



Photodegradation of selected phthalates on mural painting surfaces under UV light irradiation



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ABSTRACT

The esters of phthalic acid are considered as hazardous pollutants due to their mutagenicity, carcinogenicity and are also classified as endocrine disruptor chemicals. Several compounds of this class of substances for decades, and probably even now, were used as softeners in water-based synthetic paintings. Surfaces and structures, such as house walls painted with phthalates based paintings, can be a concern to construction workers engaged in demolition, restore and paint removal activities if they are not protected from hazardous dust inhalation. In this paper we report the results of an investigation about phthalate ester degradation by direct UV irradiation at 254 nm. The results of kinetic parameters for PAE photodegradation are reported and it shows that k values for the single PAEs ranged from 0.221 to 0.737 h^{-1} .

Moreover, the results indicate that photolysis is a successful way to remediate PEAs contaminated on mural painting.

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1. Introduction

The esters of phthalic acid ($\text{C}_6\text{H}_4(\text{COOH})_2$), generally called phthalates (PAEs), are a group of contaminants that are ubiquitous in the environment. These chemicals, generally, are colorless and odorless liquids having high boiling points, low volatility, insolubility in water and predominantly fat solubility. Not including the dimethyl phthalate (DMP) that belongs to the group of VOCs, PAEs are classified as semi-volatile organic compounds. There are no natural sources of PAEs, therefore all phthalates found in environmental matrices can be attributed to man activities [1].

In industrial countries, anthropogenic activities are the principal sources of PAEs in environmental and building matrices [2,3]. Several PAEs are considered as hazardous pollutants due to their mutagenicity, carcinogenicity and are also classified as Endocrine Disruptor Chemicals (EDCs) [4–6].

The main processes which successfully remove and eliminate PAEs from the environmental matrices include: microbiological transformation and degradation, volatilization, photo-oxidation, chemical oxidation, sorption and biological uptake [7,8]. However, some of the PAEs are recalcitrant, and biological processes are not always effective in removing them. In this context, photodegradation is an important transformation pathway for most PAEs in the environment.

The compounds considered in this paper are the most used in industrial processes which are expected to be present in indoor environments: dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DnBP), benzyl butyl phthalate (BBzP), bis(2-ethylhexyl)

phthalate (DEHP), and di-n-octyl phthalate (DnOP). Compounds with higher molecular weights, such as bis(2-ethylhexyl) phthalate (DEHP), are largely used as additives and plasticizers, while those with lower molecular weights (diethyl, di-n-butyl and dimethyl phthalate) are components of industrial solvents, adhesive, wax, ink, pharmaceutical products, insecticide materials, and cosmetic [9,10]. DEHP was found in medical disposal devices and in a number of medicine coatings. Some compounds are contained in cleaning solutions for contact lenses [11] and in food packaging films [12].

Phthalates are not chemically but only physically bound to the polymer chains; hence, they may be leached into the environment and are ubiquitously found in air, water, soils, and sediments [13–17]. People exposure to PAEs may arise from toys, child-care articles, building materials, home furnishing, car interiors, clothing, medical devices, and food-contact materials. PAEs are emitted into the atmosphere as particulates and gases [18]. Indoor environments increase the lifetime of pollutants adsorbed to the dust by minimizing or eliminating the natural decomposition processes catalyzed by natural light and rain [19].

Moreover, some phthalate esters for decades, and probably even now, were used as softeners in water-based synthetic paintings [2]. Di-n-butyl phthalate (DBP) and Bis(2-ethylhexyl) phthalate (DEHP) are the most employed. Softeners are released from the painted surface for a long time after they were applied [5]. Surfaces and structures, such as house walls painted with phthalates based paintings, can be a concern to construction workers engaged in demolition, restore and paint removal activities if they are not protected from hazardous dust inhalation.

In the last years, scientific community has focused his interest in processes that may be applied to degrade hazardous substances [20], minimizing the risk for worker exposures. Given that UV-irradiation at

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254 nm is used for wastewater and soil treatments, it is of interest to know whether this process can also be employed for phthalate degradation onto mural painting surfaces because construction work is one of the most important activities in Europe, and probably worldwide, with respect to its economic, technological, and environmental impact. Dusts containing PAEs and other hazardous substances are generated in these processes, and during transporting, storing and handling construction materials [21]. This may also be verified when certain construction processes are undertaken. Extended work times on building matrices especially in the indoor environment increase possibility of exposure to contaminants by 1000-fold compared to outdoor exposures [22]. Levels of phthalates in indoor air and dust are often higher than outdoor levels.

Currently, there is limited information concerning the UV photolysis of phthalates and in this paper we report the results of an investigation of the degradation by UV irradiation at a wavelength of 254 nm. The described approach includes the choice of appropriate irradiation conditions in order to obtain the best results.

GC/MS technique was used to quantify PAEs in samples, taken from wall surface of building located in Palermo, before and after the irradiation.

2. Experimental

2.1. Study area

The mural painting samples taken in consideration in this study were sampled in eight buildings located in Palermo area (Italy) (Table 1) [3]. Palermo is a densely populated city (about 850,000 inhabitants) characterized by conspicuous air pollution [3,23–29]. Palermo is a typically European town in building style and is generally built in stone (tuff), clay bricks and concrete.

In order to determine a possible pattern in usage of PAEs in the Palermo area, sampling was conducted in different parts of the town, in different types of buildings of different ages (Table 1). The samples were taken, during 2012 from the surface of the indoor walls and were collected by scraping off the layers or removing fragments. From each surface, a total of 5 samples were collected. About 25 g of the material was placed in glass containers. The samples were refrigerated (4 °C), avoiding the exposure to light, and taken to the laboratory where they were frozen (–20 °C) until the photodegradation was performed. About 2 g of homogenized samples of mural painting was dried at 105 °C for overnight. The water content was determined by weight loss and was utilized to correlate all the results with dry weight. Before each analysis the samples were finely pulverized in a mortar.

2.2. Photoirradiation

The mural painting samples (100–200 mg) were transferred into a Pyrex Petri dishes and directly irradiated for 8 h at $\lambda = 254$ nm by using a Mercury lamp located at 10 cm. In order to monitor the irradiation effect as a function of time, samples were collected at 0 (analyzed without irradiation) 0.5, 1, 2, 4, 6 and 8 h during the irradiation. All

the Petri dishes were randomly placed on the shelves, and sampling was performed during the irradiation with the sampled mural paintings sacrificed.

2.3. Chemical analyses

Concentrations of the PAEs in irradiated and non-irradiated samples were obtained by the following method. An aliquot of mural painting samples were transferred into 50 mL glass tubes, and mixed with hexane (100 mg of sample: 4 mL of hexane). Before extraction, surrogate standard (di-n-hexyl-phthalate- d_4) (Table 2) was added to all samples for the evaluation of the method performance (yields). Each sample was extracted for 20 min (3 times) in an ultrasonic bath, in which the water temperature was just lower than 30 °C. The mixture was then centrifuged at 5000 rpm for 5 min to separate the supernatant from the solid.

The extracts were cleaned using a short silica gel column containing anhydrous Na_2SO_4 , earlier wetted with hexane, and concentrated in a rotary evaporator at $T = 50$ °C. The final volume was around 1 mL. The last stage in the procedure involved drying the PAEs containing solution under a weak N_2 flow at room temperature. The dry residue was dissolved in 1 mL of solution containing a perdeuterated internal standard (Bis(2-ethylhexyl)phthalate- d_4) in cyclohexane. Analysis of solutions was carried out using a gas chromatograph coupled with a mass spectrometer (Shimadzu, mod. GCMS-QP2000) equipped with an SLB 5 ms (30 m 0.25 i.d., 0.5 μm) (5% diphenyl 95% dimethyl siloxane) phase fused-silica capillary column from Supelco (Milano, Italy). The mass spectrometer was operated in electron impact (70 eV) and selected ion monitoring (SIM) mode. GC oven temperature for PAEs started at 60 °C (2 min.) and ramped to 325 °C at 14.5 °C/min and maintained for 30 min.

Injection of 1 μL sample was performed by the Shimadzu Auto Injector AOC-20I. The instrument was equipped with a split/splitless injector with glass wool injection port liner and splitless time of 2 min. Total flow 21 mL/min was used. The carrier gas was helium (flow rate 1.4 mL/min). In several cases, to measure phthalates, sample extracts were diluted prior to GC analyses.

2.4. Quality assurance

The detection limits (LOD) were estimated as 3σ (three times the background noise) (IUPAC criterion) and like reported in previous

Table 2

List of the PAEs and abbreviations, the deuterated internal (underlined) and surrogate (italic) standards employed, the quantification and confirmation ions for SIM GC/MS mode.

Compound	Abbr.	N° CAS	Quantification and confirmation ions (m/z)
Dimethyl phthalate	DMP	131-11-3	163–194
Diethyl phthalate	DEP	84-66-2	121–149
Diisobutyl phthalate	DiBP	84-69-5	149–167
Di-n-butyl phthalate	DBP	84-74-2	149–150
Bis(2-methoxyethyl) phthalate	DMEP	117-82-8	59–149
Bis(4-methyl-2-pentyl) phthalate	BMPP	146-50-9	121–149
Dinonyl phthalate	DNP	86-76-4	57–71
Bis(2-ethoxyethyl) phthalate	DEEP	605-54-9	45–72
Di-pentyl phthalate	DPP	131-18-0	149–167
Dihexyl phthalate	DHxP	84-75-3	76–104
Bis(2-n-butoxyethyl) phthalate	DBEP	117-83-9	57–149
Bis(2-ethylhexyl) phthalate	DEHP	117-81-7	113–149
Di-cyclohexyl phthalate	DCHP	84-61-7	83–149
Di-n-octyl phthalate	DOP	117-84-0	149–150
Benzyl butyl phthalate	BBP	85-68-7	91–149
Diethyl phthalate- d_4	<u>DEPD₄</u>		153
Bis(2-ethylhexyl)phthalate- d_4	<u>BEHP d₄</u>		153
Di-n-hexyl-phthalate- d_4	<u>DHXP d₄</u>		153

Table 1

Descriptive profile of sampling station.

n°	Characteristic of station	Age of building
Mur 1	Stair of a building built around 1990.	23
Mur 2	Bedroom of an apartment on the first floor	25
Mur 3	Stair of the previous station	25
Mur 4	Living room of house dating from 1950 to 1 floor renovated 13 years ago.	63
Mur 5	Kitchen of an apartment on the top floor.	15
Mur 6	Garage	43
Mur 7	Kitchen	30
Mur 8	Kitchen	5

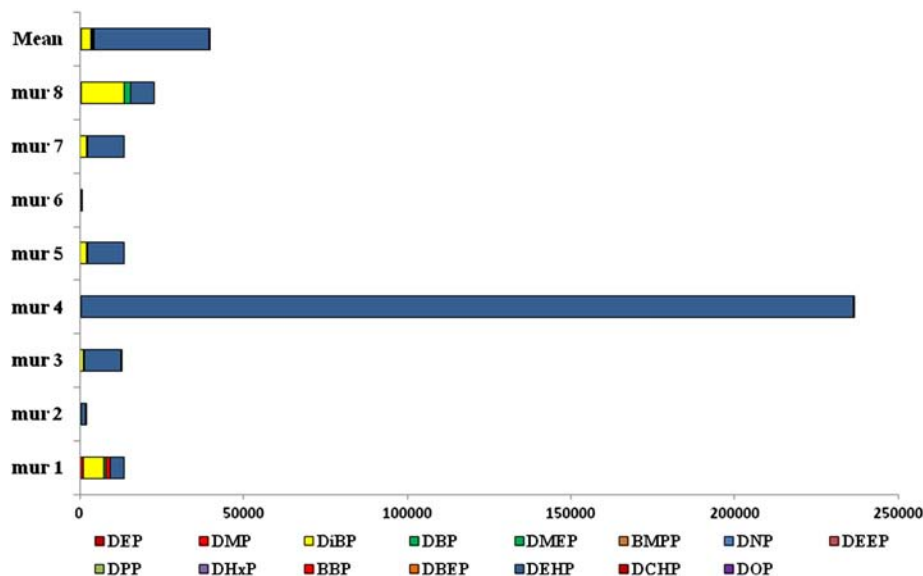


Fig. 1. Total and single PAEs (in mg/kg) (average of three analysis) concentrations in mural painting samples.

papers [2,3,25,26,28] were similar for all analyzed compounds (less than 0.3 $\mu\text{g}/\text{kg}$ for all compounds). Quantification limit (LOQ), (less than 1 $\mu\text{g}/\text{kg}$ for all compounds) was estimated as 10σ (ten times the background noise) (IUPAC criterion). LOD and LOQ were estimated in selected ion monitoring (SIM) mode [2,32 34, 36, 38]. Blank concentrations were not subtracted from sample concentrations because the levels in samples were higher than blank levels by several orders of magnitude.

The procedure was checked for recovery efficiencies as reported in a previous paper [3]. The average recoveries ranged from 85% to 99%. The relative standard deviations on the PAE recovery were less than 10%. Relative percent differences for triplicate samples were less than 14%.

3. Results and discussion

The total initial concentrations of the investigated compounds, expressed as the sum of the concentrations, ΣPAEs , in the analyzed mural painting, ranged from 0.8 to 236 mg/kg d.w. with an average of 39.4 mg/kg d.w. (Fig. 1) [3].

Among the 15 phthalates monitored only four (DEHP, DiBP, DBP and DEP) were detected in appreciable quantities [3]. BBP was significant

only for one sample and at trace levels only in two mural paintings. In all tested samples, except n° 1 and n° 8, predominates the DEHP (from 30 to 100% of total phthalates) that is in the range from 0.6 to 236 mg/kg d.w. Sporadically, DiNP was used as a substitute to DEHP, however, in our case, its occurrence was not found.

The photodegradation loss can be obtained from the following equation:

$$L = (C_N - C_I) * 100 / C_0 \quad (1)$$

where L = photodegradation loss at time t , C_0 = original concentration of single compound, C_N = concentration of compound non-irradiated mural painting sample at time t , C_I = concentration of compound irradiated sample at time t .

The photodegradation losses of single PAE versus time on mural painting surfaces are shown in Fig. 2. The loss, as sum of investigated compounds, increased rapidly during the first 60 min of the experiment, with the degradation loss being about 57%. As the photolysis reaction progressed with continuing irradiation, it was evident that the PAE degradation rate gradually reduced.

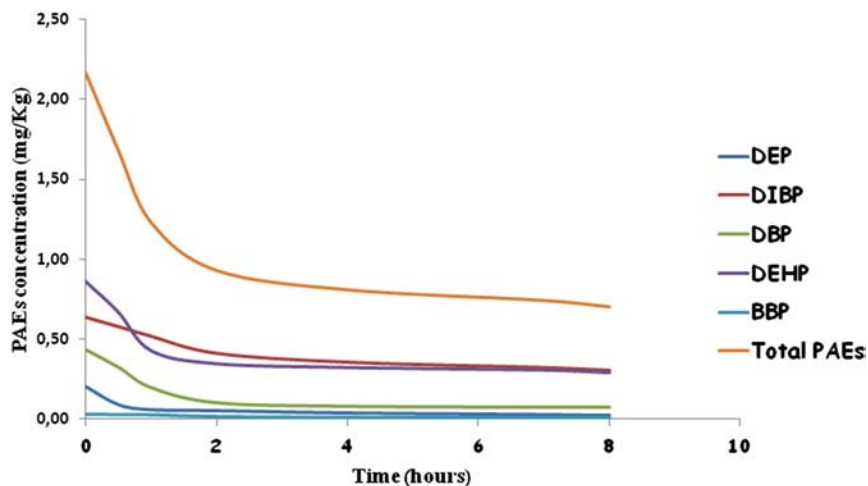


Fig. 2. Concentration of single PAE versus time on mural painting samples.

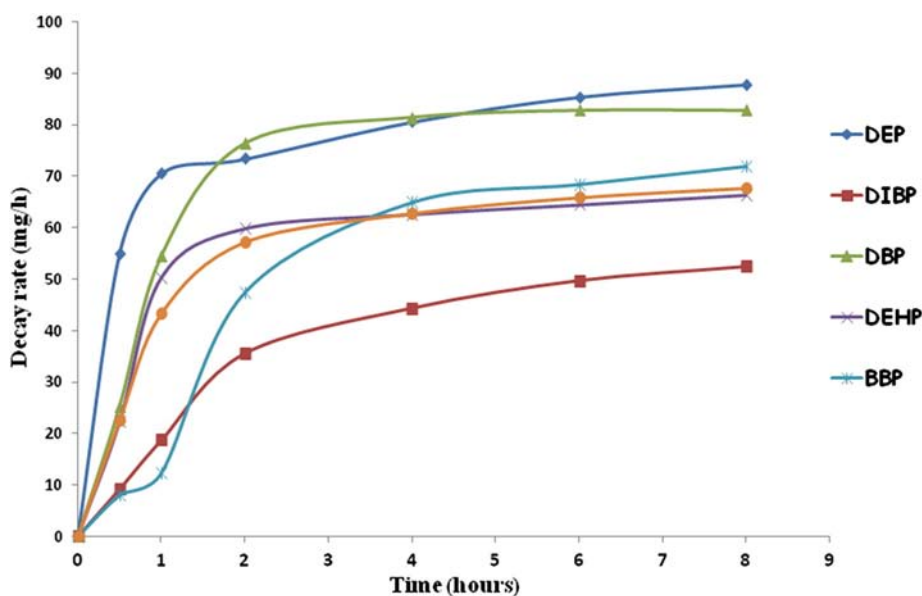


Fig. 3. Decay rate.

We can deduce that a significant removal (68%) of total PAEs can be achieved by an irradiation period of 8 h. The photolysis of the investigated compounds was then found to follow pseudo first kinetics order ($C_T = C_0 e^{-kt}$) initially; however, after a period of irradiation (60 min) the decay rate reduced, as shown in Fig. 3.

Considering the photodegradation loss of the compound found in higher concentrations in mural painting samples (DEHP) increased rapidly during the first 60 min of the treatment, with the degradation loss being about 50%.

Our study showed that PAE photodegradation was fitted to the first-order equation:

$$\ln C_0/C = kt \quad (2)$$

where C_0 and C are the PAE concentration at times zero and t respectively, and k is the rate constant. First-order degradation rate constants were determined by analysis. Half-lives $t_{1/2}$ were calculated using Eq. (3) which was derived from Eq. (2) by replacing C with $C_0/2$:

$$t_{1/2} = \ln 2/k = 0.6931/k \quad (3)$$

The results of kinetic parameters for PAE photodegradation are listed in Table 3. It shows that k values for the single PAEs ranged from 0.221 to 0.737 h^{-1} .

The direct photolysis induced by UV at 254 nm should be one of the major reaction pathways responsible for the PAE decay.

In particular, such as reported in literature, the photodegradation of phthalate esters at 254 nm involves photo-induced decarboxylation, hydroxylation, dealkylation, and scission of C–O, C–C, and O–alkyl bonds [7,30,31].

Table 3
Kinetic parameters for single PAE photodegradation.

Compound	k (h^{-1})	R	$t_{1/2}$
DEP	0.631	0.87	1.15
DIBP	0.221	0.99	2.20
DBP	0.737	0.99	1.00
DEHP	0.466	0.95	1.46
BBP	0.323	0.95	1.82
Total PAEs	0.424	0.98	1.55

4. Conclusion

The transformation and volatilization of PAEs in different aquatic systems with sunlight irradiation are irrelevant. The hydrolysis half-life of DBP is estimated at 22 years, and the atmospheric photo-oxidation half-life is reported to be between 0.6 and 6 days [32].

Photodegradation is a major degradation process which can clean up the mural paintings. According to our study, PAE photodegradation follows pseudo-first-order kinetics. The rate constant of photodegradation ranged from 0.22 to 0.74 h^{-1} .

The results of the present study suggest that the use of UV irradiation before and during the execution of renovation or restoration may be wanted in an attempt to reduce exposure to PAEs. Those data should be helpful for structuring the phthalate exposure profile and recommending local exhaust systems and personal protection equipment for construction workers.

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