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Determination of parabens in wastewater and sludge in a municipal wastewater treatment plant using microwave-assisted dispersive liquid-liquid microextraction coupled with gas chromatography-mass spectrometry

Mohammad Mehdi Amin[1,2], Majid Hashemi[3,4], Karim Ebrahimpour[1,2], Afsane Chavoshani[2,5*]

[1]Environment Research Center, Research Institute for Primordial Prevention of Non-Communicable Disease, Isfahan University of Medical Sciences, Isfahan, Iran
[2]Department of Environmental Health Engineering, School of Health, Isfahan University of Medical Sciences, Isfahan, Iran
[3]Environmental Health Engineering Research Center, Kerman University of Medical Sciences, Kerman, Iran
[4]Department of Environmental Health Engineering, School of Public Health, Kerman University of Medical Sciences, Kerman, Iran
[5]Student Research Committee, Isfahan University of Medical Sciences, Isfahan, Iran

Abstract

Background: Due to the complexities involved in the extraction of micropollutants, the information regarding micropollutants like paraben in wastewater and sludge is scarce. The aim of this study was to adopt a microwave-assisted dispersive liquid-liquid micro-extraction (MADLLME) method for the extraction of parabens in municipal wastewater treatment plant (WWTP).

Methods: A mixed stock solution of methyl-, ethyl-, propyl-, and butyl-parabens with concentration of 10 mg/mL were prepared in methanol. To validate this method, the limit of detection (LOD), limit of quantification (LOQ), linearity, and m/z were measured. To adopt this method in different condition, the effect of pH (3, 7, 9, and 12), microwave power (180, 300, 450, and 600 W), solvent type (methanol, acetone, methanol/water, acetone/water), and 1 g folorisil were assessed. After adopting MADLLME method, the paraben fate of this WWTP was evaluated through mass loading and emission.

Results: The optimum performance of MADLLME method was observed at pH = 7, microwave power = 450 W, reaction time = 30 s, and methanol as the solvent. The total concentrations of four paraben metabolites in the WWTP ranged between 2505 ng/L in influent, 1953 ng/L in effluent, and 8.03 ng/g at wet weight sludge samples. The total mass loading and emission of four parabens in this WWTP was 0.672 mg/d/1000 people and 0.186 mg/d/1000 people, respectively.

Conclusion: MADLLME method seems to be an excellent alternative, as a green extraction technique, for determining various groups of emerging micropollutants in different matrices.

Keywords: Paraben, Environment, Municipal sludge, Dispersive liquid-liquid micro-extraction, Microwave-assisted extraction

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***Correspondence to:**
Afsane Chavoshani
Email:
Chavoshani.afsane@yahoo.com

Introduction

Parabens (alkyl esters of p-hydroxybenzoic acid) as favorable ingredients consumed in personal care products (PCPs), pharmaceuticals, nutritional, and industrial products have antifungal and antibacterial properties. Because of their function in endocrine disruption and estrogenic effects, parabens consumption is banned in the EU, the United States, and Canada (1). The maximum permissible level of this substance is 0.4% in cosmetic products for single ester and 0.8% for their combination (2,3).

Parabens can be detected in wastewater, water, sediment, soil, human urine, blood, and adipose tissue (2,4-8). Studies conducted in Canada (9), the United Kingdom (10), France (11), and China (12), reported the occurrence of parabens in municipal wastewater. There are studies suggesting that in the conventional WWTPs, these chemicals are not completely removed from the water

cycle (8,13-15) and this issue remains a challenging problem due to its complex matrices.

Over the last few years, the microwave-assisted extraction (MAE) has been found to be a practical method for extracting target compounds from solid matrices (16-20). There are many studies investigated the application of this technique in different compounds extraction from different samples (17,18,20). Due to reducing consumption volume of organic solvents, reducing extraction time and improving recovery yield, the MAE is an appropriate alternative to conventional techniques (20,21). Polar solvents absorb microwave energy, which in turn increase temperature and pressure, and allow rapid transfer of target compounds from the solid matrices into the liquid phase (22).

The solid phase extraction (SPE) and liquid-liquid extraction (LLE) techniques have been introduced to improve the extraction (23,24), which are costly, time-consuming, and vulnerable to contamination and lack of sensitivity. The objective of the existing analytical techniques is to remove these restrictions and make the analytical procedure simple (21,23). One of the extraction techniques developed within the last decade is the dispersive liquid-liquid microextraction (DLLME). This technique involves the dispersion of fine droplets of extraction solvent in an aqueous sample. Due to the large surface area of the droplets, the separation of analytes into the extraction phase rapidly occurs (21). Here, the advantages of the MAE and DLLME techniques are combined to develop a simple and easy method for extracting methyl paraben (MePB), ethyl paraben (EtPB), propyl paraben (PrPB), and butyl paraben (BuPB) from wastewater and sludge samples through gas chromatography-mass spectrometry (GC–MS).

Materials and Methods

Samples collection

Influent and effluent wastewaters and sludge samples were collected from the north WWTP in Isfahan city. The chemical properties of the samples are presented in Table 1. This WWTP serves a population around 1 200 000 inhabitants with a 220-230 m^3/d influent flow rate, and consists of a conventional activated sludge (CAS) process. The samples were collected in glass bottles and immediately transferred to the laboratory.

Table 1. Chemical properties of samples in the subject WWTP

Parameter	Influent	Effluent	Sludge
Q (m^3/d)	220-230	115	
COD (mg/L)	547	55	
BOD (mg/L)	240	65	
TSS (mg/L)	304	60-70	
TKN (mg/L)	80	25	
Dried sludge production (tone/month)			4000
Wet sludge moisture content (%)			80

Reagent and chemical

The MePB, EtPB, PrPB , BuPB, and p-hydroxybenzoic acid (PHA), methanol, acetone and acetonitrile, chlorobenzene, florisil, and N-methyl-*N*-(trimethylsilyl) trifluoroacetamide (MSTFA) with a purity of greater than 98.0% were purchased from Sigma-Aldrich.

Calibration curve and performance validation

Ten milligrams of all the paraben standards were dissolved in 1 mL methanol to make a stock solution at a concentration of 10 mg/mL. The standard stock solution was sealed and kept at 4°C in the lab refrigerator before test. Working solutions with concentration of 10-100 µg/mL were prepared daily by diluting a more concentrated stock solution with deionized water.

Because the external standards are not correct due to the loss or gain that may occur during preparation of the sample, like in extraction, centrifugation, evaporation, etc., the PHA as an internal standard (20 µg/mL) was spiked to the sample at the beginning of its preparation (25). The PHA was applied to correct the errors due to external calibration curve by plotting the ratio of paraben signal to the internal standard signal. To perform a spike-and-yield relative recovery, a known concentration of parabens and internal standard was added to the sample matrices according to Eq. (1).

$$RR\% = \frac{n_{found} - n_{real}}{n_{added}} \times 100 \quad (1)$$

where n_{found} is the concentration of paraben or PHA detected after spiking the sample, n_{real} is the analytes concentration detected in the real sample, and n_{added} is the standard concentration spiked to the real sample (25). To validate this method, the limit of detection (LOD) and the limit of quantification (LOQ) expressed as Eqs. (2 and 3), were applied.

$$LOQ = \frac{10s}{S} \quad (2)$$

$$LOD = \frac{3s}{S} \quad (3)$$

where *S* is the calibration curve slope and *s* is the regression line SD (26).

The parabens mass in each sample was calculated through Eq. (4).

$$\text{Paraben mass} = \frac{C \times V}{W} \quad (4)$$

where *C* is the concentration of paraben calculated from the calibration curve equations in Table 2 (ng/mL), *V* is dilution volume, which was equal to 25 mL, and *W* is the sludge dry weight, which was equal to 3 g (25).

Sample preparation and MAE

In this study, sample preparation was designed based

Table 2. Comparative evaluation of the results of this study with those of other studies

Parabens Metabolites	Regression Equation	Linearity (r^2)	LOD (ng/g)	Retention Time (min)	LOQ (ng/g)	RR (%)	m/z	Method	Reference
MePB									
Sludge	y= 99.26 x-35.54	0.998	0.29	10	0.91	82	209, 224	MADLLME-GC/FID	This study
Sea food		0.9999	0.06	7.61	0.2		121, 151	MSPD-GC/MS	(31)
Soil	y=1x-0.145	0.999	0.3	7	0.9		177, 193, 209, 224	MSPD-GC/MS	(23)
EtPB									
Sludge	y=175.48x-106.54	0.996	0.23	13.90	0.775	133	223, 238	MADLLME-GC/FID	This study
Sea food		0.9996	0.12	7.96	0.4		121, 137	MSPD-GC/MS	(31)
Soil	y=0.432x-0.0453	0.998	0.2	8.9	0.6		193, 195, 223, 237, 238, 252	MSPD-GC/MS	(23)
PrPB									
Sludge	y=236.6x-80.08	0.997	0.14	14.50	0.47	91	193, 200	MADLLME/GC/FID	This study
Sea food		0.9996	0.12	8.61	0.4		121, 137	MSPD-GC/MS	(31)
Soil	y=0.3x-0.03	0.998	0.2	9.9	0.6		195, 197, 208, 210, 214, 237, 241, 237		(23)
BuPB									
Sludge	y=267.3x-3.96	0.999	0.125	15.20	0.44	100	195, 210	MADLLME-GC/FID	This study
Sea food		0.9994	0.3		1		121, 137	MSPD-GC/MS	(31)
Soil	0.415x-0.0467	0.999	0.1	10.8	0.4		195, 210, 251	MSPD-GC/MS	(23)

on the method of several studies (21,23,27). First, for having better interaction between microwave radiation and sample, the dried sludge granules were crushed and sieved through a 2 mm sieve to be analyzed chemically, then, 3 g this powder was diluted with 10 mL of different solvents and transferred into a glass container and exposed to microwave radiation to be analyzed at different reaction times and microwave powers. Experiments with microwave irradiation were run in a modified domestic microwave oven with a cooling system (2450 MHz, SAMSUNG Co) (Figure 1). This pilot was previously used in the study of Movahedian et al at Isfahan University of Medical Sciences (28).

After cooling, the sample was poured into a 15 mL Falcon centrifuge and centrifuged at 5000 rpm for 5 min. The supernatant phase was separated, filtered by a syringe filter and diluted in 25 mL deionized water. 10 mL of the diluted supernatant was poured into a test tube to be extracted based on DLLME method.

Dispersive liquid-liquid microextraction

Acetone and chlorobenzene were selected as the extraction solvents. According to the DLLME method, first, a mixture of 500 µL acetone and 30 µL chlorobenzene was injected into 10 mL of the sample solution to form a cloudy solution, which was next centrifuged at 5000 rpm for 5 minutes (27). The dispersed fine droplets were collected at the bottom of the test tube. A 10 µL of the sediment phase was withdrawn by applying a Hamilton microsyringe and injected into 2 mL microcentrifuge tube. The target sediment was subject to a mild flow of nitrogen until dried. The residue was, first, re-dissolved in 20 µL MSTFA, and then, 2 µL obtained solution was injected into the GC-MS (23,27,29).

GC/MS instrument characteristics

The Agilent 7890A GC-System together with MS detector was applied for the separation and quantification of parabens. Agilent 19091S-433MS column with 0.25 mm thickness, 30.0 m length, and 0.32 mm diameter was applied for the separation of parabens. The temperature of injector and detector was 280˚C and 300˚C, respectively. To begin with, the oven temperature was set at 100˚C for 4 minutes, followed by a gradual increase up to 240˚C at a 15˚C /min interval. A scan mode was devised to observe

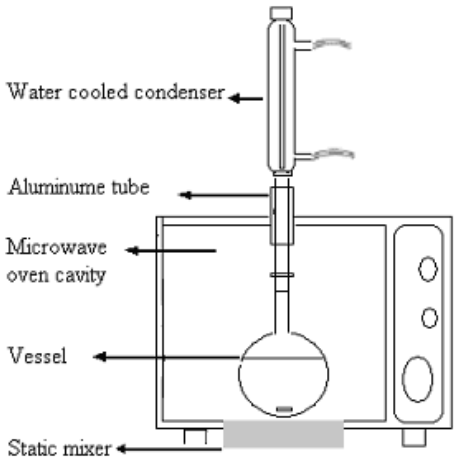

Figure 1. The schematic of the modified microwave system (28).

the elution time of each analyte, followed by a selective ion monitoring (SIM) mode running for quantitative analysis. Analyses of the results of paraben extraction subject to each variable were repeated twice.

Mass loading, removal, and emission of parabens in the Isfahan north WWTP

The mass loading, removal efficiency, and emission of parabens from the WWTP were calculated through Eqs. (5-7) (30).

$$\text{Mass load/1000 inhabitation} = C_i \times F_i \times \left(\frac{1}{10^6}\right) \times \left(\frac{1000}{population}\right) \quad (5)$$

$$\text{Removal efficiency (\%)} = \frac{(C_i \times F_i) - [(C_e \times F_e) + (C_s \times TSP)]}{(C_i \times F_i)} \times 100 \quad (6)$$

$$\text{Emission/1000 inhabitants} = [(C_e \times F_e) + (C_s \times TSP)] \times \left(\frac{1}{10^6}\right)\left(\frac{1000}{population}\right) \quad (7)$$

where C_i is the mean concentration of paraben in wastewater influent (ng/L), C_e is the mean concentration of paraben in wastewater effluent (ng/L), F_i and F_e are the daily flow of wastewater influent and effluent (L/d), respectively, *mass load/1000 inhabitants* is the mean daily weight of individual parabens introduced into WWTP (mg/d/1000 inhabitants), C_s is the mean weight of paraben in sludge (ng/g dry weight), *TSP* is the total sludge production (g/d. dry weight), *population* is the number of inhabitants serviced by the WWTP, and *emission/1000 inhabitants* is the mean daily weight of individual parabens compound discharged through wastewater effluent and sludge (mg/d/1000 inhabitants) (30).

The effects of different variables like the solvent (methanol, acetone, methanol/water, and acetone/water), pH (3, 7, 9, and 12), florisil as a salt (1 g), microwave power (180, 300, 450, and 600 W), and reaction time (15, 30, 60, and 90 s) on paraben extraction were assessed in this study, while the variables subject to the DLLME method remained constant.

Results

Method performance

To validate the paraben extraction from dried sludge through this method, regression equation, linearity, LOD, LOQ, retention time, recovery, m/z, and relative recovery (RR%) were assessed first. As shown in Table 2, a good linearity was confirmed at $r^2 > 0.99$. The LOD was confirmed in 0.125-0. 29 ng/g range, and LOQ was defined within 0.44 to 0.91 ng/g range.

The average relative recovery of all parabens in this method was within 82% to 133% range. The time required for parabens to pass through chromatography was 18.33 min. The performance results of this study are compared with that of other studies using different methods (Table 2). Figure 2 indicates structures and chromatogram of parabens in sludge samples during extraction by MADLLME method.

Effect of reaction time and microwave power on paraben extraction

To improve the MAE, both microwave power and exposure time must be considered. The effect of exposure time on the parabens extraction was examined using a constant microwave irradiation power of 180 W at reaction times of 15, 30, 60, and 90 s. The microwave irradiation of 30 s led to an increase in the paraben concentration recovery, while a shorter irradiation time (e.g. 15 s) led to a decrease in the paraben extraction. Reaction time above 30 s did not increase the parabens extraction (Figure 3). The

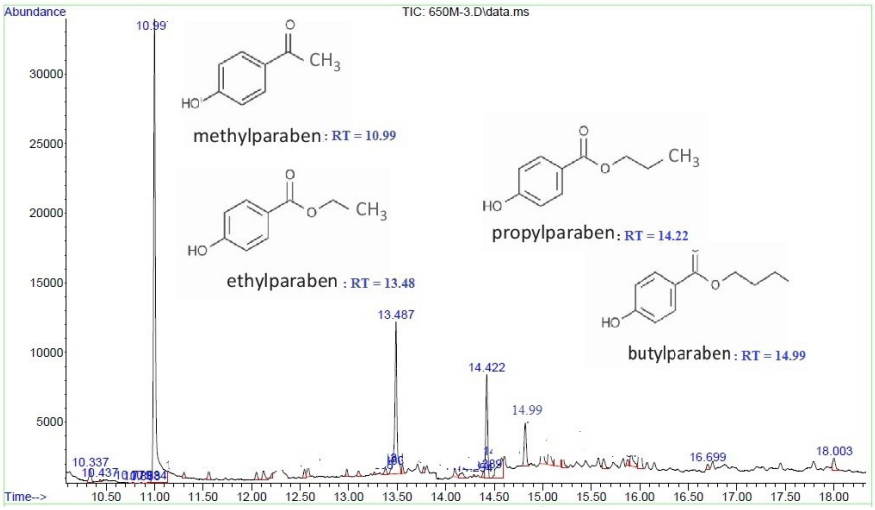

Figure 2. Structures and chromatogram of parabens in the sludge samples during extraction by MADLLME method.

results obtained at microwave irradiation of 180, 300, 450, and 600 W indicate that microwave irradiation of 450 W would be sufficient to obtain a good extraction for all parabens (Figure 4).

Effect of extraction solvent on the mean paraben extraction using microwave procedure

In order to assess the solvent type effect on paraben extraction, experiments with constant volume of methanol (10 mL), acetone (10 mL), methanol/water (5:5 v/v), and acetone/water (5:5 v/v), were performed. The MePB, EtPB, PrPB, and BuPB extractions by methanol were 15, 30, 11.5, and 0.9 ng/g, and by acetone are 4.7, 17, 5.2, and 0.9 ng/g, respectively. The parabens extraction by methanol/water was calculated to be 12.1, 25, 7, and 0.9 ng/g, respectively, and by acetone/water was 4.6, 12, 5.4, and 0.9 ng/g, respectively (Figure 5).

Effect of pH on the mean paraben extraction using microwave procedure

According to the results of experiments, pH=7 was found to be the optimum pH for paraben extraction using MADLLME method (Figure 6).

Effect of florisil on the paraben extraction using microwave procedure

To assess the florisil effect on the parabens extraction, 1 g florisil concentration was applied. In comparison with methanol alone, florisil/methanol could improve the mean extraction ± SD of MP, EP, PP, and BP from influent, wet sludge, and effluent (Figure 7).

Mass loading, removal, and emission of parabens in the subject STP

The MAE method, together with liquid-liquid microextraction, allows rapid detection of parabens in wastewater samples through GC/MS after derivatization. Through this method, it is possible to detect parabens emission into the aqueous environment from STPs. For this purpose, the mass balance method was adopted in this study.

The total of the concentrations of four paraben metabolites (∑PBs) in the STP was 2505 ng/L in influent, 1953 ng/L in

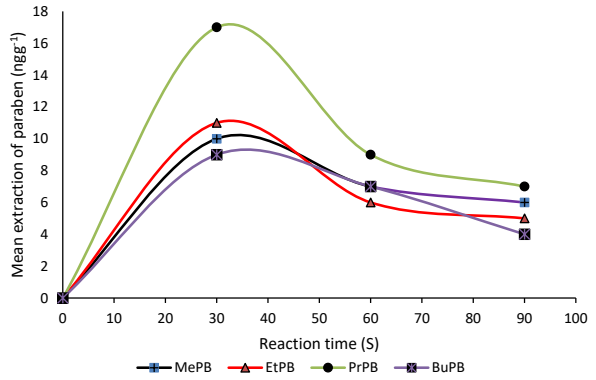

Figure 3. Effect of reaction time on the mean extraction of paraben (sludge weight: 3 g, extraction solvent: 10 mL methanol, disperser solvents: 500 µL acetonitrile and 30 µL chlorobenzene, MSTFA: 20 µL, reaction time: 15, 30, 60, and 90 s, and microwave power: 180 W).

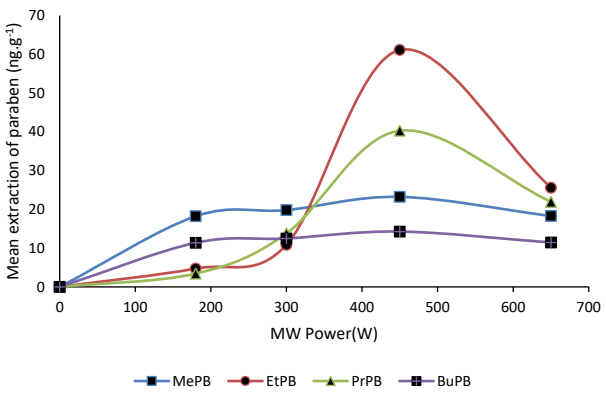

Figure 4. Effect of MW power on the mean extraction of paraben (sludge weight: 3 g, extraction solvent: 10 mL methanol, disperser solvents: 500 µL acetonitrile and 30 µL chlorobenzene, MSTFA: 20 µL, reaction time: 30 s, and microwave power: 180, 300, 450, and 600 W).

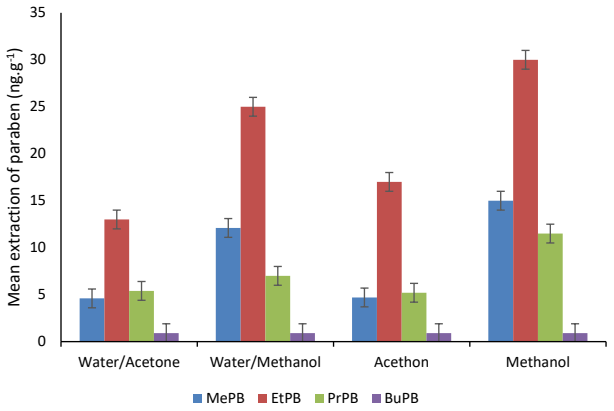

Figure 5. Effect of solvent on the mean extraction ± SD of paraben (sludge weight: 3 g, extraction solvents: 10 mL methanol, 10 mL acetone, and 10 mL methanol/water (5:5 v/v) , 10 mL acetone/water(5:5 v/v), disperser solvents: 500 µL acetonitrile and 30 µL chlorobenzene, MSTFA: 20 µL, reaction time: 30 s, and microwave power: 450 W)

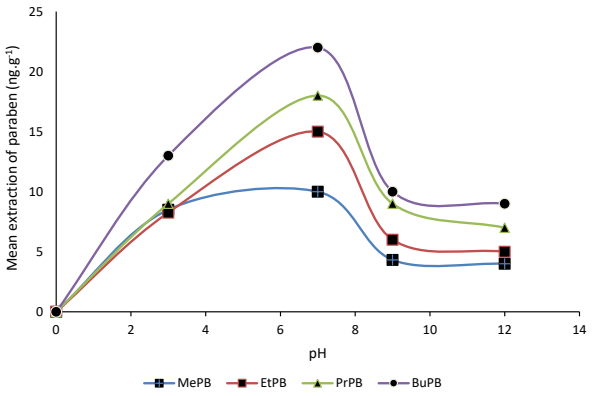

Figure 6. Effect of pH on the mean extraction of paraben (Sludge weight: 3 g, extraction solvent: 10 mL methanol, disperser solvents: 500 µL acetonitrile and 30 µL chlorobenzene, MSTFA: 20 µL, reaction time: 30 s, microwave power: 450 W, pH: 3, 7, 9, and 12).

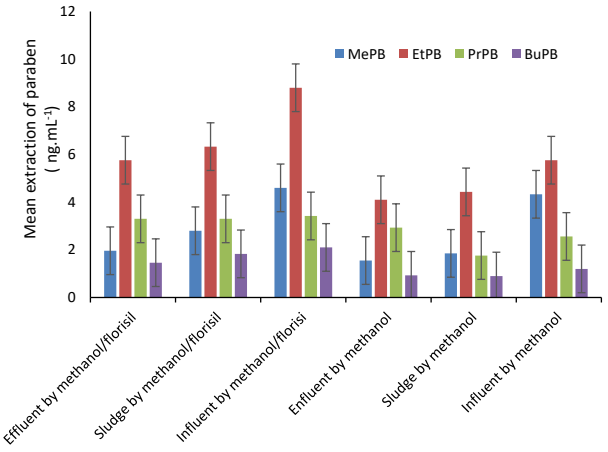

Figure 7. Effect of florisil on the mean extraction ± SD of paraben (extraction solvent: 10 mL wet sludge/methanol, 10 mL effluent/methanol, 10 mL influent/methanol (5:5 v/v), and 1 g florisil, disperser solvents: 500 µL acetonitrile and 30 µL chlorobenzene, MSTFA: 20 µL, reaction time: 30 s, and microwave power: 450 W).

effluent, and 8.03 ng/g at wet weight in sludge samples. The total of mass loading and emission of four parabens in this STP was 0.672 mg/d/1000 people and 0.186 mg/d/1000 people, respectively. The mean removal efficiencies of MePB, EtPB, PrPB, and BuPB were 75, 71, 72, and 62%, respectively (Table 3).

Discussion

MAE is known as an efficient process in determining PCPs polluted environmental aqueous matrices (34). According to the results, developed MADLLME method enables the extraction of MetPB, EtPB, PrPB, and BuPB form sludge and wastewater samples. This method also satisfies validation criterion through parameters of linearity, RR (%), LOD, and LOQ. Here, performance results are comparable with those of other studies (23,31). As microwave is highly contributed to the hydrolysis of complex matrices, so determining its optimum conditions is essential (34), which include microwave power, reaction time, solvent, and the use of Florisil as a clean-up agent. In this study, DLLME method condition including volume of the extraction and disperser solvents (chlorobenzene and acetone) and MSTFA was constant.

A review study conducted by Llompart et al showed that MAE together with different methods is able to extract micropollutants from solid matrixes (34). For example, using MAE-SPE method together with GC-MS, Azzouz and Ballesteros extracted 13 enduring disrupting compounds from sludge using 10 mL methanol/H_2O_2 (3:2 v: v), 500 W microwave power in 4 minutes reaction time, whereas the amounts of recovery and LOD were 92-98% and 4.7-5.1 ng/kg, respectively (35). Through the MAE-SPE coupled with GC-MS method, Kumirska et al extracted non-steroidal anti-inflammatory drugs and oestrogenic hormones through 10 mL water, 400 W microwave power in 15 minutes reaction time, whereas the amounts of recovery and LOD were > 50% and 0.3-5.7 ng/kg, respectively (36).

The molecular interaction using microwave radiation can increase when the microwave power increases. This phenomenon leads to more penetration of solvent into the matrix and better extraction of the solute. Microwave power should not increase the unwanted temperature and pressure (37). In the present study, it was observed that a decrease in the parabens extraction, when microwave power increased, could be due to the possible degradation of parabens (23), therefore, 450 W microwave power and 30 s reaction time were selected for the next experiments. The difference of dielectric loss of water (0.123) compared with that of other conventional solvents like methanol (0.659) or acetone (0.054) leads to a difference in the paraben recovery using different solvents or their combination with water. This phenomenon is effective in energy absorption using the proper solvent and increasing its penetration into the matrix (38-40). Solvents with a high dielectric constant and a high dissipation, promote the analytes extraction yield (41,42).

In this study, it was also found that the best extraction mean can be obtained at pH 7. Any change in the extraction recovery is explained through the change in the parabens' charges. Paraben exists in a protonated form at pH below 3, where its extraction recovery is low. This low rate is because paraben protonation may greatly weaken the hydrophobic interaction between paraben and other compounds (43,44). At pH 4-6.5, paraben mainly keeps its neutral form, with a slight increase in the extraction recovery due to its net positive charge loses and deprotonation of the hydroxyl group. At pH 7-9, paraben is in its negative charged form, due to the full deprotonation of hydroxyl group. At pH above 8, the parabens alkaline hydrolysis process begins, leading to the production of alcohol and hydroxybenzoic acid (45). It is revealed that pH value together with the organic compounds type are highly contributed in increasing the chemical reaction efficiency using microwave oven (37,46).

Florisil is usually applied to decrease the matrix interference effects on the microwave absorption through solvent and analyte (23). By applying an appropriate florisil/methanol ratio, a good extraction will be obtained (47). Florisil absorbs polar compounds of the matrix and facilitates parabens extraction by methanol (48).

In this study, the mass loading and emission of the ∑PBs were recorded as 0.672 mg/d/1000 people and 0.186 mg/d/1000 people, respectively (Table 3).

According to the results of a study conducted in two sewage treatment plants in southern India, concentrations of parent parabens were reported 131-920 ng/L in influent, 16-67 ng/L in effluent, and 104-1090 ng/g dry weight in sludge samples. But the total concentrations of their-metabolites were 4110-34 600 ng/L in influent, 2560-

Table 3. Paraben concentration in the influent, effluent, and sludge together with mass loading, emission, and removal efficiency of parabens in Isfahan WWTP and its comparison with other studies

Paraben Metabolites	Influent (ng/L)	Effluent (ng/L)	Sludge (ng/g wet. weight)	Mass Loading (mg/d/1000 people)	Emission (mg/d/1000 people)	Removal Efficiency (%)	Method	References
MePB **Isfahan**	*1219 (1000-1300)	565 (492-654)	1.87 (1-375)	0.223	0.054	75	MADLLME -GC/FID	This study
A	36.8 (21.7-56.4)	0.14 (0.14-0.14)	41.6 (35.3-68.8)	20	1.83	95.8 ±7.78	SPE-HPLC–MS/MS	(32)
B	97.9 (18.3-320)	0.14 (0.14-1.73)	58.5 (24.3-87.4)	113	3.71	95.2 ± 5.81		
SP	151	28.2	16	∑ parabens = 0.3-36	0.07-0.9		SPE-HPLC–MS/MS	(33)
BE	51	4.4	31.6					
MP	267	35.8	38.2					
UP	138	28.9	172					
CO	209	41	42					
EtPB **Isfahan**	1303 (1298-2455)	703 (245-732)	3.3 (1-2)	0.238	0.067	71	MADLLME /GC/FID	This study
A	4 (2.17-8.4)	0.3 (0.14-1.47)	2.54 (1.74- 4.80)	2.05	0.35	89.8 ± 10.9	SPE-HPLC–MS/MS	(32)
B	2.75 (0.5-66.8)	0.14 (0.14-0.29)	5.13 (1.6-12)	16.5	0.32	88.5± 7.66		
SP	40.5	8.1	5.7	∑ parabens = 0.5-7.4	∑parabens = 0.01-1.2		SPE-HPLC–MS/MS	(33)
BE	11.6	1.9	6.6					
MP	583	19.3	172					
UP	16.2	3.9	11.2					
CO	53	7.2	13.2					
PrPB **Isfahan**	761 (432-123)	400 (112-467)	1.95 (0.95-4.32)	0.139	0.038	72 ± 3.5	MADLLME -GC/FID	This study
A	12.9 (9.69-113)	1.16 (0.36-4.90)	1.38 (0.6- 2.62)	14.3	1.24	70.8 ± 15.7	SPE-HPLC–MS/MS	(32)
B	20.9 (8.19-42.3)	0.51 (0.14 – 1.10)	2.93 (0.36-4.64)	17.9	0.98	91.1 ± 4.86		
SP	68.1	9.8	82	∑ parabens = 2.2-95.3	∑ parabens = 1.06-1.9		SPE-HPLC–MS/MS	(33)
BE	38.2	2.8	519					
MP	583	19.3	172					
UP	50.2	18.4	910					
CO	55.4	8.4	404					
BuPB **Isfahan**	395 (245-432)	285 (76-306)	0.91 (0.5-2.2)	0.072	0.027	4.2	MADLLME -GC/FID	This study
A	5.80 (3.15-2.14)	0.61 (0.36-3.55)	0.57 (0.36-2.63)	4.30	1.24	70.8 ± 15.7	SPE-HPLC–MS/MS	(32)
B	7.25 (3.46-112)	0.14 (0.14-0.76)	11.2 (0.55-19)	28.2	0.91	91.1 ± 4.86		
SP	10.5	2.1	0.5	∑ parabens= 2- 0.8	∑ parabens= 0 – 0.5		SPE-HPLC–MS/MS	(33)
BE	8.9	2.9	ND					
MP	4.4	1.4	0.7					
UP	5.2	0.7	1					
CO	4.1	ND	ND					

3800 ng/L in effluent, and 1220-35 900 ng/g dry weight in sludge samples. The average removal efficiencies of parent parabens and their metabolites ranged from 80% to 100% and from 28% to 76%, respectively (30).

In two WWTPs in New York, the median concentrations of the total parabens and paraben-metabolites were 73.1-158 and 5460-10 000 ng/L in influents, and 1.96-5.57 and 2060-2550 ng/L in the final effluents. The removal efficiencies for parabens (89.6-99.9%) were higher than those for their metabolites (25.9-90.6%). The mass loadings of parabens and their metabolites were 46.3 and 6210 mg/d/1000 people for $WWTP_A$, and 176 and 63,100 mg/d^{-1}/1000 people for $WWTP_B$, respectively. The average daily environmental emission of parabens and their metabolites was 4.85–6.16 and 1270–2050 mg/d/1000 people, respectively (32).

In another study performed in Tehran, MePB and EtPB concentrations in the influent and effluent of $WWTP_A$ were 740 and 277.7 ng/L and 179.2 and 45.8 ng/L, respectively. Also, MePB and EtPB concentrations in the influent and effluent of $WWTP_B$, were 835.2 and 295.2 ng/L and 122.8 and 29.7 ng/L, respectively. In these $WWTP_s$, the removal efficiency was 83-91% (49), which is higher than that obtained in the present study (Table 3). Also, Gasperi et al evaluated the pollutant mass loads per population equivalent (PE) of parabens, triclosan (TCS), and triclocarban (TCC), where the median mass loading ranged 176 to 3040 µg/PE/d for parabens and 26 to 762 µg/PE/d for the TCS and TCC, respectively (11).

Conclusion

According to the results, the optimum condition for this method is achieved at pH = 7, reaction time = 30 s, microwave power = 450 W, and methanol as solvent. The performance of this proposed method for determination of parabens in the real wastewater and sludge samples reveals good practical results. Overall, MAE coupled with DLLME method seems to be an excellent alternative, as a green extraction technique, for determination of various groups of emerging micropollutants in different matrixes.

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Ethical issues

This study does not contain any studies with human participants or animals. The authors certify that all the data collected during the study are presented in the manuscript, and no data from the study has been or will be published elsewhere separately.

Competing interests

The author declare that they have no competing interests.

Authors' contributions

All authors were involved in data collection, analysis, and interpretation. All authors critically reviewed, refined, and approved the manuscript.

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