

Application of an ultrasonic field, hydrogen peroxide and the Fenton process in removing DEHP from bottom sediments

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ABSTRACT

The work described here considered the effectiveness with which di(2-ethylhexyl) phthalate might be removed from the solid matrix of bottom sediments using an ultrasonic field, hydrogen peroxide and the Fenton process. This was tested considering the influence of time, pH, amplitude of vibration, reagent dose and initial pollution content. The ultrasonic field applied had a vibration frequency of 20 kHz and a maximum acoustic wave intensity of 5.16 W/cm². In the event, the highest efficiency obtained was 66.20%, where C₀ = 10 mg/kg d.w., the pH value was 10 and the reaction was allowed to continue for 1 hour. Such a process proved more effective than hydrogen peroxide or the Fenton process, the removal efficiency after 1 h was at the level of 5.14% and 14.18%, respectively (pH = 3, C₀ = 10 mg/kg d.w.). The ultrasonic field was ineffective in removing DEHP in the acid reaction medium. After 1 h of the process, the efficiency of DEHP removal was 2.54%.

Keywords: Di(2-ethylhexyl) phthalate; Ultrasonic waves; Hydrogen peroxide; Fenton process; Bottom sediments

1. Introduction

A recent challenge limiting progress in various areas of life reflects the need for chemical threats arising with civilisational development to be either reduced or eliminated. This is particularly the case, given that a great many organic pollutants discharged to the environment are of low solubility and prove very resistant to degradation. This, for example, ensures retention in bottom sediments at the final stages of the processes by which water self-purifies. The greatest threat poses organic substances such as phthalic acid esters, polycyclic aromatic hydrocarbons (PAHs), pesticides, polychlorinated biphenyls, polychlorinated dibenzodioxins, polychlorinated dibenzofurans, halogenated organic compounds, nonylphenols and nonylphenol ethoxylates. These are chemical substances that are usually characterized by relative resistance to degradation, movement in the environment, toxicity to organisms and the possibility of penetration into the trophic chain and bioaccumulation [1–6].

One such notorious and commonly occurring pollutant substance is di(2-ethylhexyl) phthalate (DEHP), which proves to be detectable in air, rainfall, water intended for consumption, groundwater, surface water, the soil, bottom sediments and living organisms. Analyzing its content in bottom sediments, these values reach 322 mg/kg d.w. In addition, persistent organic pollutants include primarily pesticides and PAHs. More than 300 compounds classified as polycyclic aromatic hydrocarbons have been identified in the environment. They are considered difficult to decompose. The presence of pesticides in the environment is associated with intentional use in agriculture. Due to durability, organochlorine pesticides are particularly dangerous [7–11].

As has been noted, such chemicals of anthropogenic origin are usually less susceptible to conventional removal processes, with the result that research based on green chemistry is necessitated. Much of the relevant technology draws on advanced methods of oxidation, for example using hydrogen peroxide, ultrasound and the Fenton process [6,9,11].

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Hydrogen peroxide enjoys renown as an environment-friendly oxidant, given the typical ultimate reaction products in the form of water and CO₂. The use of ultrasound is seen as a further step in the right direction where clean green chemistry is concerned. The fact that ultrasound generates free radicals dispenses with additional chemical reagents while still ensuring a significant contribution to the process by which pollutants may be degraded [6,12,13].

This paper presents work to apply selected examples of such advanced (green chemistry-based) oxidation methods in removing DEHP from bottom sediments. The research reflects the ongoing need for detailed diagnosis of the impacts various further factors may exert as the above methods operate to remove contaminants.

2. Materials and methods

2.1. Reagents and materials

Di(2-ethylhexyl) phthalate (DEHP) and di(2-ethylhexyl) phthalate-3,4,5,6-d₄ (DEHP-3,4,5,6-d₄) were purchased from Sigma-Aldrich (Darmstadt, Germany). Reagecon (Shannon, Ireland) was in turn the source of (500 µg/mL toluene-based) standard solutions of the PAHs (acenaphthene, anthracene, benzo(a)anthracene, chrysene, fluoroanthene, fluorene, naphthalene, phenanthrene, pyrene, benzo(a)pyrene, benzo(b)fluoroanthene, benzo(g,h,i)perylene, dibenzo(a,h)anthracene, benzo(k)fluoroanthene, indeno(1,2,3-cd)pyrene and acenaphthylene); while a standard (2,000 µg/mL hexane:toluene-based) solutions of the organochlorine pesticides (α -BHC, β -BHC, γ -BHC, δ -BHC, heptachlor, aldrin, heptachlor epoxide isomer b, γ -chlordane, α -chlordane, endosulfan i, 4,4'-dde, dieldrin, endrin, endosulfan II, 4,4'-DDD, endrin aldehyde, endosulfan sulfate, 4,4'-DDT, endrin ketone and methoxychlor) were obtained from Sigma-Aldrich (Darmstadt, Germany). H₂O₂ solution (30%) and FeSO₄·7H₂O were obtained from Chempur (Piekary Śląskie, Poland); while POCH (Gliwice, Poland) was the source of purchased HCl and NaOH solutions, analytical grade n-hexane, methanol and acetone. Ultra-pure water was obtained from Purix CNX-100 (Polwater, Cracow, Poland). All glassware were submerged in NaOH solution for 24 h, dried for 5 h and then rinsed with acetone prior to heating at 280°C for 5 h [14].

2.2. Sample preparation

Bottom sediments for study were collected from Rzeszow Reservoir (Poland) using a gravity sediment corer (KC Kajak of Denmark). Samples were taken into glass amber jars from three locations located along the axis of the tank. After sampling, the sediments were dried in air at 20°C–25°C and then at 105°C to constant weight, before being ground in a mortar and passed through a 1.0 mm sieve. The collected bottom sediments characterized by a content of organic matter at the level of 8.5% and a pH of 7.9. The collected bottom sediments did not contain DEHP, which is why this pollution was introduced into the matrix for the purposes of the study. The tested applications of ultrasound, hydrogen peroxide and the Fenton process involved a synthetic matrix, prepared by washing with acetone (3 × 24 h) and then drying to constant weight. Samples of the cleaned bottom sediment weighing

1 ± 0.01 g were placed in a reactor cell into which DEHP in the appropriate amount with acetone had been introduced. The sample preparation has been described in detail in the research of Kida et al. [14]. In turn, research on the impact of the presence of other impurities on the efficiency of di(2-ethylhexyl) phthalate removal was carried out by introducing into the synthetic matrix an additional 16 substances from the group of PAHs (Σ 16 in the amount of 3.2 mg/kg d.w) and 20 substances from the group of organochlorine pesticides (Σ 20 in the amount of 4 mg/kg d.w). The whole was shaken for 1 h at 150 rpm in closed vessels, before the solvent was allowed to evaporate ($t = 24$ h).

2.3. Experimental procedures

2.3.1. Use of ultrasonic waves

The ultrasonic irradiation experiments were carried out in a laboratory reactor comprising an ultrasonic processor (Sonopuls HD 3200 from Bandelin, Berlin, Germany), a reactor cell and a water jacket. The nominal power of the processor was 200 W and the frequency 20 kHz. A titanium probe tip of diameter of 13 mm and maximum vibration amplitude 170 µm was deployed. The three vibration amplitudes (A) used were of 20%, 30% and 50%. 1 g of polluted sediment was sonicated in 40 mL of water, with the suspension maintained at 20°C ± 1°C. The tests were conducted in an open-air system to check for effective DEHP removal with no additional costs incurred (in line with real conditions capable of being sustained on a technical scale). Dissipation of ultrasonic energy in the sample was determined using a calorimetric method [15], with dissipated acoustic power (P) given by the formula:

$$P = m \cdot C_p \frac{dT}{dt} [\text{W}] \quad (1)$$

where m is the mass of liquid (g), C_p is the heat capacity of the liquid (J/g°C), and (dT/dt) is the initial slope of the curve for temperature vs. time (°C/s).

The reaction was terminated through introduction into the reaction solution of 1 M NaOH or H₂SO₄, to achieve neutral pH. The solution obtained in this way was then subjected to further analysis.

All experiments of the above kind were carried out in triplicate, and observed deviation was found to be of less than 5%. This was taken to justify the graphic presentation of average values in graphs.

2.3.2. Use of hydrogen peroxide and the Fenton process

DEHP oxidation via the Fenton process involves H₂O₂ and a source of Fe²⁺ in the form of added FeSO₄·7H₂O catalyst, with a 3 mL (1:3 w/v) aqueous phase volume as determined from the literature and experimentation. Amounts of hydrogen peroxide and iron were determined by reference to the molar ratio of reactants, with the appropriate amounts for each bottom sediment sample supplied, prior to mixing for 10 min to ensure homogeneous distribution of the catalyst in the suspension. The reaction was initiated by gradually adding the appropriate amount of 30% H₂O₂ to the sample, and the whole suspension was mixed intensively at 250 rpm.

The reaction was terminated by introducing 1 M NaOH or 1 M H₂SO₄ into the reaction mixture (until neutral pH was achieved).

2.4. Analytical methods of DEHP determination

A MARS 6 mineralizer/extractor (SELWALab, CEM, Matthews, USA) was used to isolate DEHP from bottom sediments. Average recovery in the 92%–103% range and a relative standard deviation below 10% were correctly accepted extraction conditions. The drying of sediments was carried out by adding anhydrous Na₂SO₄ – activated by roasting in a muffle furnace at 550°C for 4 h. The liquid layer was separated from the solid, and the extract obtained concentrated in a stream of nitrogen to a volume of 1 mL, before being subjected to chromatographic analysis.

Isolation of DEHP from the aqueous phase involved solvent extraction by shaking with dichloromethane. In no case in the process removing di(2-ethylhexyl) phthalate from bottom sediments was the concentration of DEHP in the aqueous phase detected.

Extracts obtained were subjected to chromatographic separation using a gas chromatograph as coupled with a mass spectrometer GC/MS (Thermo Scientific, Waltham, USA). An internal standard technique involving DEHP-3,4,5,6-d₄ was used to monitor the extraction process, and to determine extraction efficiency and analyte loss during consecutive stages of the analytical procedure.

3. Results and discussion

3.1. Use of ultrasonic waves

The effectiveness of DEHP degradation using ultrasound was as presented in Figs. 1 and 2, by reference to the $C_t/C_0 = f(t)$ relationship (where C_t is the content of di(2-ethylhexyl) phthalate in bottom sediments after time t and C_0 is the initial content of DEHP in bottom sediments). The first step, checking for the influence on DEHP removal of pH at 3, 7.95 (natural reaction) or 10 (Fig. 1a), revealed highest efficiency with an alkaline reaction. On that basis, analysis of

removal efficiency in relation to 20%, 30% and 50% amplitudes (equivalent to 34, 51 and 85 μm) was carried out with pH = 10 (Fig. 1b).

The effectiveness reported for DEHP removal at pH 10 and $t = 1$ h was 51.75%. Efficiency proved to be far lower in an acidic environment, with only 16.62% degradation achieved (after $t = 1$ h). Nor was the natural-reaction environment favourable to the removal of DEHP from bottom sediments (with just 21.10% achieved for $t = 1$ h). Reference to pKa values suggests no significant influence of pH value when it comes to the removal/degradation of DEHP using an ultrasonic field. pH value is relevant to this process where pollutants may be in neutral and/or ionised form in aqueous solution. For chemical compounds that do not have a replaceable proton, the role of the pH of the reaction medium is smaller. This may reflect the elution at this pH of various substances performing the function of so-called hydroxyl-radical scavengers (e.g., humic compounds, Ca²⁺, HCO₃⁻, CO₃⁻, phosphate and bromide ions, and many others) [15,16].

Where the role of vibration amplitude was concerned, DEHP removal from bottom sediments ($C_0 = 50$ mg/kg d.w.) over time was at the 12.58%–32.59% level for $A = 20\%$, and of 17.59%–51.75% for $A = 50\%$ (Fig. 1b). The increase of A across the 20%–50% range allowed a higher-intensity ultrasonic field in the range 3.02–5.16 W/cm² to be obtained, with acoustic power of 16.4–27.9 W [14].

Results for different process conditions show that high efficiency of removal of di(2-ethylhexyl) phthalate is even achievable where other contaminants potentially competing for HO• radicals are present (Fig. 2). A greater difference in DEHP removal efficiency was found for $C_0 = 10$ mg/kg d.w. in the presence of PAH and pesticides, as opposed to with the higher (50 mg/kg d.w.) initial content of DEHP in bottom sediments. The efficiency for $C_0 = 10$ mg/kg d.w. was in the range 34.10%–66.20% for $t = 5$ –60 min (Fig. 2a). Degradation efficiency for $C_0 = 50$ mg/kg d.w. was slightly lower, but the presence of 3.2 mg/kg d.w. of PAH or 4.0 mg/kg d.w. of pesticides did not impact on the process significantly (Fig. 2b). In turn, for $C_0 = 10$ mg/kg d.w., the efficiency of elimination of di(2-ethylhexyl) phthalate was of 10.92% for $t = 5$ min, 7.44% for $t = 15$ min, 12.52% for $t = 30$ min and 7.47% for $t = 60$ min.

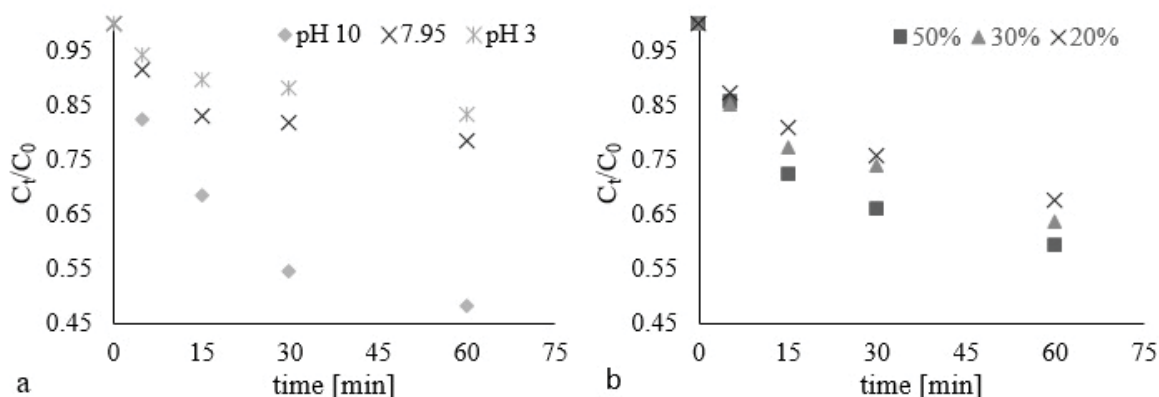


Fig. 1. Application of an ultrasonic field in removing DEHP from bottom sediments ($C_0 = 50$ mg/kg d.w.): (a) effect of pH ($A = 50\%$) and (b) effect of vibration amplitude (at pH 10).

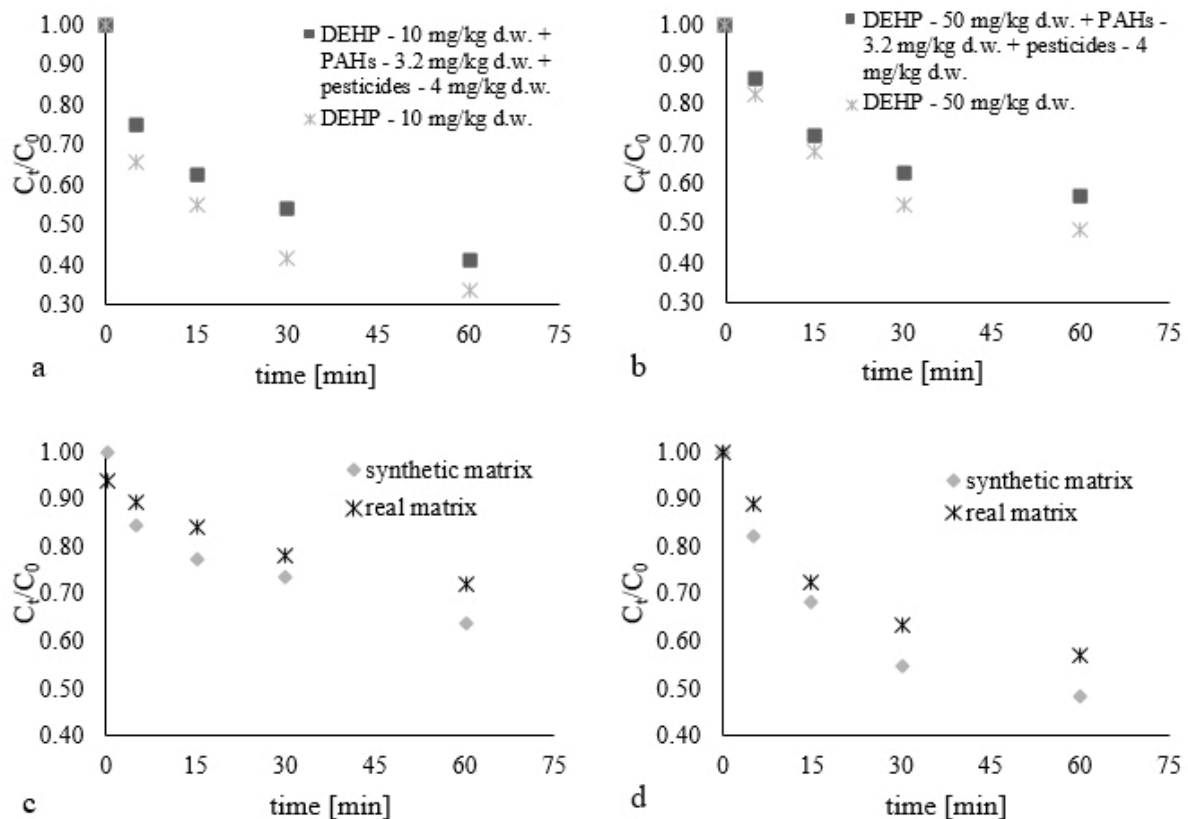


Fig. 2. Effect of (a) other non-degradable pollutants on the efficiency of removal of DEHP via the US process (at pH = 10) for $C_0 = 10$ mg/kg d.w., $A = 50\%$; (b) $C_0 = 50$ mg/kg d.w., $A = 50\%$; (c) the treatment of bottom sediments by organic solvent washing on DEHP decomposition via the US process (pH = 10) $A = 30\%$; and (d) $A = 50\%$.

The presence of other substances, especially in comparable amounts, contributes to increased competitiveness with access to HO^\bullet radicals, with the result that removal efficiency is reduced.

Similar results were obtained from work using uncleaned bottom sediments as sources of di(2-ethylhexyl) phthalate for removal (Figs. 2c and d). The test results showed a slightly lower efficiency of removal of DEHP from real as opposed to synthetic sediments, albeit with the difference within the 4.47% – 8.15% range for $A = 30\%$ and between 3.76% and 8.58% for $A = 50\%$. The most likely main reason for the lower efficiency of DEHP removal in real bottom sediments was the presence of other pollutants rinsed with solvent.

3.2. Use of hydrogen peroxide

The effectiveness of removal of DEHP from bottom sediments was analysed using a molar ratio $\text{DEHP}:\text{H}_2\text{O}_2$ of constant DEHP concentration equal to 0.13 mM/kg d.w. (Fig. 3). As H_2O_2 offered a less effective method of removing DEHP than the ultrasonic field, processes with its participation were carried out for $t = 1, 2, 4, 12$ and 24 h.

It did not prove possible to note any significant effect on DEHP removal efficiency of increasing amounts of hydrogen peroxide in the molar ratio $\text{DEHP}:\text{H}_2\text{O}_2$ from 2:1 to 1:50. Thus, a degradation efficiency of 8.58% at $t = 60$ min (where pH = 3 and the $\text{DEHP}:\text{H}_2\text{O}_2$ molar ratio was 2:1), increasing

to 18.53% after 24 h, compared with a situation in which a doubling of the H_2O_2 dose ($\text{DEHP}:\text{H}_2\text{O}_2$ 1:1) was associated with very similar removal efficiencies of 9.72% and 19.55%, respectively, at $t = 2$ h and $t = 24$ h. Under the same background conditions, testing of a molar ratio as high as 1:50 revealed degradation of just 13% of the DEHP after 1 h and 21.39% for $t = 24$ h.

The greater efficiency of removal of DEHP in an acidic environment compared with an alkaline one may reflect ease of access to iron ions contained in the sediments analysed, because non-catalytic oxidation of organic substances with hydrogen peroxide is usually most effective in alkaline conditions. The extent of the removal of the tested compound for pH = 7.95 was in the range 7.01%–18.04% for $t = 24$ h, depending on the dose.

The best results in degrading di(2-ethylhexyl) phthalate in bottom sediments using hydrogen peroxide to come where H_2O_2 was introduced in a quantity of 650 mM/kg d.w. A higher H_2O_2 dose increases oxidation effects in relation to pollutants, though too much hydrogen peroxide in relation to the oxidised substrate may lead to the binding of hydroxyl radicals [17]. In any event, an increased dose of hydrogen peroxide is obviously associated with higher costs of the process.

Chen et al. [18] tested a wide range of doses of hydrogen peroxide in a process seeking to removing tetracycline from aqueous solution. Usefulness of this method was analysed

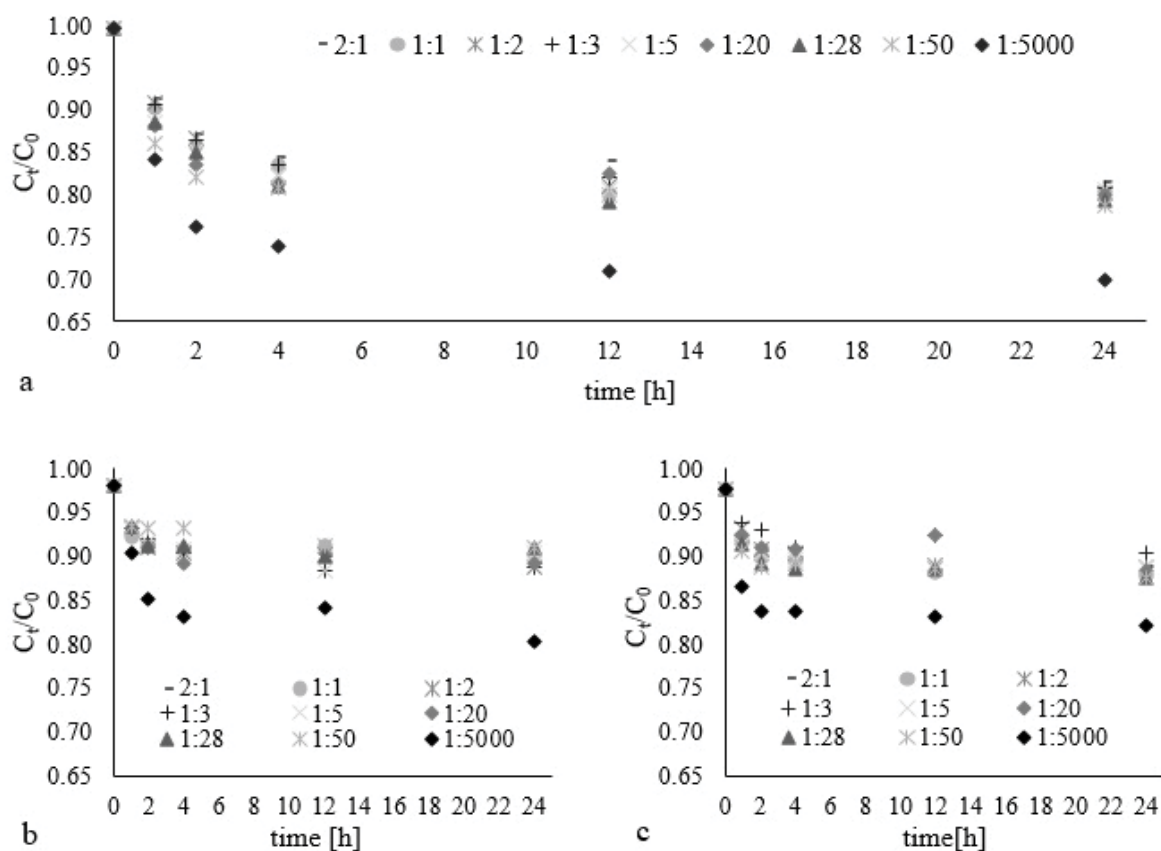


Fig. 3. Effectiveness of the use of hydrogen peroxide on removal of DEHP from bottom sediments in relation to the DEHP: H_2O_2 molar ratio and (a) pH = 3; (b) pH = 7.95; and (c) pH = 10.

over the 193–3,869 mM/L H_2O_2 range, for $t = 10$ –180 min. Efficiencies of removal of the antibiotic (at 400 mg/L) in aqueous solution were in the 44.89%–88.23% range after 1 h, and with hydrogen peroxide doses of between 193 and 1,161 mM/L. A further increase in the amount of H_2O_2 was associated with a level of efficiency of tetracycline degradation about 10% higher. At $t = 2$ h, no significant differences in process efficiency were found for $H_2O_2 \geq 1,161$ mM/L. Given the relative costs, the optimal dose of hydrogen peroxide recommended for removing tetracycline at a concentration of 400 mg/L was 1,161 mM/L [18].

As in the case of sonification, no significant impact on H_2O_2 -mediated degradation was noted due to the presence of selected polycyclic aromatic hydrocarbon pollutants (dosed at 3.2 mg/kg d.w.) or organochlorine pesticides (dosed at 4 mg/kg d.w.) for $C_0 = 50$ mg/kg d.w. (Fig. 4). However, where the process entailed removing a content of di(2-ethylhexyl) phthalate only one-fifth as high, the more limited access of this substance to hydroxyl radicals was associated with a lower efficiency of removal of DEHP from bottom sediments. In the process where other pollutants were absent, the highest efficiency achieved for $C_0 = 10$ mg/kg d.w. was 21.58% ($t = 24$ h). This value was only 2.03% higher than with $C_0 = 50$ mg/kg d.w. In the presence of other pollutants, the effectiveness of removal of DEHP ($C_0 = 10$ mg/kg d.w.) was lower by 6.57% (at $t = 24$ h).

Although hydrogen peroxide is referred to as a strong yet environment-friendly oxidant, used on its own it appears to be too weak to provide for effective degradation of di(2-ethylhexyl) phthalate present in bottom sediments. The effectiveness of DEHP removal using an ultrasonic field was three times greater at $t = 1$ h (pH = 10, $C_0 = 10$ mg/kg d.w.) than with hydrogen peroxide at $t = 24$ h (molar ratio DEHP: H_2O_2 1:1, pH = 3, $C_0 = 10$ mg/kg d.w.). In addition, a lowering of pH requires the subsequent alkalisation of bottom sediments. The advantage of using oxidation processes lies in the increased susceptibility to biodegradation of organic pollutants [19]. The low efficiency of removal of DEHP achieved using H_2O_2 indicates the need for combined methods.

3.3. Use of the Fenton process

Investigations centred on the effect of the DEHP: H_2O_2 : Fe^{2+} molar ratio in various variants involving a constant DEHP content of 0.13 mM/kg d.w., as well as $t = 1, 2, 4, 12, 24$ h and pH = 3 (Fig. 5).

The highest efficiency of degradation of di(2-ethylhexyl) phthalate for $t = 1$ h was recorded where the dose of H_2O_2 : Fe^{2+} (at 28:1). It was at an average level of 13.39%. In other variants, values were only slightly lower than this, except where no oxidiser was introduced (DEHP: H_2O_2 : Fe^{2+} 1:0:1). After 24 h, the efficiency of removal of di(2-ethylhexyl) phthalate

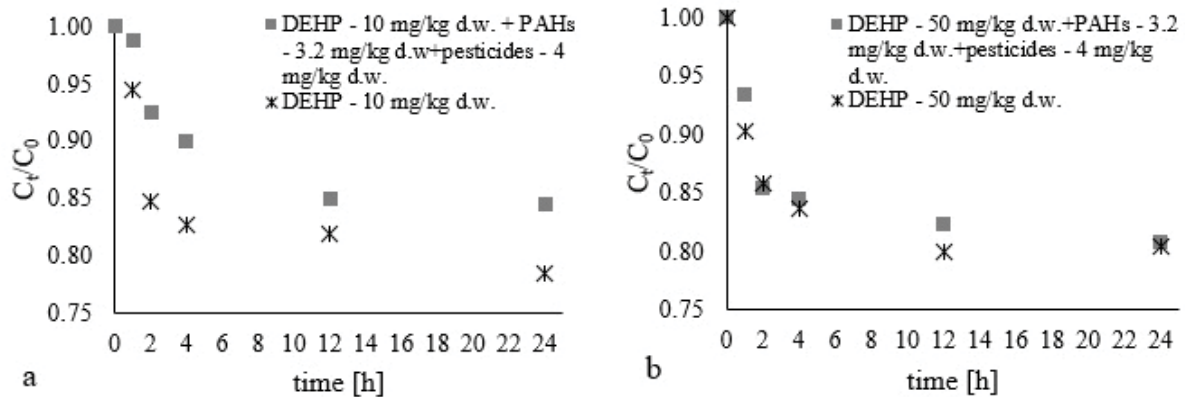


Fig. 4. Effect of other non-degradable pollutants on the efficiency of removal of DEHP (at pH = 3, molar ratio DEHP:H₂O₂ 1:1) for (a) $C_0 = 10$ mg/kg d.w.; (b) $C_0 = 50$ mg/kg d.w.

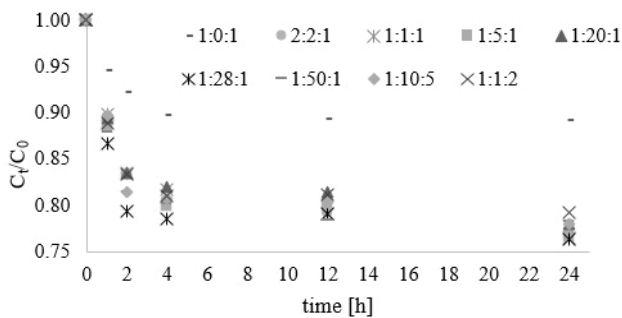


Fig. 5. Effect of DEHP:H₂O₂:Fe²⁺ molar ratio on DEHP degradation (at pH = 3).

had only doubled for each reagent dose (20.51%, H₂O₂:Fe²⁺ 28:1, $t = 24$ h).

Determination of an optimal molar ratio for H₂O₂:Fe²⁺ avoids unwanted radical reactions that may occur where either reagent is present in excess [20]. In this case, the process was anyway proved ineffective in removing DEHP from bottom sediments. An increase in amounts of hydrogen peroxide does not increase this efficiency significantly.

Similar results were obtained by Cheng et al. [21], who analysed the decomposition of atrazine in soil ($C_0 = 617.5$ mg/kg) using the Fenton reagent. The process took place effectively in the first 2 h, but after a further 18 h the authors obtained only a twofold increase in the level of degradation. This effect was also observed in our own research in a self-conducted process with hydrogen peroxide, in which a value for this parameter about 3% lower with respect to the Fenton reagent was obtained. Such a small difference may reflect the presence in bottom sediments of naturally occurring iron ions available during the process.

Greatest effectiveness was achieved in an acidic reaction environment (Fig. 6). Removal of DEHP after 24 h was at the levels of 23.57% and 23.69% for pH = 3 and respective doses of DEHP:H₂O₂:Fe²⁺ in the ratios 1:1:1 and 1:28:1. In contrast, at pH = 7.95, the corresponding values of effectiveness were 10.56% and 10.50%, and for pH = 10–14.34% and 14.12%.

A further important factor determining the efficiency of DEHP removal from bottom sediments via this process was

the presence of selected pollutants, that is, 3.2 mg/kg d.w. of 16 substances from the PAH group, as well as 4.0 mg/kg d.w. of 20 organochlorine pesticides, for $C_0 = 10$ mg/kg d.w. (Fig. 7a). The highest efficiencies of DEHP removal from bottom sediments noted with the Fenton process applied for $C_0 = 10$ mg/kg d.w. were 11.14% and 25.94%, respectively, for $t = 1$ and 24 h. By comparison, in the process using hydrogen peroxide the $t = 1$ h efficiency was 5.17% (at pH = 3), while with the ultrasonic field the percentage was as high as 66.20 (at pH = 10).

In the presence of these other pollutants, the effectiveness of di(2-ethylhexyl) phthalate removal was on average lower by 10.64%, for $C_0 = 10$ mg/kg d.w. No significant differences from that were noted in the first 4 h of the process where the initial content of DEHP was higher (at $C_0 = 50$ mg/kg d.w.; Fig. 7b). Compared with the process in which the oxidant was hydrogen peroxide, the Fenton reaction provided for a greater reduction in the content of DEHP in bottom sediments (maximally by 5.55% at $t = 60$ min where $C_0 = 10$ mg/kg d.w.).

The susceptibility of PAHs in soil, sewage sludge and bottom sediments to degradation using Fenton's reagent was investigated by Flotron et al. [22]. They showed that the amounts of reagents needed for an efficient process depended on type and characteristics of the matrix. Efficiencies of removal of different polycyclic hydrocarbons were at different levels, with oxidation of benzo(a)pyrene for example, are more effective than that of fluoranthene. There was ready sorption of hydrocarbons such as benzo(b)fluoranthene. Using the Fenton process to remove PAHs from soil, Silva et al. [23] obtained 94% phenanthrene removal after 4 h, as opposed to less than 50% in the case of pyrene.

Across the analysed range of parameters, the Fenton process also proved ineffective at removing DEHP from bottom sediments, with results achieved only a few percentage higher than with hydrogen peroxide. In contrast, the Fenton process is known to be very effective at removing pollutants from aqueous solutions, as Esmali et al. [24] confirmed.

However, if pollutants are to be removed from a solid matrix, they must first be desorbed. pH correction of the reaction environment is also required. However, advantages of the process include the easy access to reagents and the lack of any need for specialised equipment.

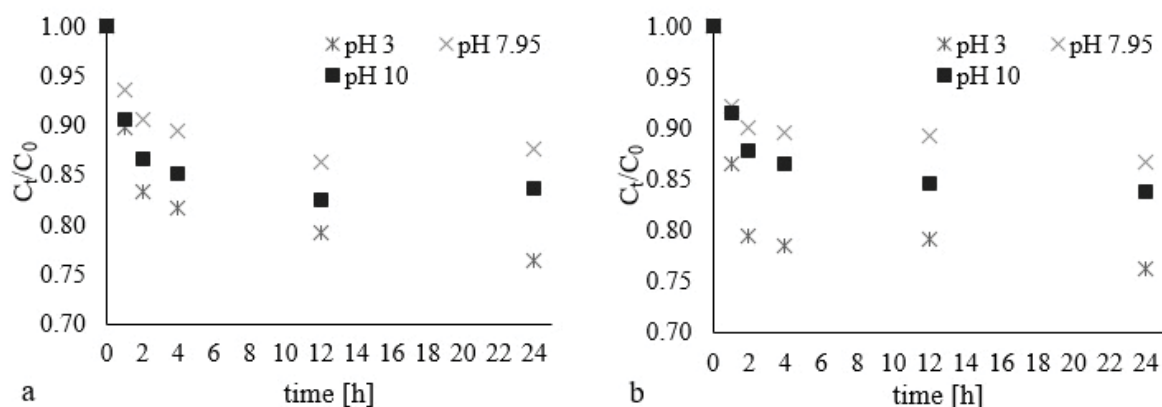


Fig. 6. Effect of pH on DEHP decomposition for the DEHP:H₂O₂:Fe²⁺ molar ratios of: (a) 1:1:1 and (b) 1:28:1.

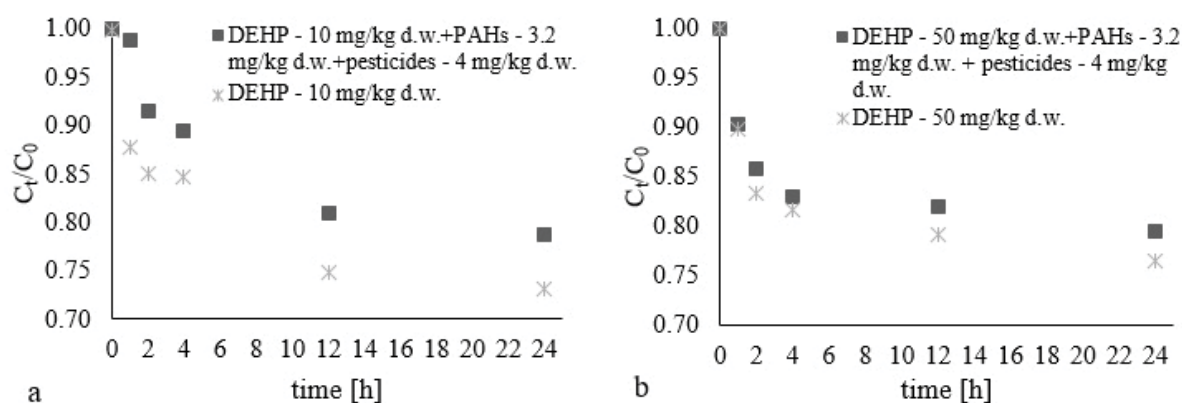


Fig. 7. Effect of other non-degradable pollutants on the efficiency of removal of DEHP (at pH = 3, with a DEHP: H₂O₂:Fe²⁺ molar ratio of 1:1:1), for C₀ equal to (a) 10 mg/kg d.w.; (b) 50 mg/kg d.w.

4. Conclusions

It can be concluded that:

- an ultrasonic field allowed for the most efficient removal of DEHP from bottom sediments, also in a much shorter time than the other processes analysed.
- the use of hydrogen peroxide and the Fenton process requires prior desorption of pollutants from bottom sediments to allow for effective removal.
- efficiency of DEHP removal from bottom sediments was particularly influenced by initial DEHP content and the presence of other pollutants such as PAHs and pesticides in comparable quantity.
- optimal process conditions may only be fully determined where testing provides information on such parameters as characteristics of the pollutant to be removed, process specificity and occurring phenomena and matrix characteristics.

References

- [1] L. Bartoszek, P. Koszelnik, R. Gruca-Rokosz, M. Kida, Assessment of agricultural use of the bottom sediments from eutrophic Rzeszów reservoir, *Rocz. Ochr. Sr.*, 17 (2015) 396–409.
- [2] K. Maj, P. Koszelnik, Methods of bottom sediment management, *JCEEA*, 63 (2016) 157–169.
- [3] D. Papciak, J. Kaleta, A. Puzskarewicz, B. Tchórzewska-Cieślak, The use of biofiltration process to remove organic matter from groundwater, *J. Ecol. Eng.*, 17 (2016) 119–124.
- [4] K. Pochwat, Hydraulic analysis of functioning of the drainage channel with increased retention capacity, *E3S Web Conf.*, 17 (2017) 00075.
- [5] M. Gajewska, Ł. Kopec, H. Obarska-Pempkowiak, Operation of small wastewater treatment facilities in a scattered settlement. *Rocz. Ochr. Sr.*, (Annual Set the Environment Protection), 13 (2011) 207–225.
- [6] S. Ziembowicz, M. Kida, P. Koszelnik, Removal of dibutyl phthalate (DBP) from landfill leachate using an ultrasonic field, *Desal. Wat. Treat.*, 117 (2018) 9–14.
- [7] S. Książek, M. Kida, P. Koszelnik, The occurrence and source of polycyclic aromatic hydrocarbons in bottom sediments of the Wisłok river, *Polish J. Natural Sci.*, 31 (2016) 373–386.
- [8] M. Starzec, J. Dziopak, D. Styś, K. Pochwat, S. Kordana, Dimensioning of required volumes of interconnected detention tanks taking into account the direction and speed of rain movement, *Water*, 10 (2018) 18–26.
- [9] M. Smol, M. Włodarczyk-Makuła, K. Mielczarek, J. Bohdziewicz, D. Włóka, The use of reverse osmosis in the removal of PAHs from municipal landfill leachate, *Polycycl. Aromat. Comp.*, 36 (2016) 20–39.
- [10] M. Smol, M. Włodarczyk-Makuła, B. Skowron-Grabowska, PAHs removal from municipal landfill leachate using an

- integrated membrane system in aspect of legal regulations, *Desal. Wat. Treat.*, 69 (2017) 335–343.
- [11] M. Zolfaghari, P. Drogui, B. Seyhi, S.K. Brar, G. Buelna, R. Dubé, Occurrence, fate and effects of Di (2-ethylhexyl) phthalate in wastewater treatment plants: a review, *Environ. Pollut.*, 194 (2014) 281–293.
- [12] S. Ziembowicz, M. Kida, P. Koszelnik, The impact of selected parameters on the formation of hydrogen peroxide by sonochemical process, *Sep. Purif. Technol.*, 204 (2018) 149–153.
- [13] C.Y. Teh, T.Y. Wu, J.C. Juan, An application of ultrasound technology in synthesis of titania-based photocatalyst for degrading pollutant, *Chem. Eng. J.*, 317 (2017) 586–612.
- [14] M. Kida, S. Ziembowicz, P. Koszelnik, Study on the suitability of using low-frequency ultrasonic field for removing di (2-ethylhexyl) phthalate from bottom sediments, *Sep. Purif. Technol.*, 233 (2020) 116010.
- [15] S. Koda, T. Kimura, T. Kondo, H. Mitome, A standard method to calibrate sonochemical efficiency of an individual reaction system. *Ultrason. Sonochem.*, 10 (2003) 149–156.
- [16] C. Pétrier, The use of power ultrasound for water treatment, *Power Ultrasonics*, (2015) 939–972.
- [17] J. Długosz, Fenton method and its modifications in the treatment leachate-for review, *Arch. Environ. Prot.*, 16 (2014) 33–42.
- [18] Y.Y. Chen, Y.L. Ma, J. Yang, L.Q. Wang, J.M. Lv, C.J. Ren, Aqueous tetracycline degradation by H₂O₂ alone: removal and transformation pathway, *Chem. Eng. J.*, 307 (2017) 15–23.
- [19] K. Józwiakowski, M. Marzec, J. Fiedurek, A. Kamińska, M. Gajewska, E. Wojciechowska, S. Wu, J. Dach, A. Marczuk, A. Kowalczyk-Juśko, Application of H₂O₂ to optimize ammonium removal from domestic wastewater, *Sep. Purif. Technol.*, 173 (2017) 357–363.
- [20] H.W. Sun, Q.S. Yan, Influence of pyrene combination state in soils on its treatment efficiency by Fenton oxidation, *J. Environ. Manage.*, 88 (2008) 556–563.
- [21] M. Cheng, G. Zeng, D. Huang, C. Lai, P. Xu, C. Zhang, Y. Liu, J. Wan, X. Gong, Y. Zhu, Degradation of atrazine by a novel Fenton-like process and assessment the influence on the treated soil, *J. Hazard. Mater.*, 312 (2016) 184–191.
- [22] V. Flotron, C. Delteil, Y. Padellec, V. Camel, Removal of sorbed polycyclic aromatic hydrocarbons from soil, sludge and sediment samples using the Fenton's reagent process, *Chemosphere*, 59 (2005) 1427–1437.
- [23] V.L.D. Silva, B.D.B. Neto, M.O. Simonnot, Phenanthrene and pyrene oxidation in contaminated soils using Fenton's reagent, *J. Hazard. Mater.*, 161 (2009) 967–973.
- [24] R. Esmaeli, A.H. Hassani, A. Eslami, M. Ahmadi Moghadam, A.A. Safari, Di-(2-ethylhexyl) phthalate oxidative degradation by Fenton process in synthetic and real petrochemical wastewater, *Iran. J. Environ. Health Sci. Eng.*, 8 (2011) 201–206.