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A comparative evaluation of ozonation and heterogeneous photocatalytic oxidation processes for reuse of secondary treated urban wastewater

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ABSTRACT

This study aimed to optimize two oxidation processes for wastewater reuse of an urban wastewater treatment plant (UWWTP) effluent intended for human consumption. Ozonation and TiO_2 photocatalytic oxidation (PCO) processes were compared for their effectiveness in terms of organic matter degradation (measured as UV absorbance at 254 nm, UV_{254}), disinfection by products formation (measured as trihalomethanes formation potential, THMFP), and ecotoxicity (evaluated by *Daphnia magna* and *Lepidium sativum*), on secondary treated wastewater collected from a UWWTP in the province of Salerno (southern Italy). Accordingly, ozonation experiments using 28 mg/L ozone dose and PCO experiments using 250 W lamp (emission range: 315–400 nm; emission peak: 14.7 $\mu W/cm^2$ at 340 nm) and varying TiO_2 dose from 1 to 3 g/L were carried out. Ozonation ($t_{1/2} = 71.6$ min) was not found as effective as PCO for organic matter degradation at all TiO_2 doses, and 3 g/L of TiO_2 was found to be the most effective photocatalyst loading ($t_{1/2} = 41.8$ min). Moreover, PCO-treated samples resulted in a lower THMFP compared to ozonation process. While ozonation did not increase toxicity to *D. magna* severely (10% of immobilization), PCO-treated samples exhibited varying toxicity end-points possibly due to formed oxidation intermediate products. However, Cl_2 disinfection of treated wastewater samples played an improving role in toxicity of PCO-treated samples. In particular, in 30 min oxidized samples, toxicity to *D. magna* was decreased up to 50% (from 40 to 20% of immobilization) while germination index of *L. sativum*, a phytotoxicity test used for irrigation quality testing purpose, improved at 30% after Cl_2 disinfection in 3 g/L of TiO_2 treated sample.

Keywords: Advanced oxidation processes; Disinfection by products; Ecotoxicity; Ozonation; Photocatalysis; Phyto-toxicity; Trihalomethanes; Wastewater reuse

1. Introduction

Wastewater reuse has been a highlighting issue in the last decade in arid and semi-arid areas. Reclaimed wastewater may be reused for irrigation of agricultural and urban areas, in industrial plants (as cooling water), as well as for enrichment of groundwater bodies. Thus, wastewater reuse may strengthen water savings generating supplementary water sources,

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which are especially important in areas with limited rainfall [1]. However, the conventionally treated effluents may/may not assure the safeguard limits of reuse although there is a need of using proper treatment and disinfection technologies in arid and semi-arid areas [2]. The various existing national guidelines and regulations on wastewater reuse tend to focus mainly on risks from pathogens and convential parameters [3,4], with other trace pollutants only marginally addressed. The wide range of trace chemical contaminants persisting in urban wastewater after conventional treatment includes inorganic compounds, heavy metals, persistent organic pollutants like endocrine disrupting compounds, pharmaceutically active compounds, disinfection by-products (DBPs), and many other complex compounds [5,6]. Thus, various advanced wastewater treatment technologies have been proposed for the production of effluents with a quality complying with the specific applications of wastewater reclamation and reuse. Among advanced treatment methods, coagulation [7], membranes [8], and ozonation [9,10] have been proposed in countries where strict limits on DBPs exist; for instance, a 30 μg/L of trihalomethanes (THMs) limit was set in Italy for wastewater reuse [3]. Disinfection is a very important treatment to achieve a safe discharge or to safely reuse reclaimed water, because it removes or inactivates pathogenic organisms responsible for waterborne diseases such as cholera, typhoid fever, and dysentery. In particular, chlorination is a widely used, very efficient, and low-cost method of disinfection. However, the reaction of chlorine with organic matter can produce a wide range of halogenated organic substances, among which THMs and haloacetic acids, which can have adverse health effects [11]. Thus, alternative disinfectants such as ozone [12], ozone/UV [13], and chlorine dioxide/peracetic acid [14] have been attempted also to effectively remove DBPs precursors and trace organics. Advanced oxidation processes (AOPs) have gained importance and have been studied intensively to remove emerging pollutants such as pharmaceuticals, personal care products, pathogens, etc. from urban wastewater treatment plants (UWWTPs) effluent in recent years [15,16]. AOPs results in the formation of extremely reactive species (such as hydroxyl radicals) capable of oxidizing a wide range of organics occurring in wastewater [16,17]. Among AOPs, heterogeneous photo-catalytic oxidation (PCO) has drawn particular attention in academic studies [18,19], with the advantage of being a green technology regarding the possibility of exploiting solar energy [20]. Anyhow, water reuse strategies are intended to address the problem of water scarcity without aggravating other environmental problems, thus reflecting the need of an environmental assessment-based approach [10,21] as well as to minimize effluent toxicity [7,11].

Color removal using ozone and ultrasonics [15] and particularly, the synergetic effect of ozonation and PCO processes in the organic matter mineralization and color removal from reclaimed water, were investigated [22]. However, none of these studies has dealt with DBPs' formation and ecotoxicity. Thus, this work is, to our knowledge, the first one where ozonation and PCO processes were comparatively evaluated in terms of organic matter degradation (measured as UV absorbance), DBPs formation (measured as THMs formation potential, THMFP), and ecotoxicity (evaluated by *Daphnia magna* and *Lepidium sativum*), as a cumulative and useful tool to evaluate the adverse effects of intermediates formed during oxidation [23].

2. Materials and methods

2.1. Wastewater sampling

Samples were collected from an UWWTP located in the province of Salerno (Southern Italy) receiving (1/3 ratio) secondary treated wastewater from a leather tannery district. The UWWTP is composed of tertiary treatment with denitrification unit followed by sand filtration.

2.2. Photocatalytic oxidation tests

Photocatalytic oxidation experiments were performed using a 250 W UV lamp (UV Power Supply 482, PROCOM, Italy) with a light emission range of 310–480 nm and a maximum emission peak at 340 nm (Fig. 1). Four doses (0.5, 1, 2, and 3 g/L) of TiO_2 (Degussa P25, Germany) were used. A spectrometer model HR-2000 from Ocean Optics (Dunedin, FL, USA), equipped with cosine corrector with Spectralon diffusing material, was used to measure the irradiation intensity of the UV lamp (Fig. 1). Cylindrical Pyrex reaction vessel (300 mL) filled inwith 100 mL wastewater sample was irradiated until to 60 min, after 2 min of pre-sonication in order to provide a uniform dispersion of the catalyst in the solution [24]. The reactor was illuminated from the top and slowly mixed by a magnetic stirrer. The samples were filtered by means of 0.45 μm Millipore Millex-HA cellulose-based membrane filters to remove TiO_2 particles before analytical measurements. Process efficiency was assessed in terms of degradation of the aromatic fraction of organic matter, by means of UV absorbance at 254 nm (UV_{254}) measurements in filtered samples. Control tests with (i) UV lamp switched on, but in

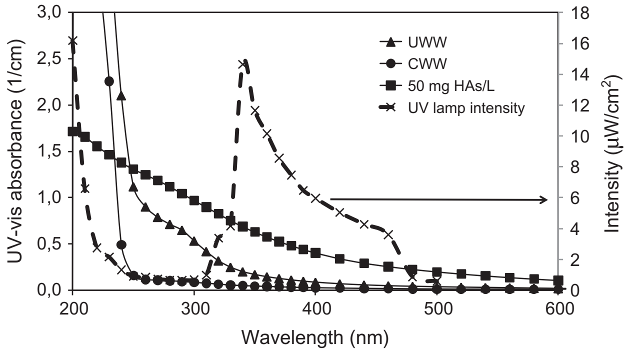

Fig. 1. UV absorbance spectra of studied tertiary treated wastewater (UWW1) compared with humic acid (50 mg/L) and another urban wastewater effluent without industrial discharge mixture (CWW).

absence of TiO_2 particles and (ii) presence of TiO_2 particles but under dark conditions (UV lamp switched off) were carried out in parallel, using 2.0 g/L as catalyst loading. The tests were carried out in duplicate and average values were plotted.

2.3. Ozonation tests

Ozone was supplied by a generator (Microlab, Aeraque I.T., Italy) with a maximum capacity of 1.5 g O_3/h and a maximum gas flow rate of 200 NL/h with a working pressure of 0.5 bar. The ozone gas was forced to pass into 180 cm height and 15 cm diameter Plexiglas cylindrical reactor. The ozonation tests were carried out by using 3 L raw wastewater samples. The experiments were performed by applying an ozone dose of 28 mg/(L min) for 1 h and samples were taken from the reactor at different times to obtain degradation kinetics. Ozone dose was set according to previous experiments [15]. Ozone concentrations and demand were monitored according to Standard Methods [25].

2.4. Chlorination procedure

Raw and treated water samples were chlorinated to measure the THMFP. Chlorine was dosed in excess using a 7% NaOCl (Carlo Erba, Italy) solution in order to obtain a free chlorine residual as high as 5 mg/L after being held for seven days at 25°C and pH 7, according to 5710B method (for THMFP measurement) from Standard Methods [25]. The chlorine effect was stopped by adding sodium thiosulphate to each one sample at the end of seven days period.

2.5. Analytical measurements

Molecular absorption spectra of the samples were recorded on a Perkin Elmer Lambda12 (USA) spectrophotometer with 1.0 cm quartz cells. Moreover, UV_{254} measurements were achieved by reading UV–vis absorbance values at the wavelength of 254 nm [24]. Chlorine residual was measured by a photometer (Pocket Colorimeter^{TM} analysis system) from Hach, designed for single wavelength colorimetric measurements and characterized by both an accuracy of ±0.02 mg/L at 25°C and repeatability of 0.01 mg/L at 25°C. The THMs (namely chloroform, dichlorobromomethane, dibromochloromethane, and bromoform) measurements in raw and treated wastewater samples were carried out according to a standard procedure explained in detail elsewhere [26], using liquid–liquid extraction with methyl-tert-butyl ether, followed by gas chromatography–electron capture detector (GC–ECD) determination. The instrumentation used included a Hewlett–Packard GC 5890 Series II with a ^{63}Ni ECD, helium (He ECD) as carrier gas and nitrogen (purity 99.999%) as make-up gas. The injection technique was splitless. The column used was fused silica DB-1, $10\,m \times 0.53\,mm$ i.d. $\times$ 0.25 μm film thickness.

2.6. Toxicity and phytotoxicity tests

D. magna acute toxicity test was performed according to ISO 6341 method [27] using 24 h new born daphnids for 24 h exposure time. Experiments were carried out in quadruplicate without sample dilution. Five daphnids were tested in each test beaker with 50 mL of effective volume. The number of immobilized organisms was divided by the total number of tested organisms to record the immobilization percentage for each tested sample. Phytotoxicity was evaluated using *L. sativum* (seed cress) seeds. The seeds were incubated for three days with the samples. The germinated percentile and root lengths of the seeds were recorded for the calculation of germination index by multiplying germinated seed percentile with root length in each data-set, as described elsewhere [19].

3. Results and discussion

3.1. Organic characteristics of wastewater sample

The UWWTP where wastewater samples were taken from receives a mixture of civil and industrial wastewater. The industrial wastewater comes from the effluent of a wastewater treatment plant from a leather tannery district employing chemical–biological-based processes. The wastewater characteristics of the UWWTP effluent investigated in this work are the following: pH 7.6, COD 72.2 mg/L, TSS 51.0 mg/L, chromium 1.1 mg/L, and iron 0.2 mg/L. To better explain the aromatic character of the organic matter occurring in the investigated wastewater sample, the effluent of the UWWTP (UWW) was compared in terms of UV absorbance spectra with both 50 mg/L of humic acid solution and another treated urban wastewater effluent (CWW) not affected by industrial wastewater (Fig. 1).

Absorbance variation of UWW displays a significant increase between 250 and 350 nm wavelengths with respect to CWW sample which was collected from a small domestic wastewater treatment plant (a district of Salerno city) just for comparison. As can be observed, the behavior of UV absorbance curve of UWW sample, in the same range of wavelengths, is quite similar to humic acids solution. This rapid increase in UV absorbance at 280 nm wavelength is attributed to the aromatic organic matter fraction originated from the leather tannery treated effluent which contain tannins and dyes both used in tanning process [28].

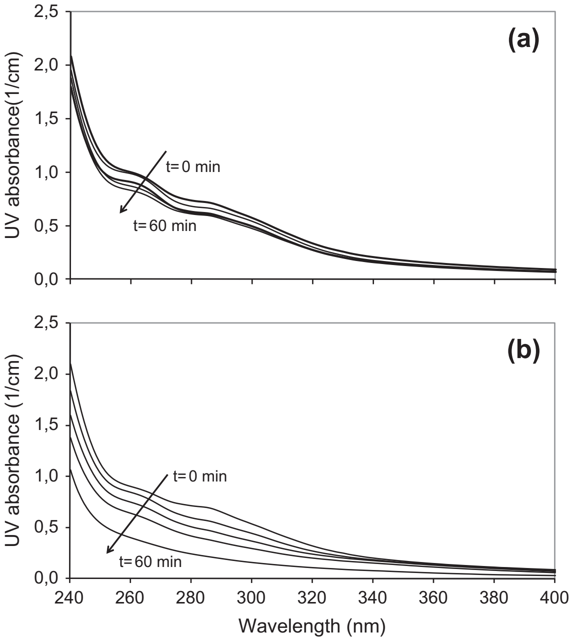

Fig. 2. Evolution of UV absorbance spectra vs. time ($t = 0$, 5, 15, 30 and 60 min) of UWW1 sample under dark (a) and PCO conditions (b) (TiO_2 1 g/L). UV absorbance at $t = 0$ refers to the raw sample.

3.2. Effect of photocatalysis on organic matter degradation

According to Fig. 2(a), the evolution of UV absorbance under dark condition shows that adsorption of organic matter on TiO_2 catalyst occurred during 30 min. However, a greater part of organic matter was removed after 60 min under illumination condition (Fig. 2(b)). Moreover, the gradual disappearance of the bumps at 260 and 280 wavelengths, respectively (Fig. 2(b)), indicated that aromatic structure was oxidized to smaller molecular structured organic compounds [19]. On the opposite, adsorption process on TiO_2 particles did not affect organic matter structure (the bumps are unchanged in spite of absorbance decrease, Fig. 2(a)), because the process just results in a phase separation where the organic aromatic contaminants pass from the liquid phase (wastewater) to the solid phase (catalyst particles).

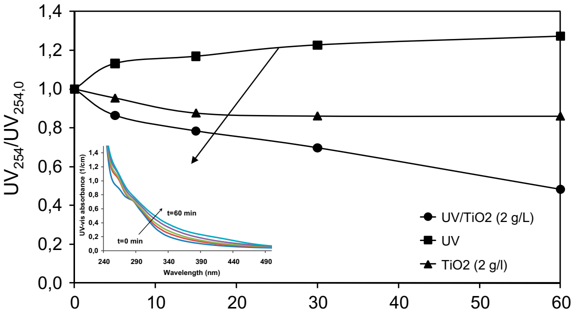

Fig. 3. Evolution of UV_{254} during PCO (UV/TiO_2), only light (UV), and dark (TiO_2) conditions in UWW1 sample.

The results of control tests including only adsorption (TiO_2), only illumination (UV), and PCO (TiO_2/UV), in terms of UV_{254} absorbance removal, using 2 g TiO_2/L as catalyst dose, are shown in Fig. 3. The presence of photo-sensitive organic compounds resulted in the formation of organic oxidation intermediates because of UV radiation treatment. The smaller plot in Fig. 3 clearly shows the gradual disappearance of some organics: bumps at 260 and 280 nm decrease already after 5 min of UV irradiation, until to totally disappear after 60 min treatment. In parallel, an upward shift of UV–vis absorbance curves, as irradiation time increased, was observed thus confirming that the degradation of some organic parent compounds (with characteristic peaks at 260 and 280 nm) resulted in the formation of organic oxidation intermediates with a higher capacity to absorb UV radiation at 254 nm wavelength [19].

A 50% of organic matter removal was obtained after 60 min of PCO using 2 g/L of TiO_2. According to Fig. 4, organic matter removal increased from 40 to 60% when TiO_2 dose was increased from 0.5 to 3 g/L during 60 min of illumination. Previous studies on TiO_2 photocatalytic treatment of tannery wastewater showed a quite poor efficiency in terms of organic matter removal (<6% of COD) when high organic loading wastewater (initial COD 2,365 mg/L) was investigated [29]; but comparable results were

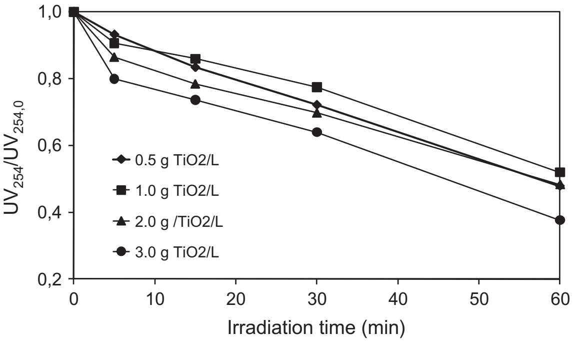

Fig. 4. Effect of catalyst dose on removal efficiency of absorbance during PCO of UWW1 sample.

observed (65.7% of COD removal) when diluted tannery wastewater (COD 200 mg/L) was investigated [30].

3.3. *Effect of ozonation on organic matter degradation*

Organic matter degradation vs. time during ozonation is depicted in Fig. 5. As can be observed, organic matter was hardly degraded during the first 5 min of the oxidation. However, after 10 min of ozonation, absorbance started to decrease and after 60 min of ozonation, a 50% of organic matter removal was observed, in accordance with previous findings dealing with ozonation of domestic wastewater effluent [15].

The UV_{254} normalized absorbance curve shows an increase during the first 5 min of ozonation, possibly due to the formation of intermediate oxidation products (Fig. 6). However, after 10 min of ozonation, absorbance started to decrease and after 60 min of ozonation, a 50% of organic matter removal was observed. This result is in agreement with a previous study where ozonation process was comparatively investigated with other AOPs in the oxidation of tannery wastewater and it was found to preferentially degrade compounds with an aromatic organic structure [29].

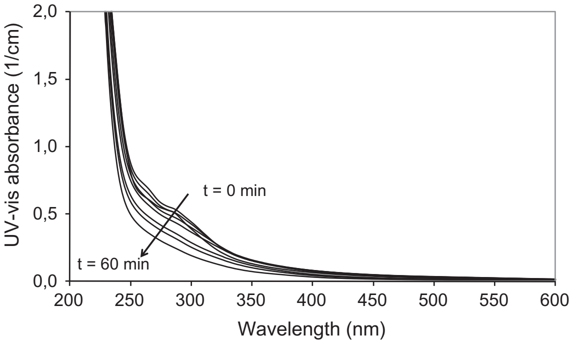

Fig. 5. Evolution of UV absorbance vs. time ($t = 0$, 3, 5, 10, 15, 30 min) during ozonation of UWW 1 sample (applied ozone dose: 28 mg/(L min)). UV absorbance at $t = 0$ refers to the raw sample.

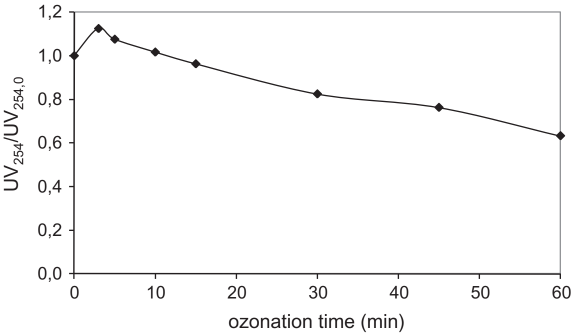

Fig. 6. Variation of UV_{254} vs. time during ozonation of UWW1 sample (applied ozone dose: 28 mg/(L min)).

3.4. *Kinetics of organic matter removal: comparison between photocatalytic oxidation and ozonation processes*

The comparison between PCO and ozonation processes, in terms of organic matter removal, showed a higher efficiency of PCO process. In particular, experimental data have been modeled according to a pseudo-first-order kinetic equation:

$$dC/dt = -kC \tag{1}$$

where "C" is UV_{254} at time "t" and "k" is a constant. The integration of Eq. (1) between initial time ($t_0 = 0$ min) and "t" results in the following equation:

$$-\ln(C/C_0) = kt \tag{2}$$

where "C_0" is UV_{254} at initial time (raw wastewater) and "k" is the kinetic constant (L/min). A plot of Eq. (2) gives a straight line with a slope of k. The half-life of a first-order reaction is independent of the starting concentration and is given by $t_{1/2} = \ln(2)/k$. Table 1 shows k, $t_{1/2}$ and R^2 values for all investigated catalyst loadings.

The lower $t_{1/2}$ for the degradation of UV_{254} (42 min) was observed for 3 g/L of TiO_2 (Table 1). The same removal was obtained within approximately 72 min of ozonation at 28 mg/(L min) of ozone flow rate according to kinetics evaluation (Table 1). The superiority of photocatalysis for organic matter degradation has been noted elsewhere too [22,24].

Table 1
Organic matter removal in terms of UV_{254}: comparison of kinetics parameters during ozonation and photocatalytic oxidation of UWW1 sample

Parameter	Photocatalytic oxidation				Ozonation
	0.5 g TiO_2/L	1.0 g TiO_2/L	2.0 g TiO_2/L	3.0 g TiO_2/L	
k (1/min)	0.0121	0.0104	0.0113	0.0149	0.0087
R^2	0.996	0.976	0.982	0.970	0.948
$t_{1/2}$ (min)	51.5	59.9	55.1	41.8	71.6

Table 2
THMFP (μg/L) of chloroform ($CHCl_3$), dichlorobromomethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$), and bromoform ($CHBr_3$) in chlorinated samples after photocatalytic and ozone treatment (3 gTiO_2/L; Cl_2 = 5 mg/L; applied ozone dose: 28 mg/(L min)

Sample description	pH	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$
UWW1 + Cl_2	7.80	6.5	1.1	0.7	ND
UWW1 + O_3(1 h) + Cl_2	7.99	5.5	1.1	0.7	ND
UWW2 + Cl_2	7.69	7.8	1.2	0.7	ND
UWW2 + O_3(1 h) + Cl_2	7.96	6.7	1.1	0.7	ND
5 min PC oxidized UWW1 + Cl_2	8.01	ND	1.1	0.7	ND
15 min PC oxidized UWW1 + Cl_2	7.41	1.5	1.1	0.7	ND
30 min PC oxidized UWW1 + Cl_2	8.06	2.2	1.1	0.7	ND

ND: not detected; PCO: photocatalytic oxidation.

Table 3
Toxicity to *Daphnia magna* and phytotoxicity to *Lepidium sativum* in raw and oxidized samples (3 gTiO_2/L; Cl_2 = 5 mg/L; applied ozone dose: 28 mg/(L min))

Sample description	pH	% Immobilization *Daphnia magna*	% Germination index *Lepidium sativum*
UWW1	7.87	0	71.08
UWW1 + Cl_2	7.80	10	80.12
UWW2	7.75	0	NM
UWW2 + Cl_2	7.69	0	
UWW1 + O_3(1 h) + Cl_2	7.99	0	
UWW2 + O_3(1 h) + Cl_2	7.96	5	
5 min PC oxidized UWW1	7.83	0	62.71
5 min PC oxidized UWW1 + Cl_2	8.01	20	67.57
15 min PC oxidized UWW1	7.94	0	60.54
15 min PC oxidized UWW1 + Cl_2	7.41	0	58.43
30 min PC oxidized UWW1	7.97	40	57.32
30 min PC oxidized UWW1 + Cl_2	8.06	20	80.92

NM: not measured; PC = photocatalytic treatment.

3.5. Effect of oxidation processes on THMFP

Photocalaytically oxidized samples resulted in lower concentrations of THMs than ozonated samples, as shown in Table 2. PCO was found to be superior to ozone for DBPs formation in drinking water since it is more effective to mineralize organics in water [24]. Chloroform ($CHCl_3$) was the dominant compound among other THMs in the ozonated samples, while none of the samples showed any bromoform ($CHBr_3$) formation potential. According to our previous findings, similar THMFP was recorded for a TOC range of 3.5–4.5 mg/L for alum coagulated, coagulated–ozonated, ultrasonics, and ozone combination treatment (data not shown). However, all chlorinated samples shown in Table 2 resulted in total THMs concentrations lower than the maximum contaminat level (30 μg/L) set by Italian legislation for wastewater reuse [3].

3.6. Effect of oxidation processes on toxicity and phyto-toxicity

Raw wastewater samples (UWW1 and UWW2) did not exhibit any toxicity to *D. magna* while a slight toxicity (10% of immobilization) was observed in UWW1 sample after chlorination (Table 3).

This slight toxicity was reduced to zero after 1 h ozonation treatment. In 5 min phocatalytically treated sample, the toxicity increased after chlorination, while after 15 min of PCO treatment, no toxicity was observed even after chlorination. On the other hand, toxicity increased to 40% immobilization after 30 min PCO treatment, and decreased to 20% after chlorination. The percent germination index of *L. sativum* increased after chlorination at 10% displaying a positive input of chlorination to oxidize harmfull substances in raw wasteater [6,10,21]. However, germination index indicated a gradual decrease in photocatalytically treated samples vs. time, in UWW1 sample. On the other hand, the toxicity increased after chlorination in 30 min oxidized sample too. These results were attributed to intermediate formation during treatment and further oxidation with chlorination, which may oxidize these intermediates or may form new intermediates due to the complex mixture of wastewater samples [1,11,19,24].

4. Conclusion

In this study, two oxidation processes (namely ozonation and PCO) were compared in the advanced treatment of an UWWTP effluent for possible wastewater reclamation. The main results achieved can be summarized as follows:

- Degradation of organic matter increased as TiO_2 dose was increased, and a 3 g/L dose was used to optimize effluent quality regarding THMFP and ecotoxicity.
- Degradation kinetics of organic matter calculated by means of UV_{254} showed a superiortiy of PCO even at the lowest TiO_2 concentration compared to ozonation.
- PCO treated samples yielded lower concentrations of THMs compared to ozonated samples, while effluent toxicity varied between the two processes. However, a 30 min PCO treatment was found to produce an effluent to comply with THMs limit set by Italian regulation for wastewater reuse, as well as with irrigation purpose evaluated by *L. sativum*.

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