85.3 ± 1.8	51.3 ± 2.3	40.5 ± 2.5	59.4 ± 1.8	60.2 ± 0.9	52.3 ± 2.1	63.4 ± 1.6
200	66.4 ± 1.6	70.9 ± 1.1	52.3 ± 2.0	42.4 ± 2.5	80.3 ± 0.2	51.5 ± 2.1	62.4 ± 2.0
300	90.3 ± 0.1	84.4 ± 1.3	79.8 ± 0.8	80.7 ± 0.7	85.7 ± 0.7	83.5 ± 1.4	82.5 ± 1.2
400	66.4 ± 1.5	74.4 ± 1.4	40.4 ± 0.2	51.3 ± 2.4	70.7 ± 0.8	41.3 ± 2.7	65.5 ± 1.7
Flow rate[b]							
Low	88.7 ± 0.6	82.4 ± 1.2	78.3 ± 1.4	77.8 ± 0.6	85.2 ± 0.2	80.8 ± 0.7	83.4 ± 1.4
Medium	72.0 ± 2.1	65.8 ± 0.9	62.4 ± 1.6	56.4 ± 1.9	72.3 ± 1.6	51.9 ± 3.1	41.7 ± 1.4
High	76.3 ± 1.6	60.9 ± 0.8	61.4 ± 1.8	66.9 ± 0.6	41.9 ± 3.9	46.3 ± 2.6	51.4 ± 2.2
Type of eluting solvent[c]							
Acetonitrile	89.5 ± 1.0	81.4 ± 1.3	83.3 ± 1.4	78.4 ± 1.3	83.4 ± 1.1	77.4 ± 1.4	90.4 ± 1.4
Methanol	62.0 ± 1.0	51.4 ± 2.0	36.4 ± 2.8	47.7 ± 1.8	54.4 ± 2.1	41.5 ± 0.3	44.4 ± 2.3
Volume of eluting solvent “CAN” (mL)[d]							
1	70.7 ± 1.2	69.4 ± 1.7	71.2 ± 1.6	57.4 ± 2.1	67.4 ± 1.5	64.3 ± 1.8	61.3 ± 2.0
2	81.9 ± 1.9	80.9 ± 0.8	51.5 ± 2.3	60.8 ± 0.9	71.4 ± 1.6	74.3 ± 1.6	72.3 ± 1.6
3	91.2 ± 1.4	86.3 ± 1.4	83.4 ± 1.4	80.8 ± 0.8	85.5 ± 1.3	78.2 ± 0.6	86.0 ± 0.5
4	86.2 ± 0.5	78.6 ± 1.3	72.0 ± 2.2	75.5 ± 0.2	77.3 ± 1.5	71.4 ± 1.6	80.8 ± 0.7
Sample volume (mL)[e]							
50	80.8 ± 0.7	77.4 ± 1.3	72.5 ± 1.3	82.6 ± 1.3	82.9 ± 0.6	80.9 ± 0.7	76.4 ± 1.4
100	83.9 ± 0.7	76.4 ± 1.4	76.4 ± 1.3	77.4 ± 1.5	70.2 ± 1.0	82.3 ± 1.4	80.3 ± 1.4
150	86.8 ± 0.7	83.4 ± 1.2	85.4 ± 1.9	78.1 ± 0.8	80.4 ± 1.4	84.6 ± 1.0	90.5 ± 1.0
200	62.4 ± 1.8	48.8 ± 1.1	40.4 ± 2.8	57.5 ± 1.4	81.4 ± 1.7	65.4 ± 1.5	51.4 ± 2.3
400	60.3 ± 1.0	56.4 ± 1.8	47.8 ± 1.1	35.4 ± 2.9	65.4 ± 1.8	81.2 ± 1.5	64.5 ± 1.5

[a] OW-ethanol-200 sorbent; loading 150 mL of water sample at low flow rate, elution with 3 mL ACN.
[b] 300 mg of OW-ethanol-200 as sorbent, loading 150 mL of water sample, elution with 3 mL ACN.
[c] 300 mg of OW-ethanol-200 as sorbent, loading 150 mL of water sample at low flow rate, elution with 3 mL eluting solvent.
[d] 300 mg of OW-ethanol-200 as sorbent, loading 150 mL of water sample at low flow rate, elution ACN.
[e] 300 mg of OW-ethanol-200 as sorbent, loading water sample at low flow rate, elution with 3 mL ACN.

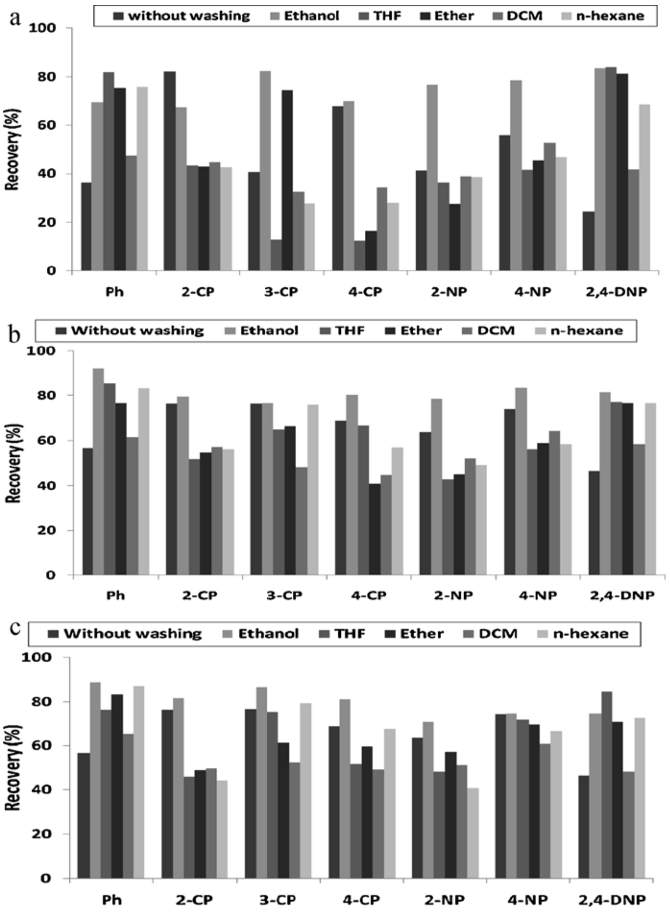

Fig. 1. Effect of (a) washing OW, (b) washing with various solvents then pyrolysis at 200 °C, (c) pyrolysis at 200 °C then washing with various solvents, on % recovery of various phenols by SPE from water. %RSD range: (a) [0.7–9.8%]; (b) [0.3–4.0%]; (c) [0.5–3.4%].

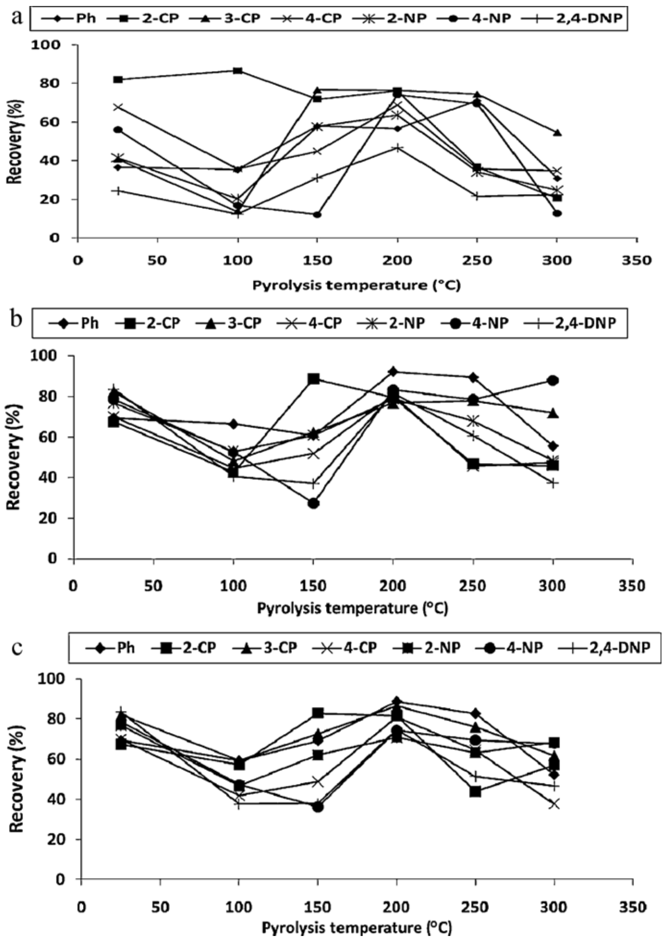

Fig. 2. Effect of order of treatment of OW on % recovery of various phenols by SPE from water (a) pyrolysis only, (b) washing with ethanol then pyrolysis, (c) pyrolysis then washing with ethanol. %RSD range: (a) [0.7–9.5%]; (b) [0.4–4.8%]; (c) [0.3–5.5%].

and thus more acidic groups were exposed after washing [33]. As a consequence, uptake of MB decreased, which may indicate that MB adsorption generally occurred on those basic compounds on the OW surface. It is also noted that carbon content was slightly decreased after washing OW, while pH_{pzc} have slightly increased. From Table 2, it is noted that adsorption of chloro-phenols (K_D values) has significantly increased after washing, while uptake of phenol and nitro-phenols (K_D values) have only slightly increased. This may reflect the role of acidic surface groups in sorption of phenolic compounds [31].

The results of SPE of phenols are summarized in Table 2. It is noted that washing OW with organic solvents has greatly affected the SPE performance. The best washing solvent was ethanol where the recovery range was 67.4–83.5%, while the recovery with raw OW was 24.5–82.1%. This may be attributed to the fact that many polar organic compounds were removed by ethanol washing, thus more active sites became available for binding phenolic compounds. Fig. 1a presents detailed description of the recoveries of phenols for various washed-OW sorbents. The following observations may be drawn: (1) washing OW with any of the solvents has generally increased the recovery of Ph and 2,4-DNP but decreased the recovery of 2-CP. (2) Ethanol washing of OW has generally increased the recovery of all phenols (except 2-CP). (3) Washing OW with THF, ether, DCM or n-hexane has generally decreased the recovery of 2-CP, 3-CP, 4-CP, 2-NP and 4-NP. Based on these observations, it seems that ethanol washing has the best positive influence on the SPE of almost all the phenols. So that ethanol was recommended as the washing solvent of OW for subsequent optimization steps.

3.2. *Effect of OW pyrolysis*

Thermal degradation of wood was reported by Bridgwater [34]. He reported that cellulose degradation usually starts at 200 °C by losing adsorbed water and water produced from β-elimination of the cellulose hydroxyl groups. As the temperature increases, the degree of cellulose polymerization decreases. At 400 °C, aliphatic, alcoholic and monoaromatic groups became very weak, while other groups, such as aldehyde and etheric groups disappeared. Hemicellulose degradation occurs in the temperature range 220–320 °C, with first decomposition of the polymeric chain into water-soluble fragments, then conversion to monomeric units that in turn decomposes into volatiles. In lignin degradation, the relatively weak aliphatic bonds are first broken to release large hydrocarbon molecules (tar), which then undergoes secondary reactions such as cracking and polymerization. So that, it was proposed that pyrolysis of OW at various temperatures would produce sorbents of various SPE properties. Grioui et al. [35] reported that the thermal degradation of olive wood during carbonization notably increases the porosity of the carbonized samples. The largest variation is observed when the temperature of degradation varies between 523 and 548 K. They also reported that the carbonization does not change the structure of olive wood but the thickness and cracking of the cell walls were affected.

The effect of partial pyrolysis of OW at various temperatures on sorbents' characteristics was also studied. From Table 1, it is noted that the surface acidity has increased while surface basicity has decreased. This may be explained by releasing volatile basic compounds attached to the OW surface during pyrolysis. MB adsorption has also decreased after pyrolysis which may support the role of the basic groups on MB sorption as in the previous section. This is contrary to sorption of phenolic compounds, which has increased after pyrolysis. The carbon content has increased after pyrolysis due to gradual loss of volatile compounds and water. Almost 63% of the OW mass was lost after pyrolysis at 300 °C, which represents the total loss of water, volatile compounds and degradation products.

The results of SPE of phenols on pyrolyzed and non-pyrolyzed sorbents are summarized in Table 2. It is noted that pyrolysis at 200 °C gave almost the best recovery range for all the phenols (46.6–76.4%), compared with (24.5–82.1%) for the non-pyrolyzed OW. Details of recoveries of phenols are shown in Fig. 2a. Almost recovery of all phenols decreased after pyrolysis at 100 °C due to loss of water which plays a role in phenols sorption, but started to increase after pyrolysis at 150 and 200 °C. Recovery then declined again after pyrolysis at 250 and 300 °C, probably due to depolymerization of lignocellulosic material which started at 250 °C [34]. So that 200 °C was recommended as the pyrolysis temperature of OW for subsequent optimization of the SPE procedure.

3.3. *Effect of combined washing and pyrolysis of OW*

The effect of washing OW with various sorbents prior to pyrolysis at 200 °C on sorbents characteristics (Tables 1 and 2) was also studied. Compared to OW-200, it is noted that washing OW prior to pyrolysis at 200 °C reduced the mass loss and MB sorption. The other properties (total acidity, total basicity, pH_{pzc}, sorption of phenolic compounds) were very close to those of OW-200. Reversing the order of treatment (pyrolysis at 200 °C then washing) did not significantly change the properties of the produced sorbents except for the MB adsorption.

The effect of washing OW with ethanol prior to pyrolysis at various temperatures on sorbents characteristics was also studied (Tables 1 and 2). Compared to OW-ethanol, the total acidity and phenols sorption decreased. Compared to the pyrolyzed sorbents (OW-100, OW-150, OW-200, OW-250, OW-300), washing OW with ethanol prior to pyrolysis has significantly reduced the mass loss and phenols sorption, while the MB adsorption has randomly changed. Reversing the order of treatment (pyrolysis at various temperature then ethanol washing) did not significantly change the properties of the produced sorbents.

The results of SPE of phenols are shown in Figs. 1 and 2. Fig. 1b shows the effect of washing OW with various solvents then pyrolysis at 200 °C, while Fig. 1c shows the opposite sequence. Fig. 2b shows the effect of washing OW with ethanol then pyrolysis at various temperatures, while Fig. 2c shows the opposite sequence. Recovery ranges for each set of experiments are summarized in Table 2. From Table 2 it is noted that sometimes there are large differences in recoveries when reversing the sequence of treatment. This may be attributed to the fact that washing OW will remove the organic compounds covering the lignocellulosic surface, leaving a clean OW surface prior to pyrolysis. On the other hand, if OW is first pyrolyzed, then both the lignocellulosic skeleton and the adsorbed organic compounds will be pyrolyzed simultaneously. Thus at high temperature, there is a possibility of interaction between the pyrolyzed surface and the adsorbed organic compounds, which may lead to different surface properties. From Table 2, it is noted that the percentage recovery range for phenols is the highest (77–92%) for OW-ethanol-200 compared with 25–82% for untreated OW. Using OW-200-ethanol sorbent gave slightly lower recovery range than OW-ethanol-200. So that OW-ethanol-200 was selected as the optimum sorbent for SPE of phenolic compounds from water. This sorbent exhibited moderate surface area; and low amounts of acidic and basic groups.

3.4. *Effect of sorbent type on the loading flow rate*

The effect of pyrolysis and/or washing of OW on sample loading flow rate through the sorbent under the force of gravity was studied. The results are shown in Table 2, from which it is noted that washing OW with any of the selected solvents has generally doubled or tripled the sample loading flow rate. This may be explained by the hypothesis that some compounds covering (or filling) the OW pores hinder water flow [35]; so that washing these compounds removed them from the pores and thus water flow became easier. Similar observations were also observed for OW pyrolysis (washing then pyrolysis) and (pyrolysis then washing). The maximum flow rate (4.7 mL min^{-1}) was achieved by washing with ethanol followed by pyrolysis at 200 °C (sorbent OW-ethanol-200) compared with 1.0 mL min^{-1} for the untreated sorbent OW. Reversing the order of OW treatment (using OW-200-ethanol sorbent) resulted in slightly lower sample flow rate. The effect of pH on sample loading flow rate was studied for OW-ethanol-200 (the results are not shown). It was found that the maximum flow rate was recorded at pH 7. This pH is slightly higher than pH_{pzc}, which means that the surface is almost neutral or slightly negatively charged. So that the electrostatic attraction between the surface and solution components is minimum, and thus the flow rate is maximum.

3.5. *Effect of pH*

The pH of water sample is an important parameter that affects SPE of phenols because phenols are weak acids. Based on pK_a values of phenols, changing the sample pH will cause deprotonation of phenolic groups and the functional groups on the treated OW surface. The extraction efficiency of phenols depends on the sample pH.

A set of experiments were carried out to investigate the influence of sample pH over the pH range from 1.0 to 11.0 using various sorbents (OW-ethanol, OW-ethanol-100, OW-ethanol-150, OW-ethanol-200, OW-ethanol-250 and OW-ethanol-300). Fig. 3 shows the dependence of the recovery of the phenols on the sample pH for OW-ethanol and OW-ethanol-200. Other sorbents are not shown. The highest recoveries of almost all the phenols were achieved at pH 7 where the phenols and the surface functional groups are present in the protonated form. This will facilitate H-bonding between the surface and the neutral phenols. At pH 7.0, 2,4-DNP (pK_a 4.96) presents in the phenolate anionic form and thus it will repel the surface. Slightly lower recoveries were obtained in solutions adjusted to pH 9.0; this was probably due to repulsion between the negatively charged phenolate anions in solution and the deprotonated functional groups on the sorbent surface. Low recoveries were recorded for pH values 1.0–5.0 due to high competition from hydronium ions towards the active surface sites. Since the highest recoveries were achieved at pH 7 using OW-ethanol-200, it was selected as the optimum pH in the proposed SPE method.

3.6. *Effect of pK_a of phenols on K_D values*

Phenolic compounds has the following pK_a values: Ph (9.89), 2-CP (8.5), 3-CP (8.8), 4-CP (9.2), 2-NP (7.17), 4-NP (7.15), 2,4-DNP (4.96). From Table 2, it is noted that the extraction powers of nitrophenols (as indicated by its K_D values) are generally lower than those of chlorophenols. This is probably due to nitrophenols are more acidic (have lower pK_a values) and thus at pH 7, they produce more phenolate anions than the chlorophenols. The point of zero

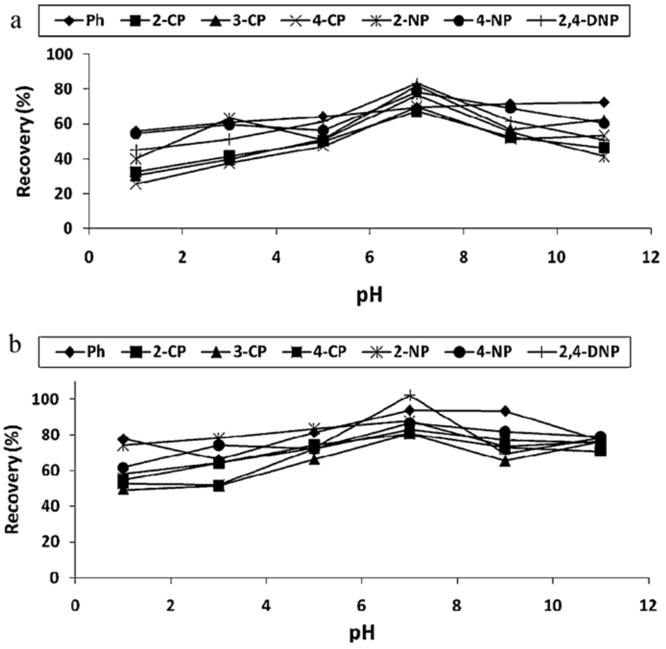

Fig. 3. Effect of pH on % recovery of various phenols by SPE on different sorbents: (a) OW-ethanol; (b) OW-ethanol-200%RSD range: (a) [0.3–2.8%]; (b) [1.0–3.5%].

charge of OW sorbents ranges from 5 to 7, so that the surface is negatively charged at pH 7. So that nitrophenols exhibited higher repulsion to the surface than did chlorophenols.

The extraction power (K_D) of OW-based sorbents towards chlorinated phenols was in the order: 4-CP > 3-CP > 2-CP. This is opposite to the order of decreasing acidity of the respective phenols. This is also explained by the fact that phenols of higher acidity (lower pK_a values) produce more phenolate anions and they repel more the negatively charged OW surface.

The trend for nitrophenols was not proportional to the pK_a values, in which 2-NP and 2,4-DNP gave lower K_D values than those of 4-NP. This is probably due to the intra-molecular hydrogen bonding between the phenolic hydrogen and the oxygen of the nitro substituent in the ortho position. This makes the phenolic proton of 2-NP less available for interaction with the functional groups of the OW surface.

3.7. *Optimization of other SPE parameters*

To get the best conditions for SPE of the phenolic compounds, it is necessary to optimize other parameters such as: mass of sorbent, flow rate, volume of loaded sample, type and volume of eluting solvent. All experiments were conducted using OW-ethanol-200 at pH 7. The results are shown in Table 3.

Effect of mass of sorbent: SPE experiments with various sorbent masses (OW-ethanol-200) were executed. It was aimed to use the minimum mass of adsorbent that is sufficient to completely retain the analytes, and to allow desorption of the retained analytes with the minimum volume of eluent. The results are shown in Table 3. It was noted that the highest recoveries were achieved when 300 mg of sorbent was used. Larger masses did not increase the recovery of phenols.

Effect of sample loading flow rate: Flow rate of sample solution may be used to control the analytical speed of the method without a decrease in recovery. Three different flow rates were tested: low flow rate (4.7 mL min^{-1}); moderate flow rate (9 mL min^{-1}); and high flow rate (25 mL min^{-1}). The results are shown in Table 3. The highest recoveries were recorded when loading the sample slowly; this was probably due to longer contact time between the phenols and the sorbent and thus more time is available to attain equilibrium.

Effect of eluting solvent: The effect of eluting solvent type (acetonitrile or methanol) is shown in Table 3. Different elution efficiencies would be obtained when different eluting solvents are used because of the physical and chemical properties of the involved organic solvents and the characteristics of the sorbents and analytes in the cartridge. In our study, it was found that acetonitrile gave better elution performance for the seven phenols than methanol. Therefore, it was selected for subsequent optimization steps.

In SPE, to get the highest enrichment factor, it is necessary to elute all the retained analytes with minimum eluting solvent volume. Various volumes of acetonitrile were tested: 1, 2, 3 and 4 mL. The results are shown in Table 3. It was noted that 3 mL of acetonitrile was enough to maintain high recovery for most phenols. So that it was selected as the optimum volume of eluting solvent.

Effect of water sample volume: breakthrough volume: Volume of the loaded sample has a proportional effect on enrichment factor. Various volumes of samples were tested. The results are shown in Table 3. Considering the need for high recovery and high enrichment factor; 150 mL was selected as an appropriate water sample volume above which the recovery of phenols significantly decreased.

3.8. *Analytical performance*

Some analytical parameters, such as linear range, detection limit, accuracy, and precision, should be evaluated. For that purpose, purified distilled water was spiked with the seven targeted phenols simultaneously with the following concentrations: 5, 10, 20, 40, 60, 80, 100, 150 and 200 μg L^{-1}; the proposed SPE procedure was then applied (n = 3). The linearity of the calibration curve of each phenol was determined by plotting the average peak area against the concentration of each phenol. The linearity was estimated based on R^2 value of the calibration curve. The detection limits were estimated as three times the standard deviation of the blank signal. Accuracy of the methods was estimated based on the % recovery of the phenols while the precision of the method was estimated based on the %RSD of triplicate samples.

The analytical figures of merit of the method are shown in Table 4. The method was linear up to 100 μg L^{-1} for 2-CP, 3-CP, 4-CP and 2,4-DNP; up to 150 μg L^{-1} for 2-NP; up to 200 μg L^{-1}

Table 4
Analytical figures of merit of the optimum SPE procedure.

	Limit of linearity (μg L^{-1})	R^2	LOQ (μg L^{-1})	%RSD range (%)	Sensitivity (peak are/(μg L^{-1}))	LOQ[36] (μg L^{-1})	LOQ [37] (μg L^{-1})	LOQ [12] (μg L^{-1})
Ph	200	0.9964	0.48	0.6–7.6	0.95	12.11	23.0	–
2-CP	100	0.9911	0.28	0.5–5.9	1.50	–	–	–
3-CP	100	0.9966	0.33	0.5–8.8	0.66	–	–	0.33
4-CP	100	0.9911	0.29	1.4–9.3	0.64	–	–	0.26
2-NP	150	0.9927	0.23	0.1–3.3	2.42	2.21	5.28	–
4-NP	200	0.9812	0.24	0.3–5.6	1.66	0.83	11.88	–
2,4-DNP	100	0.9858	0.20	0.5–10.3	1.73	2.15	13.53	–

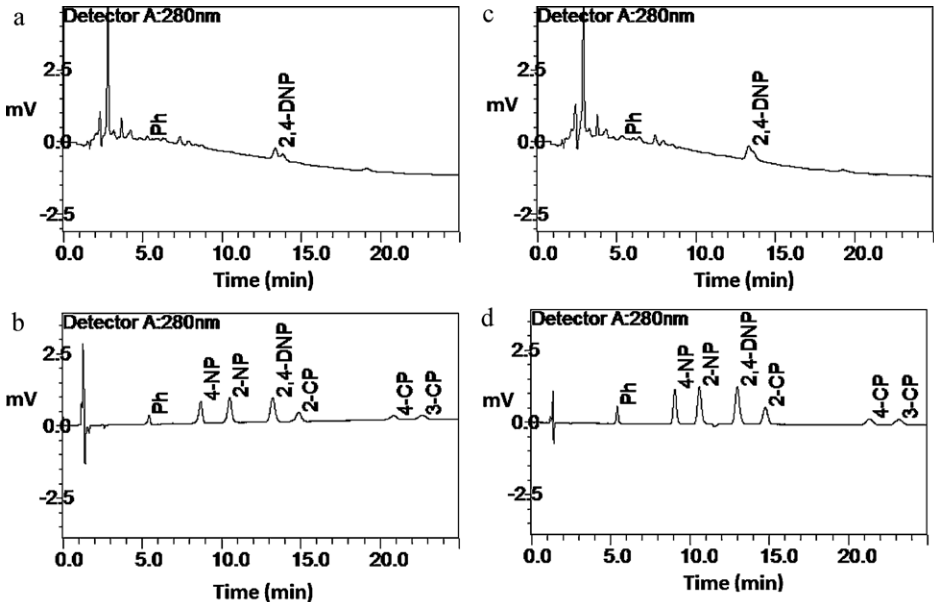

Fig. 4. Chromatograms from the proposed SPE method using industrial wastewater: (a) unspiked, OW-ethanol-200, (b) spiked with 5 ppb, OW-ethanol-200, (c) unspiked, C-18, and (d) spiked with 5 ppb, C-18.

Table 5
Recovery of the seven targeted phenols from industrial waste water samples after application of the proposed optimum method (*n* = 4).

Spike conc.	Recovery ± RSD (%)			
	C18		OW-ethanol-200	
	2 μg L^{-1}	5 μg L^{-1}	2 μg L^{-1}	5 μg L^{-1}
Ph	91.1 ± 4.4	96.4 ± 3.7	84.1 ± 4.0	91.4 ± 2.9
2-CP	90.2 ± 4.8	93.4 ± 2.6	81.3 ± 4.7	88.5 ± 3.2
3-CP	91.3 ± 4.2	90.4 ± 2.3	85.4 ± 4.6	89.2 ± 2.0
4-CP	92.5 ± 3.3	95.4 ± 3.7	87.4 ± 2.9	90.3 ± 3.4
2-NP	86.3 ± 3.8	91.4 ± 2.4	80.2 ± 3.9	87.3 ± 2.7
4-NP	88.2 ± 1.5	93.1 ± 5.1	89.5 ± 1.3	83.5 ± 5.5
2,4-DNP	92.1 ± 1.3	97.4 ± 1.1	85.3 ± 1.4	90.6 ± 1.1

for Ph and 4-NP. The method showed relative errors ranging from −2.2% to −23.6%. Limits of quantifications (LOQ) for all the studied phenols ranged between 0.20 and 0.48 μg L^{-1}. It is noted that the limits LOQ for 3-CP and 4-CP reported in our work are very close to those reported by Cai et al. [12]. On the other hand, our method gave much lower LOQs for Ph, 2-CP, 2-NP, 4-NP and 2,4-DNP than those reported by Liu et al. [36] and Penalver et al. [37]. The precision of the method was acceptable as indicated by the %RSD range (0.1–10.3%) for all the studied phenols. Based on the above discussion, it is clear that the proposed SPE method is capable of accurate determination of all the phenols.

3.9. *Real water samples*

The optimum method was applied on industrial wastewater samples to test the applicability of the proposed method for environmental use. Two of studied phenolic compounds were found: Ph: 72.5 ± 1.3 μg L^{-1} and 2,4-DNP: 78.6 ± 0.5 μg L^{-1}. For the purpose of comparison, SPE of phenols was applied (after optimization) using 500 mg/3 mL Hypersep C-18 cartridges (Thermo electron corporation). The following concentrations were recorded: Ph: 78.5 ± 1.6 μg L^{-1}; and 2,4-DNP: 87.1 ± 0.7 μg L^{-1}. All experiments were performed in five replicates (*n* = 5).

To validate the method, the industrial water samples were then spiked with two different concentrations: 2 and 5 μg L^{-1}. The proposed method was then applied using OW-ethanol-200 and C-18. Typical chromatograms are shown in Fig. 4. The obtained recoveries are shown in Table 5. The recovery range using OW-ethanol-200 is 81.3–91.4% (%RSD range 1.1–5.5%), while the recovery range using C-18 is 86.3–97.4% (%RSD range 1.1–5.1%). This means that the sorbent OW-ethanol-200 gave slightly lower recoveries than C-18, but the precision was very similar as seen by the F test for the comparison of standard deviations. Application of the *t*-test showed that there is no significant difference between OW-ethanol-200 and C-18 for almost all sets of data based on 95% confidence level. Almost all the calculated *t* values were lower than the critical *t* value at the 95% confidence level.

4. Conclusions

Washing and/or pyrolysis of OW has noticeably affected its surface characteristics, SPE/adsorption performance and loading flow rate of the water sample through it. This may be attributed to the hypothesis that washing and/or pyrolysis will remove the compounds filling up or covering the pores. These pores, along with the surface acidic groups, seem to play a major role in phenols sorption. The leached compounds seem to possess some basic functional groups covering the acidic functional groups on OW surface. The most efficient SPE sorbent was OW-ethanol-200, which gave the highest recovery and the highest sample loading flow rate. The order of treatment (pyrolysis/washing or washing/pyrolysis) of OW has only slight effect on the SPE of phenols. The sorbent OW-ethanol-200 gave comparable results to C-18 sorbent in terms of recovery and precision.

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