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Partially pyrolyzed olive pomace sorbent of high permeability for preconcentration of metals from environmental waters

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ABSTRACT

The aim of this work is to develop a preconcentration procedure of Cd^{2+}, Zn^{2+} and Cu^{2+} in environmental waters using olive pomace (OP) prior to their determination by flame atomic absorption spectrometry (FAAS). Raw OP as preconcentrating sorbent was found to have low permeability towards the passed water samples and thus long time was needed. Even reducing the vacuum pressure caused cartridge blockage. Novel preconcentrating sorbents of high permeability were then prepared by heat pretreatment under inert atmosphere (partial pyrolysis) of OP at various temperatures (100, 150, 200, 250 and 300 °C). The permeability of OP pyrolyzed at 200 °C (sorbent OP-200) was enhanced 11 times relative to the raw OP, which significantly reduced the time required in the preconcentration process. A preconcentration procedure was optimized using OP-200 as preconcentrating sorbent, in which the detection limits were 42 ng L^{-1} for Cu^{2+}, 76 ng L^{-1} for Zn^{2+} and 172 ng mL^{-1} for Cd^{2+}. The method was linear within the studied concentration range (2–100 ng mL^{-1}). The proposed method gave recoveries from 83 ± 6 to $103 \pm 5\%$ for determination of metals in tap water; and recoveries from 81 ± 6 to $100 \pm 6\%$ in well water. The method was validated by comparison with independent method and by analysis of lake sediments LKSD-4 certified reference material.

1. Introduction

Due to their toxicity, the presence of heavy metals in water causes harmful effects to human health. The direct determination of metals in water at ultra-trace level by flame atomic absorption spectrometry (FAAS) is not feasible without a preconcentration step. Preconcentration of metals was reported by many authors [1–3]. Preconcentration using solid phase extraction (SPE) sorbents is a very attractive technique to achieve low detection limits [4].

Agricultural by-products are promising sorbents due to their minimum cost and high sorption ability [5–16]. Biosorbents are prepared from naturally abundant waste biomass. Igwe and Abia [6] and Veglio and Beolchini [11] have reviewed bioseparation processes for removing heavy metals from wastewater using agricultural by-products, such as, juniper wood and bark [5], maize-cob and husk [17], sunflower stalk [18], *Medicago sativa* (Alfalfa) [19], cassava waste [20], tree fern [14,21], sawdust [22], chitosan [23], peanut skins [24], shea butter seed husks [25], banana pith [26], sugar-beet pulp [27] and wheat bran [28].

Olive mill solid residue, also called olive pomace (OP), is very abundant in the *Mediterranean* area. Oil production leaves ~30% (by weight) solid residue [9,29]. Disposal of this solid residue is a serious problem in the oil industry. Olive waste may be used for preparation of SPE material for the aim of using it in preconcentration of metal ions from environmental water.

Olive waste materials have been used by many authors for removal of metal ions from aqueous solutions [9,12,30–35], such as removal of Cd by olive stones [30], adsorption of Hg, Pb, Cu, Zn and Cd by hexane-treated olive mill solid residues [9,33]. Fiol et al. [31] found that maximum sorption of Pb(II), Ni(II), Cu(II) and Cd(II) on solid olive waste occurs at pH 5.5–6.0. Gharaibeh et al. [12] found that processed solid residue of olive mill products can be used to remove Pb(II) and Zn(II) from aqueous solutions by adsorption but did not remove Cr(III), Ni(II) and Cd(II).

Many works have reported modification the properties of lignocellulosic sorbents, such as, the use of OP treated with phosphoric acid and hydrogen peroxide for adsorption of Cu and Cd [32], the use of thioglycollic acid-modified cassava waste biomass to enhance the adsorption of Cd, Cu and Zn from aqueous medium [20], the removal of Cr^{6+} by polyacrylamide-grafted sawdust [22], adsorption of Au(III) ions onto *N*-carboxymethyl chitosan [23], modification of coconut fiber and sawdust by carboxymethylation and thiolation for removal of Pb(II), Hg(II) and As(V) [17], the use of cationized cotton fibers, wood sawdust and maize-cob flour for use as scavengers for anionic surfactants [7], the use of lanthanum-treated lignocellulosic sorbents to remove orthophosphate [8].

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Preliminary experiments in our lab showed that using raw OP as preconcentrating sorbent of metal ions from water samples is very slow process due to low permeability of raw OP. Although many authors have used olive waste and other lignocellulosic sorbents for adsorption of metals from aqueous medium, however, none of the researchers have paid attention to the low permeability of the lignocellulosic sorbents. Thus it was proposed that altering the chemical and textural properties of OP might enhance the permeability of the OP sorbent. This may be achieved by pyrolysis.

Pyrolysis is a process, which involves heating a carbonaceous material at high temperature under inert atmosphere to prepare activated carbon [36–40]. Partial pyrolysis (heating the sorbent at low temperature under inert gas atmosphere) is expected to change the chemical and textural characteristics of the sorbent without forming activated carbon. Pagnanelli et al. [41] reported the chemical changes of olive pomace upon thermal treatment (carbonization) and chemical treatment. In this work, novel olive pomace-based sorbents were prepared by heat pretreatment at low temperature (100–300 °C) under inert atmosphere to enhance the permeability of the sorbent and thus reduce the time required for the preconcentration process. The prepared sorbent were tested for preconcentration of Cd^{2+}, Zn^{2+} and Cu^{2+} from environmental waters. The effect of pretreatment temperature on the sorbent permeability is also reported. The raw and heat-pretreated OP sorbents were characterized to follow the surface changes of the sorbents upon partial pyrolysis.

2. Materials and methods

2.1. Materials

Standard stock solutions (1000 μg mL^{-1}) were purchased from the following suppliers: Cd^{2+} standard solution from Aldrich (Taufkirchen, Germany), Cu^{2+} and Zn^{2+} standard solutions from Scharlau (Barcelona, Spain). Working standard solutions were prepared by appropriate dilution of the stock standard solutions using doubly distilled water. All the reagents used were of analytical grade or better. The following buffers were used to control the pH of the solutions: hydrochloric acid–glycine (pH 1), sodium acetate–acetic acid (pH 3 and 5), disodium hydrogen phosphate-sodium dihydrogen phosphate (pH 7), and ammonium chloride–ammonia (pH 9). Concentration of all buffers was 0.050 M.

Lake Sediments Reference Material LKSD-4 was purchased from Canadian Certified Reference Materials Project CCRMP (Ottawa, Canada).

Olive pomace was supplied by an olive oil producer from Ajloun, Jordan. It was dried overnight at 60 °C, ground, passed through a 1 mm sieve, homogenized and labeled as “OP” sorbent.

To prepare partially pyrolyzed OP sorbents, samples of OP were heated at various temperatures (100, 150, 200, 250 and 300 °C) under inert atmosphere. Heat treatment was conducted using an F47910-26 BARNSTEAD/Thermolyne furnace (Dubuque, IOWA, USA) under N_2 gas flowing at 8.0 L min^{-1}. Temperature was maintained for 1 h after which the furnace was switched-off and N_2 gas continued flowing until furnace temperature reached room temperature. The obtained sorbents were labeled according to the pyrolysis temperature (100, 150, 200, 250 and 300 °C) as follows: OP-100, OP-150, OP-200, OP-250 and OP-300, respectively.

2.2. Apparatus

An Analyst 300 Perkin-Elmer atomic absorption spectrometer (Waltham, MA, USA) was used for the quantitative determination of metals under the conditions described elsewhere [42]. In electro-thermal atomic absorption spectrometry ET-AAS, the heating cycles were also similar to those described in a previous work [42].

A Varian Cary 100 Bio UV–vis spectrophotometer (Palo Alto, CA, USA) was used for the determination of the remaining concentrations of methylene blue in sorbent characterization. A visiprep-12-port vacuum manifold (Supelco, USA) connected to a vacuum pump (KNF NEUBERGER D-7800, Germany) was used to control the vacuum pressure inside the vacuum manifold. Moulinex mill (type code 719 211, France) was used for grinding the raw olive waste sorbents.

2.3. Cartridge preparation and preconcentration procedure

Typically, cartridge was prepared by placing exactly 500 mg of OP-200 in an empty 6 mL polypropylene SPE-tube (Supelco, USA). Polyethylene frits of 20 μm porosity (Supelco, USA) were used to hold the adsorbent packing in the cartridge. Cartridge was preconditioned by washing with 6 mL of 1.0 M HNO_3, followed by 12 mL of doubly distilled water, then 12 mL of buffer solution (pH 5), ahead of the preconcentration procedure. 150 mL of water sample, spiked with 20 ng mL^{-1} of each metal ion simultaneously and buffered to pH 5 were pumped through the cartridge at a flow rate of 4.3 mL min^{-1} (vacuum pressure inside the manifold was −6 kPa). Subsequently, metal ions retained on the cartridge were eluted with 5 mL of 0.50 M HNO_3. The eluate was then analyzed directly by flame atomic absorption spectrometer (FAAS).

2.4. Characterization of the sorbents

Metal contamination of the raw OP was conducted by passing 10 mL of 1.0 M HNO_3 through 0.200 g of OP. Eluates were then analyzed for the determination of metals. The metals present in raw OP were as follows (expressed as μg metal per g sorbent): Cd, 0.35 ± 0.04; Zn, 0.12 ± 0.01; Cu, not detected. Relative surface area of the sorbents was studied by using methylene blue adsorption method, as described by many authors [39,42–44], in which similar procedure was followed. Iodine numbers were determined as described by the standard ASTM method (method number D 4607–94) [45]. The determination of total acidity and total basicity of the sorbents was determined by following similar procedures as described by Boehm [46] and other researchers [39,42,44]. The chemical composition of OP was estimated following the methods described by Doree [47], Browning [48] and Sjostrom [49]. Adsorption capacity of raw and partially pyrolyzed OP sorbents towards metal ions was separately estimated for each metal (at pH 5) by passing 50 mL of 10 μg mL^{-1} of the metal ion solution was through a 0.200 g sorbent packed and preconditioned in the cartridge. The adsorbed metals were eluted with 10 mL of 1.0 M HNO_3.

2.5. Permeability of the sorbents

The vacuum pressure of the manifold was maintained at −6 kPa to avoid cartridge blockage. The permeability of the raw and partially pyrolyzed sorbents was estimated by pumping 150 mL of water sample through a 500 mg of the sorbent packed and preconditioned in the 6 mL cartridge as described in Section 2.3. 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.

2.6. Sampling and sample preparation

Sampling of the three types of environmental waters (tap water, well water and treated wastewater) was similar to that described elsewhere [42]. The optimum SPE procedure was applied on unspiked and spiked water samples with the target metal ions. To ensure reproducibility of the results, SPE procedures were applied in five replicates ($n = 5$), after which each extract was analyzed for metal ions as separate sample.

3.947 g portions of Lake Sediments Reference Materials LKSD-4 (Ottawa, Canada) were transferred into beaker. 30 mL of nitric acid, 10 mL of hydrochloric acid and 40 mL of water were added to the beaker, heated for 2 h. The supernatant was separated and the solution was made up to 150 mL and the pH was adjusted to 5.

3. Results and discussion

3.1. *Characterization of the raw OP and partially pyrolyzed olive pomace*

Characteristics of the raw OP and partially pyrolyzed olive pomace sorbents are shown in Table 1. The chemical and elemental composition of the raw olive pomace are presented in Table 2, while the chemical composition of the partially pyrolyzed OP sorbents could not be estimated due to unknown chemical changes of olive pomace upon partial pyrolysis.

The total acidity/basicity of the raw and pyrolyzed OP sorbents are shown in Table 1. It is noted that the total acidity generally decreased with increasing the pyrolysis temperature, while the total basicity generally increased.

The methylene blue relative surface area and iodine number (which give a relative indicator of the porosity and the surface area of the sorbent) are shown in Table 1. It is noted that there is no systematic trend in these values with the temperature of pyrolysis. However, OP-200 gave the highest methylene blue relative surface area, while OP-150 gave the highest iodine number value. On the other hand, OP-300 gave the lowest iodine number and relative surface area values.

The adsorption capacity values of the raw and pyrolyzed OP sorbents towards Cu^{2+}, Cd^{2+} and Zn^{2+} at pH 5 are given in Table 1. For Cu^{2+}, it is clear that pyrolysis of olive pomace generally lowered the adsorption capacity towards Cu^{2+} relative to the raw OP sorbent. For Zn^{2+} and Cd^{2+}, the highest adsorption capacity was observed for OP-150, while OP-200 showed adsorption capacity towards Zn^{2+} and Cd^{2+} very close to that of raw OP. Many authors, who did research on adsorption of metals on olive waste sorbents, reported close adsorption capacity values to our values (see Table 1). For example, de Hoces et al. [30] reported 4.5 mg g^{-1} for Cd^{2+} using olive stones, while Gharaibeh et al. [12] reported 5.4 mg g^{-1} for Zn^{2+} using olive mill products. Fiol et al. [31] reported 2.0 mg g^{-1} for Cu^{2+} and 7.7 mg g^{-1} using olive stone waste. Pagnanelli et al. [33] reported an adsorption capacity of 4.5 mg g^{-1} for Cu^{2+} and 6.7 mg g^{-1} for Cd^{2+} using raw olive pomace. Some authors reported the effect of chemical treatment of olive waste material on its adsorption capacity. For example, Martin-Lara et al. [32] reported the effect of phosphoric acid treatment and hydrogen peroxide treatment. They found that phosphoric acid treatment noticeably increased the adsorption capacity of OP towards Cu^{2+} and Cd^{2+} three times relative to the untreated OP. Pagnanelli et al. [9] found that the adsorption capacity of OP treated with pH 5 water towards $Cu^{2+}$was higher than OP treated with pH 4 water and OP treated with hexane.

In evaluating the preconcentration performance of the sorbent, it is necessary to consider many factors, such as adsorption characteristics, the recovery of the analyte and the permeability of the sorbent.

Although the adsorption capacity and other sorbent characteristics play an important role in the preconcentration performance of the sorbent, however, other factors should be considered in the choice of the sorbent for a preconcentration procedure, such as the permeability of the adsorbent.

Table 1

Characteristics of the raw and partially pyrolyzed OP sorbents and comparison of the adsorption capacity with other olive waste sorbents.

	MB relative surface area, $m^2\,g^{-1}$	Iodine number, mg g^{-1}	Total basic groups, mmol g^{-1}	Total acidic groups, mmol g^{-1}	Adsorption capacity[a]			Permeability of sorbents[b]				
					Cu^{2+}	Cd^{2+}	Zn^{2+}	pH 1	pH 3	pH 5	pH 7	pH 9
OP	291 ± 9	27 ± 2	0.03 ± 0.00	0.18 ± 0.02	8.0 ± 0.6	5.1 ± 0.4	4.8 ± 0.4	0.4 ± 0.0	0.4 ± 0.0	0.3 ± 0.0	0.3 ± 0.0	0.3 ± 0.0
OP-100	252 ± 9	51 ± 2	0.03 ± 0.00	0.18 ± 0.01	7.1 ± 0.6	4.9 ± 0.4	4.9 ± 0.4	0.7 ± 0.0	0.7 ± 0.0	0.7 ± 0.0	0.5 ± 0.0	0.6 ± 0.0
OP-150	249 ± 8	55 ± 2	0.03 ± 0.00	0.17 ± 0.01	5.3 ± 0.4	7.0 ± 0.6	5.1 ± 0.4	1.7 ± 0.0	1.5 ± 0.0	1.5 ± 0.1	1.1 ± 0.1	0.8 ± 0.0
OP-200	451 ± 9	52 ± 3	0.05 ± 0.00	0.15 ± 0.02	6.5 ± 0.5	5.2 ± 0.4	4.6 ± 0.3	4.9 ± 0.1	4.7 ± 0.2	4.3 ± 0.2	3.7 ± 0.3	4.1 ± 0.2
OP-250	270 ± 8	25 ± 2	0.09 ± 0.01	0.10 ± 0.01	4.0 ± 0.3	3.7 ± 0.2	1.7 ± 0.2	3.0 ± 0.1	2.3 ± 0.1	1.8 ± 0.1	2.3 ± 0.2	2.3 ± 0.1
OP-300	174 ± 7	12 ± 1	0.10 ± 0.01	0.09 ± 0.00	6.5 ± 0.5	3.0 ± 0.2	1.9 ± 0.2	4.7 ± 0.1	5.2 ± 0.2	5.0 ± 0.2	3.8 ± 0.4	4.9 ± 0.1
Other olive pomace sorbents from the literature												
Olive stones [27]					–	4.5	–					
Olive stone waste [28]					2.0	7.7	–					
Olive mill products [9]					–	–	5.4					
Olive pomace [30]					4.5	6.7	–					
Olive pomace [29]					11.4	3.4	–					
Olive pomace treated with phosphoric acid [29]					31.8	11.2	–					
Olive pomace treated with hydrogen peroxide [29]					12.1	5.6	–					
Olive pomace treated with water at pH 4 [6]					8.0	–	–					
Olive pomace treated with water at pH 5 [6]					12.5	–	–					
Olive pomace treated with *n*-hexane [6]					4.0	–	–					

[a] mg metal per g sorbent at pH 5.

[b] Expressed as flow rate of water solutions through sorbents, mL min^{-1}.

Table 2
Proximate analysis (%w/w ± σ) and ultimate (elemental) analysis (%w/w ± σ) of raw olive pomace (OP).

	OP
Proximate analysis	
Moisture, %	6.5 ± 0.1
Ether extract[a], %	7.0 ± 0.1
Alcohol extract[a], %	0.8 ± 0.0
Hemicellulose[a], %	20.9 ± 0.2
α-Cellulose[a], %	24.5 ± 0.8
Lignin[a], %	37.8 ± 0.9
Ash content[a], %	2.6 ± 0.2
Ultimate analysis	
C, %	54.4 ± 0.6
H, %	7.7 ± 0.3
N, %	0.9 ± 0.0

[a] Estimated on dry basis.

3.2. *Preconcentration of metal ions using raw OP and partially pyrolyzed olive pomace sorbents*

3.2.1. *Using raw OP sorbent*

Raw OP was initially used for preconcentration of metal ions in the pH range 1–9. These experiments were conducted under gravity. From Fig. 1, it is noted that at pH 5, OP gave a recovery range of 85–97% for Cu^{2+}, Cd^{2+} and Zn^{2+}. This is slightly higher than that at pH 7. It is clear that satisfactory recoveries could be achieved for all metals with OP. However, the problem in using raw OP was that the loading flow rate of water solution through OP cartridge was too slow (flow rate between 0.3 and 0.4 mL min^{-1}, Table 1). This is impractical due to long loading time.

3.2.2. *Heat-pretreated olive pomace sorbents: effect of pyrolysis temperature and pH of water sample on preconcentration recovery of metals*

Olive pomace sorbents pyrolyzed at various temperatures were tested for preconcentration of metals in the pH range of 1–9. Two parameters were considered to choose the best pyrolysis temperature: the metals' recovery (Fig. 1) and the sorbent permeability (flow rate of water sample, Table 1). It was primarily proposed that the best pyrolyzed sorbent is the one that will give the highest permeability with maximum recovery. Permeability of the sorbents is discussed later in Section 3.3.

From Fig. 1a, it is noted that the highest recoveries towards Cu^{2+} were achieved using OP-100 (100%) and OP-150 (97%) at pH 5. For Cd^{2+} (Fig. 1b), the highest recoveries were achieved at pH 5 using OP-150 (recovery 98%), OP-100 (recovery 93%) and OP-200 (recovery 87%). For Zn^{2+} (Fig. 1c), almost all partially pyrolyzed sorbents gave the highest recoveries at pH 5.

The abnormal recovery values of OP-100, OP-150 and OP-200 may be due to the presence of relatively high amount of total acidic groups, which then decreased in OP-250 and OP-300. Generally saying, sorbent OP-150 at pH 5 gave recovery >95% for all metals; while OP-200 gave recoveries ∼100% for Zn^{2+}; and 90% for Cd^{2+} and Cu^{2+}. However, there still another factor that should be considered, which is the permeability of the sorbent.

3.3. *Permeability of the sorbents*

All the preconcentration experiments were performed under constant vacuum pressure (−6 kPa). Permeability's of the raw and partially pyrolyzed olive pomace sorbents (expressed as flow rate, in mL min^{-1}, of the water sample through the cartridge) are shown in Table 1. It is noted that the permeability of the raw OP sorbent was very low (flow rate was between 0.3 and 0.4 mL min^{-1} at various pH values). An attempt to enhance the flow rate was performed by further reducing the vacuum pressure in the manifold. Unexpectedly, a cartridge blockage occurred upon reducing the vacuum pressure. Thus another approach should be used to enhance the flow rate of the sample through the cartridge. It was proposed that partial pyrolysis of the raw OP may change its textural and surface properties and therefore the sorbent permeability may be changed.

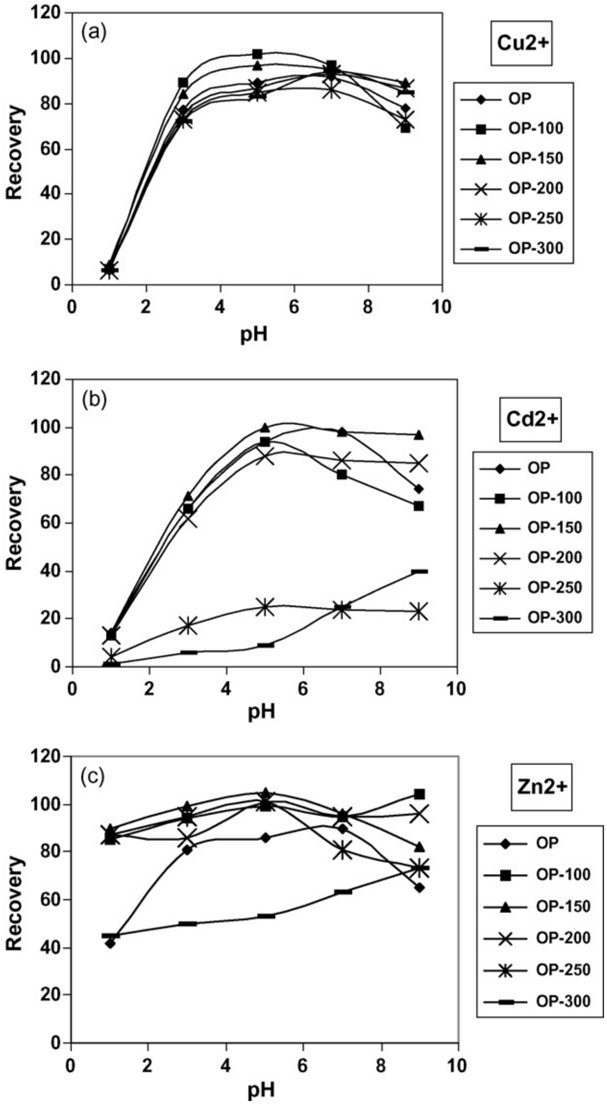

Fig. 1. Effect of pH on preconcentration performance of metals: (a) Cu^{2+}, (b) Cd^{2+}, and (c) Zn^{2+} using various olive pomace-based sorbents pyrolyzed at various temperatures. (150 mL of water spiked with 20 ng mL^{-1} metal (each), 300 mg sorbent, elution with 10 mL of 0.50 M HNO_3).

3.3.1. *Partially pyrolyzed olive pomace sorbents*

The permeability's of the partially pyrolyzed olive pomace sorbents towards water solution are presented in Table 1 at various pH values. The permeability was in the order: OP-300 > OP-200 > OP-250 > OP-150 > OP-100. It is noted that, at pH 5, while the flow rate using OP-150 was 1.5 mL min^{-1}, it was 4.4 mL min^{-1} for OP-200. Thus OP-200 is preferred over OP-150 in terms of permeability. On the other hand, OP-150 is slightly better than OP-200 in terms of metal recovery (by ∼8% for Cu^{2+}, 11% for Cd^{2+}, 5% for Zn^{2+}). Thus OP-200 was selected as the preconcentrating sorbent in this work (pH of water sample: 5, sample flow rate: 4.3 mL min^{-1}).

Table 3
Effect of various parameters on the preconcentration recovery of 20 ng mL^{-1} of metals using OP-200 at pH 5[*].

Parameter	Recovery, % Cu^{2+}	Cd^{2+}	Zn^{2+}
Mass of OP-200 (mg)[a]			
100	60	71	78
300	85	88	101
500	101	98	102
700	103	100	103
Eluent[b]			
0.10 M HNO_3	90	101	97
0.50 M HNO_3	101	102	101
1.00 M HNO_3	104	103	103
Volume of 0.50 M HNO_3 (mL)[c]			
5	101	102	98
8	102	101	101
10	100	100	101
Sample volume (mL)[d]			
50	102	101	102
100	104	101	101
150	101	103	102
200	89	78	73
400	74	45	39

[*] Values reported were average of triplicate measurements (R.S.D. < 8.0%).

[a] Sample volume: 150 mL, flow rate: 4.3 mL min^{-1}, eluent: 10 mL of 0.50 M HNO_3.

[b] Sample volume: 150 mL, flow rate: 4.3 mL min^{-1}, mass of OP-200: 500 mg, volume of eluent: 10 mL.

[c] Sample volume: 150 mL, flow rate: 4.3 mL min^{-1}, mass of OP-200: 500 mg, eluent: 0.50 M HNO_3.

[d] Flow rate: 4.3 mL min^{-1}, mass of OP-200: 500 mg, eluent: 10 mL of 0.50 M HNO_3.

3.4. Optimization of metal preconcentration method using OP-200 at pH 5

To ensure high preconcentration levels of metals, a preconcentration procedure for Cd^{2+}, Cu^{2+} and Zn^{2+} (using OP-200 as sorbent, pH of sample was 5) was optimized by studying various parameters, such as eluent concentration and volume; mass of sorbent; volume of water sample. The influence of various parameters on the preconcentration recovery of 20 ng mL^{-1} are shown in Table 3.

In solid phase extraction, it is necessary to elute all the adsorbed analytes on the adsorbent surface using minimum volume of eluent, to get the highest enrichment factor. Nitric acid was used as the eluent in this work based on its strong ability to dissolve metals. The effect of concentration and volume of nitric acid on the preconcentration process was investigated. Various concentrations and volumes of nitric acid solutions were used for elution. From Table 3, it is clear that 5 mL of 0.50 M HNO_3 is sufficient to elute the maximum amount of the adsorbed metal ions (recovery >99%). Higher volumes and concentrations gave similar recoveries (>99%). Therefore, 5 mL of 0.50 M HNO_3 was selected as the optimum eluent. The optimum mass of sorbent (OP-200) was 500 mg, while the breakthrough volume was 150 mL.

Table 4
Tolerance limits for various coexisting ions (μg mL^{-1}) towards the targeted metal ions.

Coexisting ion	Cu^{2+}	Cd^{2+}	Zn^{2+}
Na^+	2000	3000	800
K^+	700	3000	500
$SO_4{}^{2-}$	60	300	60
Ca^{2+}	80	50	80
Mg^{2+}	100	200	200
$HCO_3{}^-$	80	100	250
Fe^{3+}	8	8	8

Table 5
Analytical parameters of the optimum preconcentration method followed by FAAS determination of the targeted metals.

	R^2	Detection limit, ng L^{-1}	Precision, %R.S.D. range ($n = 5$)	Slope, AU, ng mL^{-1}
Cu^{2+}	0.9960	42	0.75–10.5	0.55
Cd^{2+}	0.9730	172	0.63–6.2	1.38
Zn^{2+}	0.9960	76	0.42–12.4	3.80

3.4.1. Effect of common ions

In solid phase extraction, it is necessary to study the effect of interferences from other ions that may affect the preconcentration process. This was investigated by using 20 ng mL^{-1} solution of the metal ions containing some interfering ions and then treated according to the optimum preconcentration procedure (see Section 2.3). The tolerance limits of each coexisting ion on each metal ion are shown in Table 4. Tolerance limit was defined as concentration of coexisting ion needed to reduce the recovery of the metal into 90%.

3.5. Analytical performance of the method

Some important analytical parameters of the optimum method are to be explored such as: linearity, detection limit, sensitivity, accuracy, and precision. For that purpose, 150 mL of doubly distilled water samples (at pH 5) were spiked with various concentrations of the metal ions (simultaneously): 2, 5, 20, 40, 60, 80 and 100 ng mL^{-1} and then preconcentrated using OP-200 according to the optimum preconcentration procedure. Preconcentration experiments were performed in five replicates ($n = 5$). The results in Table 5 indicate that precision was satisfactory at a very low level and the relative standard deviations %R.S.D. ($n = 5$) was between 0.42 and 12.4%. It was found the method is linear within the studied concentration range (2–100 ng mL^{-1}). Satisfactory correlation coefficients were obtained and were in the range 0.996–0.973. The detection limit of the method for each metal ion was calculated from the average blank signal of each metal ion plus three times its standard deviation ($n = 10$). The detection limits range of the metals was 42–172 ng L^{-1}.

3.6. Validation of the method

In order to validate the proposed method for analysis of Cd^{2+}, Cu^{2+} and Zn^{2+}, this method was compared with an independent method of analysis "electro-thermal vaporization atomic absorption spectrometer (ET-AAS)". For that purpose, treated wastewater samples were analyzed according to the optimum proposed preconcentration method (using sorbent OP-200 at pH 5) followed by analysis with flame atomic absorption spectrometer (FAAS). Similar treated wastewater samples were analyzed directly by (ET-AAS) as an independent method of analysis. The results are given in Table 6, from which it is clear that the two methods gave comparable results.

The optimum preconcentration method followed by FAAS analysis was also applied on other environmental waters (well water and tap water samples) to examine the validity of the method. The metal ions were found in the un-spiked real water samples as shown in

Table 6
Concentrations of metals (ng $mL^{-1} \pm \sigma$, $n = 5$) in treated wastewater using the optimum preconcentration method (using OP-200) followed by FAAS and comparison with electro-thermal atomic absorption spectrometry ET-AAS.

	Preconcentration method: FAAS	ET-AAS
Cu^{2+}	23 ± 2	20 ± 1
Cd^{2+}	21 ± 2	18 ± 1
Zn^{2+}	39 ± 0	37 ± 1

Table 7
Concentrations of metals ($\text{ng mL}^{-1} \pm \sigma$, $n = 5$) in un-spiked environmental waters and their spike recoveries using OP-200.

Element	Added	Tap water		Well water	
		Found	Recovery, %	Found	Recovery, %
Cu^{2+}	0	ND	–	ND	–
	20	17 ± 1	86	16 ± 1	82
	50	44 ± 1	87	41 ± 3	81
Cd^{2+}	0	ND	–	ND	–
	20	19 ± 1	93	17 ± 1	83
	50	42 ± 3	83	42 ± 1	83
Zn^{2+}	0	3 ± 0	–	6 ± 1	–
	20	24 ± 1	103	25 ± 2	96
	50	48 ± 2	88	56 ± 3	100

ND, not detected.

Table 7. Only zinc could be detected by the proposed method, while cupper and cadmium were lower than the limits of detection of the proposed method. So that environmental waters were then spiked with the metal ions (simultaneously) at various concentrations (20 and 50 ng mL^{-1}). Spike recoveries of the target metal ions in real water samples are shown in Table 7. Spike recovery range of all the metals was 81.0–103.1%. The results indicate that the proposed method has a good validity for simultaneous determination of Cu^{2+}, Cd^{2+} and Zn^{2+} in complex water samples.

The proposed method was applied for analysis of Zn, Cu and Cd in certified reference material (Lake Sediments LKSD-4). The analytical values (for Zn: $188.7 \pm 13.7\ \mu\text{g g}^{-1}$, for Cu: $29.0 \pm 1.9\ \mu\text{g g}^{-1}$, for Cd: $1.8 \pm 0.1\ \mu\text{g g}^{-1}$, $n = 3$) were in good agreement with the certified values (for Zn: 189 $\mu\text{g g}^{-1}$, for Cu: 30 $\mu\text{g g}^{-1}$, for Cd: 1.9 $\mu\text{g g}^{-1}$). These results indicate that the proposed method can be used for analysis of LKSD-1 certified material.

4. Conclusion

Olive pomace can be use for preconcentration of metals from aqueous medium but its permeability is very low. It was found that partial pyrolysis of olive pomace has a significant effect on the permeability of olive pomace. It was found that partial pyrolysis of olive pomace at 200 °C produced sorbent (OP-200) that has 11 times permeability relative to the raw olive pomace (OP). Optimization of the preconcentration parameters of the selected metals from water (using OP-200 at pH 5) yielded a preconcentration procedure, followed by FAAS determination, which can be applied for analysis of metals in real complex water samples. Comparable results were achieved with the proposed preconcentration procedure (followed by FAAS determination) to those obtained with electro-thermal vaporization atomic absorption spectrometry (ET-AAS).

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