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Research Paper

Effect of microplastics on urban wastewater disinfection and impact on effluent reuse: Sunlight/H_2O_2 vs solar photo-Fenton at neutral pH

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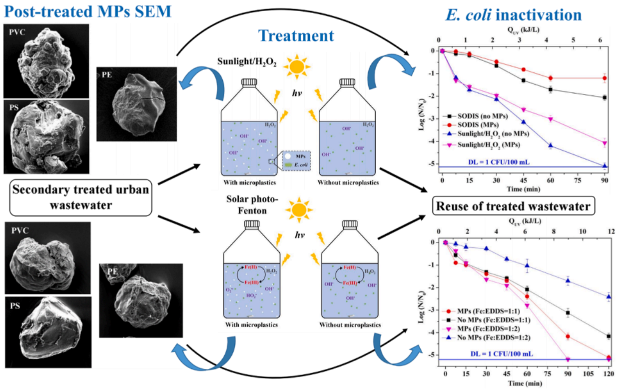
HIGHLIGHTS

- Microplastics (MPs) type affected disinfection efficiency and biofilm formation.
- Solar-photo Fenton (SPF) was more effective than sunlight/H_2O_2 with MPs.
- SPF was less effective than sunlight/H_2O_2 without MPs.
- Lower *E. coli* regrowth observed in tests with MPs compared to tests without MPs.
- SPF less effective in controlling regrowth of *E. coli* than sunlight/H_2O_2.

GRAPHICAL ABSTRACT



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ABSTRACT

The interference of three types of microplastics (MPs) on the inactivation of *Escherichia coli (E. coli)* by advanced oxidation processes (AOPs) (namely, sunlight/H_2O_2 and solar photo-Fenton (SPF) with Ethylenediamine-N,N′-disuccinic acid (EDDS)), in real secondary treated urban wastewater was investigated for the first time. Inactivation by sunlight/H_2O_2 treatment decreased as MPs concentration and H_2O_2 dose were increased. Noteworthy, an opposite behaviour was observed for SPF process where inactivation increased as MPs concentration was increased. Biofilm formation and microbial attachment on surfaces of post-treated MPs were observed on polyethylene (PE) and polyvinyl chloride (PVC) MPs by field emission scanning electron microscopy. In presence of PE MPs, a complete inactivation of *E. Coli* was achieved by SPF with EDDS (Fe:EDDS = 1:2) after 90 min treatment unlike of sunlight/H_2O_2 treatment (~4.0 log reduction, 40 mg/L H_2O_2 dose, 90 min treatment). The lower efficiency of sunlight/H_2O_2 process could be attributed to the blocking/scattering effect of MPs on sunlight, which finally reduced the intracellular photo Fenton effect. A reduced *E. coli* regrowth was observed in presence of MPs. SPF (Fe:EDDS = 1:1) with PE MPs was less effective in controlling bacterial regrowth (~120 CFU/100 mL) than sunlight/H_2O_2 (~10 CFU/100 mL) after 48 h of post-treatment. These results provide useful information about possible interference of MPs on urban wastewater disinfection by solar driven AOPs and possible implications for effluent reuse.

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1. Introduction

Water shortage is one of the greatest challenges throughout the world because of growing population, climate change, industrialization and agricultural practices. Lack of water availability would provide more pressure on natural water resources and water basins, thus creating socio-economic and political instability in a country [1]. Reuse of treated urban wastewater for anthropic activities is one of the best alternatives to solve the problem of water scarcity [2]. However, wastewater reuse for crop irrigation is often limited due to risks associated with pathogenic bacteria contained in the treated effluent, which potentially affect human health in the form of infectious diseases [3]. Under these circumstances, European Union (EU) has recently introduced Water Reuse Risk Management Plans in the recently approved regulation on *minimum requirements for use of reclaimed water* (2020/741), where the minimum concentration of *Escherichia coli (E. coli)* after tertiary treatment is between ≤10 (class A water) and ≤10000 (class D water) CFU/100 mL depending on the type of crops for irrigation [4]. Therefore, an effective disinfection technique as a tertiary treatment should be implemented at urban wastewater treatment plants (WTPs) for safe reuse of wastewater for crop irrigation.

Recent studies on water/wastewater disinfection revealed that disinfection performance could be negatively affected by the presence of tiny plastic particles called microplastics (MPs) [5-7]. MPs are small particles less than 5 mm in diameter, frequently detected in the effluent of WTPs ranging between 29 and 447 particles/L [8]. These tiny plastic particles can skip the primary and secondary treatment trains and reach tertiary treatment stage, where they interact with pathogenic bacteria and subsequently interfere with the disinfection process. Till date, a few studies investigated the effects of MPs on wastewater disinfection, focusing on chemical disinfection [7], membrane filtration [9] and ultraviolet (UV) irradiation [5]. Such studies concluded that low disinfection performance in presence of MPs is due to different hindering mechanisms during treatment process. Specifically, MPs hindered the action of chlorine on microorganism by rapid decay of disinfectants, thereby protecting microorganism from inactivation [10]. Membrane filtration is an effective technique for water/wastewater disinfection, however, fouling of membrane and pore blockage due to interaction of MPs with membrane surface and other substances is a major drawback [11]. Although UV irradiation is a robust and viable disinfection technique, MPs can negatively affect UV disinfection efficiency by blocking/scattering/absorbing UV light, resulting in shielding microorganism from inactivation [5]. The detrimental effects of MPs on disinfection performance not only reduce treatment efficiency but also offer some other drawbacks. For example, additional amount of chemical disinfectant dose would be required to achieve complete wastewater disinfection [6]. Membrane fouling would reduce the lifetime of membrane and require regular maintenance [12]. UV disinfection may require longer treatment time to achieve complete inactivation of bacteria. Therefore, alternative disinfection techniques should be investigated to evaluate the effects of MPs as well as if they can perform better than conventional disinfection processes.

Among the best available treatment techniques, solar driven-advanced oxidation processes (solar-AOPs), and particularly solar photo Fenton (SPF) with a chelating agent (to effectively operate the process at neutral pH) and sunlight/H_2O_2, have found to be an effective and sustainable solution for wastewater disinfection in small WTPs [13,14] [15]). Unlike conventional treatment processes, solar driven-AOPs take advantage of natural sunlight, making disinfection process energy-efficient and environmentally friendly. Although solar based disinfection processes are considered as an attractive and sustainable option, the effect of MPs on process efficiency has not been explored yet. The only studies available in literature are related to interference of suspended solids/particles on water/wastewater disinfection. For example, it was reported that presence of suspended solids in wastewater negatively affected solar disinfection performance by increasing bacteria inactivation time from 5 min (without solid particles) to 120 min [16]. Similarly, Walters et al. [17] also observed that solid particles in municipal wastewater acted as a barrier for sunlight penetration and protected pathogenic bacteria from inactivation. To the best of author's knowledge, the effect of engineering MPs on solar driven AOPs, including sunlight/H_2O_2 and solar photo-Fenton process for disinfection purpose have not been reported so far.

Besides the direct interference of MPs (UV light blocking, scattering and reflecting) on disinfection performance, microorganisms attached to microplastic surface during disinfection cannot be ignored [5], which could potentially affect the disinfection performance. Bacteria associated with MPs, referred to as the "plastisphere" [18], are capable to survive under harsh environmental conditions [19]. In fact, characteristics of microplastics (type and morphology) and wastewater environment are the key factors affecting the attachment of MPs with bacteria [20].

In this study, interference of MPs on the inactivation of indigenous *E. coli* by solar driven AOPs processes, namely sunlight/H_2O_2 and SPF with Ethylenediamine-N,N′-disuccinic acid (EDDS) complex were investigated in real secondary treated urban wastewater under different H_2O_2 doses, MPs concentrations and Fe:EDDS ratio. Disinfection experiments were carried out using 3 MPs including polyethylene (PE), polystyrene (PS) and polyvinyl chloride (PVC) as a model because i) they are common and frequently detected MPs in influent and effluent of WWTPs [21]; ii) microbial attachment on these MPs has been widely observed [22]; iii) density of each polymer type is different in water and iv) they can be affected in different ways by AOPs providing different protections to bacteria through biofilm formation. The effect of MPs on post-treatment events (regrowth of *E. coli*) was also investigated to better understand possible related risk for wastewater reuse.

2. Materials and methods

2.1. Chemicals and reagents

PE MPs (powdered, average particle size: 150 μm) were purchased from Goodfellow Cambridge Ltd. (London, UK). PS and PVC MPs (powdered: average particle size: 150 μm) were supplied by Zhenjiang Chimei Chemical Company Limited (China) and Inner Mongolia Junzheng Chemical Company Limited (China), respectively. Characteristics of MPs used in this study are given in supplementary material file (SM, Table S1)·H_2O_2 (30%, w/v), EDDS water solution (35%, w/v) and bovine liver catalase were purchased from Sigma Aldrich. $Fe_2(SO_4)_3 \cdot H_2O$ (75% w/v), purchased from Titolchimica S.P.A., was used as a source of Fe in SPF experiments. Titanium (IV) oxysulfate (99.99%), ascorbic acid, 1,10-phenanthroline, acetic acid and ammonium acetate (Sigma Aldrich) were used for measurement of residual H_2O_2 concentration and dissolved iron in wastewater. Tryptone bile X-glucoronide (TBX) Agar and Nutrient Brooth (NB) were purchased from Biolife.

2.2. MPs characterization

To evaluate the effect of AOPs on MPs as well as on biofilm formation, the surface and morphology of pristine and treated MPs were analysed using field emission scanning electron microscopy (FeSEM, FEI Inspect-F). Prior to analysis, pristine MPs samples were washed with deionized water and dried at room temperature. Treated MPs samples after incubation were separately frozen at − 2 °C in sealed petri dish to avoid cross contamination. All MPs samples were coated with thin gold layer of 65.0 nm by a conventional sputtering instrument to avoid electrostatic interaction with signals created by FeSEM to produce clear images [23]. High magnified images of MPs were captured with an accelerated voltage and working distance of 10.0 kV and 11.0 mm, respectively.

2.3. Wastewater characteristics

The wastewater used in this study was collected from the secondary effluent of a WTP in the province of Salerno, southern Italy, serving 650,000 population. The basic characteristics of collected samples are shown in Table 1.

2.4. Bacterial suspension

Bacterial suspensions of *E. coli* were prepared according to method and procedure followed in our previous study [24]. Firstly, *E. coli* strains were isolated from wastewater sample inoculating 0.1 mL of the sample on Tryptone Bile X-glucuronide (TBX) Agar medium and incubated at 37 °C for 24 h. After incubation, a single colony of *E. coli* was inoculated into sterilized tube containing Nutrient-Broth Agar I (14 mL) and incubated at 37 °C for 20 h. The formed pellet was collected after centrifugation at 3000 rpm for 15 min. After discarding the supernatant, the pellet was resuspended in a 14 mL sterilized phosphate-buffer saline (PBS, Oxoid) solution. The initial concentration of *E. coli* spiked in wastewater for disinfection tests was 10^5 CFU/100 mL, which is consistent with the concentration in real urban wastewater.

2.5. Experimental design and set-ups

The effect of MPs on inactivation of *E. coli* by sunlight/H_2O_2 was investigated in real urban wastewater at different H_2O_2 doses (0, 20, 40 and 60 mg/L), MPs concentrations (0.25, 0.5 and 1.0 g/L), MP type (PE, PVC and PS) and wastewater matrix (real and DI water). The range of H_2O_2 dose used in sunlight/H_2O_2 test was in accordance with the doses applied at pilot-scale [25]. The range of concentration of MPs selected for this work is a compromise solution between realistic concentrations in wastewater [5] and experimental needs. Before starting the actual experiment, control test using same operational conditions as sunlight/H_2O_2 was performed in the dark at room temperature to determine intracellular oxidative decay of *E. coli* bacteria. SPF tests were carried out at different Fe:EDDS complex ratio (1:1 and 1:2) and MP type (PE, PVC and PS) in real wastewater matrix. To evaluate the interference of MPs, SPF tests were initially operated using 1:1 Fe:EDDS complex ratio (0.1 mmol/L of Fe and 0.1 mmol/L EDDS) as it was considered optimum ratio for inactivation of *E. coli* in a previous study [15]. The concentration of MPs (0.5 g/L) and H_2O_2 dose (40 mg/L) in SPF experiments were selected according to the results obtained by sunlight/H_2O_2 process.

2.5.1. Disinfection tests

Sunlight/H_2O_2 experiments were performed in batch mode with borosilicate glass (DURAN, Schott, Germany) vessel reactors, magnetically stirred at 100 rpm throughout the experiments. Total irradiated wastewater volume and illuminated surface area were 500 mL and 0.014 m^2, respectively. All experiments were performed under natural sunlight irradiation at the University of Salerno, Fisciano Campus located at 40° 76′ N and 14° 79′ W. Prior to sunlight exposure, previously autoclaved real wastewater samples were added with weighted MPs and magnetically stirred for 30 min. After MPs mixing in wastewater, bacterial solution containing *E. coli* was spiked and the reactor was left under stirring condition for 10 min, followed by H_2O_2 addition. Residual concentration of H_2O_2 in wastewater was monitored periodically during experiments.

Table 1
Basic characteristics of secondary treated urban wastewater.

Parameter	Mean value
pH	7.8 ± 0.2
Turbidity (NTU)	9.4 ± 0.4
Total suspended solids (mg/L)	15.4 ± 1.0
Conductivity (mS/cm)	2.4 ± 0.2
Dissolved organic carbon (DOC) (mg/L)	20.5 ± 3.4
Chlorides (mg/L)	126.11 ± 11
Bicarbonates (mg/L)	401.6 ± 10
Chlorides (Cl^-) (mg/L)	126 ± 11
NO_3^- (mg/L)	2 ± 0.2

Iron complex (Fe:EDDS) for SPF disinfection tests was prepared by dissolving $Fe_2(SO_4)_3 \cdot H_2O$ (75%) in Milli-Q grade water, followed by EDDS addition in dark due to instability of EDDS with light. Then, Fe:EDDS solution was added to wastewater samples spiked with *E. coli* and mixed for 5 min in the reactor. After adding 40 mg/L H_2O_2 in wastewater and further 30 s mixing, the reactor was uncovered and exposed to direct sunlight. UV radiation of sunlight was monitored through a radiometer (BLACK-Comet Stellar Net UV–VIS, StellarNet, Tampa, FL, USA) which gives data in terms of incident radiation (W/m^2) in the range 280–400 nm. The results were plotted as a function of accumulated UV energy per unit of treated wastewater volume (Q_{UV}, kJ/L) at a given time [26], details are provided in SM. All experiments were performed at natural pH of wastewater (~7.8). Wastewater samples taken at each time were spiked with catalase (20 μL of 0.1 g/L catalase stock solution) to quench residual H_2O_2 concentration and immediately analysed. All experiments were performed in duplicates and results were plotted with error bars.

2.6. Bacterial regrowth tests

Regrowth tests of *E. coli* bacteria was performed by incubating wastewater samples at 20 °C for 24 and 48 h. Wastewater samples were taken at mid and end of each sunlight/H_2O_2 and SPF with EDDS test. Bacterial count was performed in duplicates.

2.7. Microbial analysis and analytical measurements

Enumeration of target bacteria was carried out by membrane filtration method. Wastewater samples containing residual bacteria (10–20 μL) were filtered through a 0.45 μm pore size membrane filters and placed on TBX agar petri dish for cultivation, followed by incubation for 24 h at 37 °C. Representative colonies of *E. coli* on agar plate were counted on each sample corresponding to free bacteria (green colonies) and microplastics-associated bacteria (green colonies on MPs). The detection limit (DL) of this method was 1 CFU/100 mL. Inactivation of *E. coli* was plotted as $Log\ (N/N_0)$ Vs time and Q_{UV}, N and N_0 being total bacterial concentration (free plus microplastics-associated bacteria) at time t and initial time, respectively.

Concentration of iron and H_2O_2 was monitored spectrophotometrically by a UV/Vis Lambda-25 spectrophotometer (Perkin Elmer). In particular, residual concentration of H_2O_2 and dissolved Fe were analyzed according to DIN 38402H15 and ISO 6332 methods, respectively (more details in the SM file).

3. Results and discussion

3.1. Microplastics characterization

To evaluate the possible changes in surface and morphology of neat and treated MPs they were analysed by FeSEM (Fig. 1**)**. Pristine PVC MPs exhibited a rugged and bumped morphology (Fig. 1**A**), whereas pristine PS showed relatively smoother surface texture (Fig. 1**D**). Compared with pristine PVC and PS MPs, pristine PE presented a rough and porous surface feature (Fig. 1**G**), which is in accordance with the available literature [27]. After sunlight/H_2O_2 treatment, a complex network of honeycomb-like pattern of extracellular polymeric substance (EPS)

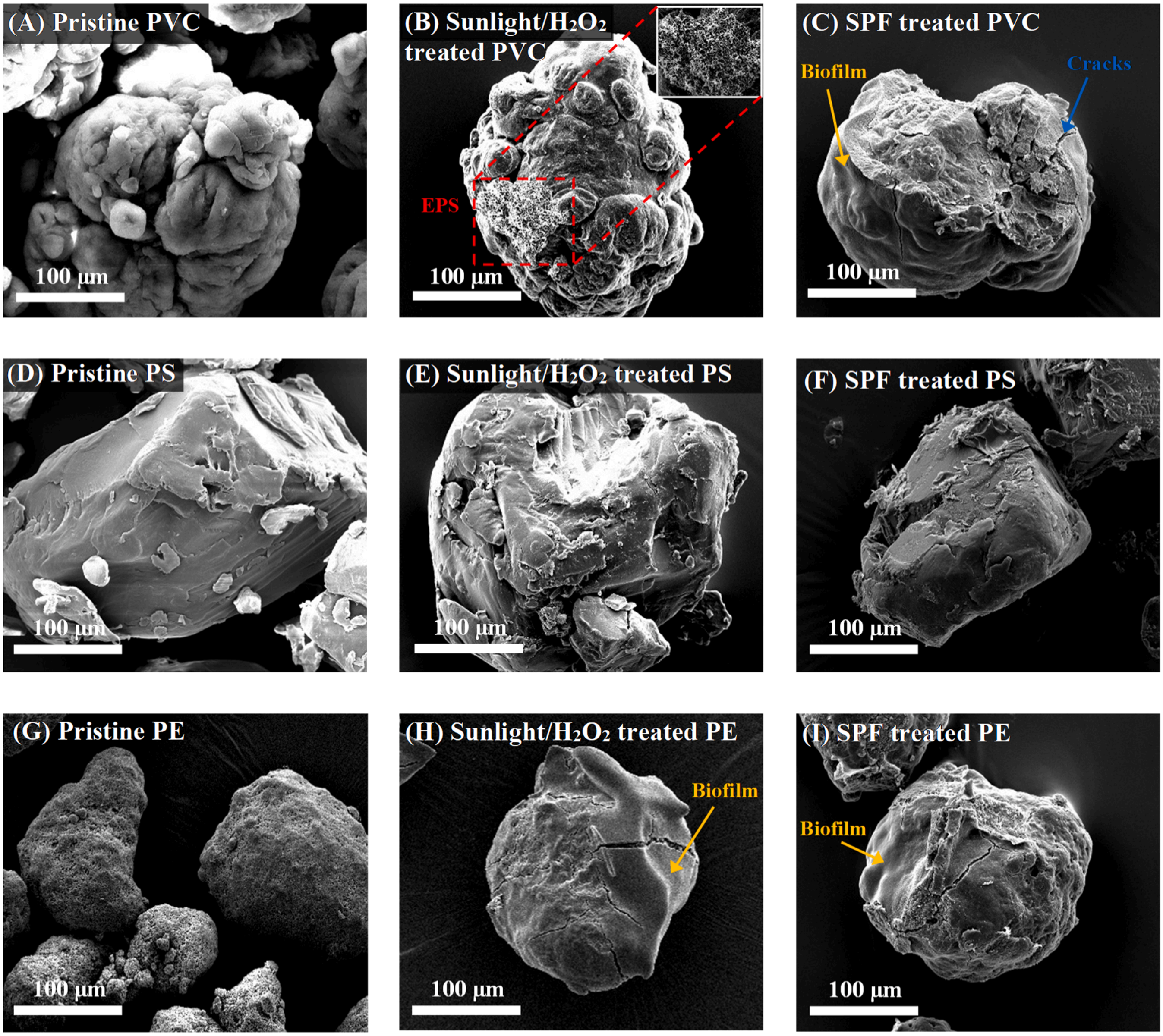

Fig. 1. FeSEM images of pristine and treated (sunlight/H_2O_2 and SPF) MPs. Experimental conditions: sunlight/H_2O_2 = 90 min treatment. SPF = 120 min treatment time, 1:1 (Fe:EDDS). Concentration of H_2O_2 and MPs in both treatments were 40 mg/L and 0.5 g/L, respectively.

matrix was noticed on the surface of PVC microplastic (Fig. 1**B**), which can stimulate the attachment of bacterial cells and promote the formation of biofilm [28]. A similar pattern of EPS matrix was observed on grains of sediments [29] and mounds [30], which were colonized by microbes in nature. A formation of biofilm with some cracks appeared on the surface of SPF treated PVC (Fig. 1**C**). In contrast, no formation of biofilm on surface of treated PS microplastics can be observed, except occurrence of surface erosion after sunlight/H_2O_2 treatment (Fig. 1**E**). In case of PE treated MPs, unlike PS MPs, the entire surface area was coated with biofilm after disinfection (Fig. 1**H and I**). Above all, SEM images of pristine and treated MPs revealed that PS MP exhibited stronger resistance to form microplastisphere in comparison to PE and PVC MPs, which could be attributed to surface hydrophobicity of microplastics [31]. High abundance of bacterial attachment on PE and PVC MPs in this study are in accordance with the observation of another study which reported higher enrichment of microorganisms for PE and PVC than other MPs [32]. Moreover, the cracks on SPF treated PVC MP as well as surface erosion on sunlight/H_2O_2 treated PS MPs could be attributed to the oxidation of MPs surface by hydroxyl radical ($^{\bullet}OH$) produced during treatment. Such a difference (cracks Vs erosion) may be due to the higher $^{\bullet}OH$ production rate for SPF compared to sunlight/H_2O_2, because of the different mechanisms $^{\bullet}OH$ formation. In particular, in the photolysis of H_2O_2 is the UV-C radiation that breaks down H_2O_2 molecule promoting the formation of $^{\bullet}OH$ but in sunlight spectrum only less than 4% is the UV-C radiation [33].

3.2. *Effect of MPs on E. coli inactivation*

3.2.1. *Sunlight/H_2O_2 disinfection*

3.2.1.1. Effect of initial H_2O_2 concentration. The effect of hydrogen peroxide on *E. coli* inactivation by sunlight/H_2O_2 process was evaluated with and without presence of PE-MPs (1.0 g/L) in the range between 0 and 60 mg/L of H_2O_2, as shown in Fig. 2. The possible effect of H_2O_2 on bacteria inactivation due to intracellular oxidation was investigated through control experiments in dark. H_2O_2 concentration of 20 mg/L alone did not reduce concentration of *E. coli* in wastewater after 90 min of standalone process (Fig. S1). Solar disinfection (SODIS) tests without

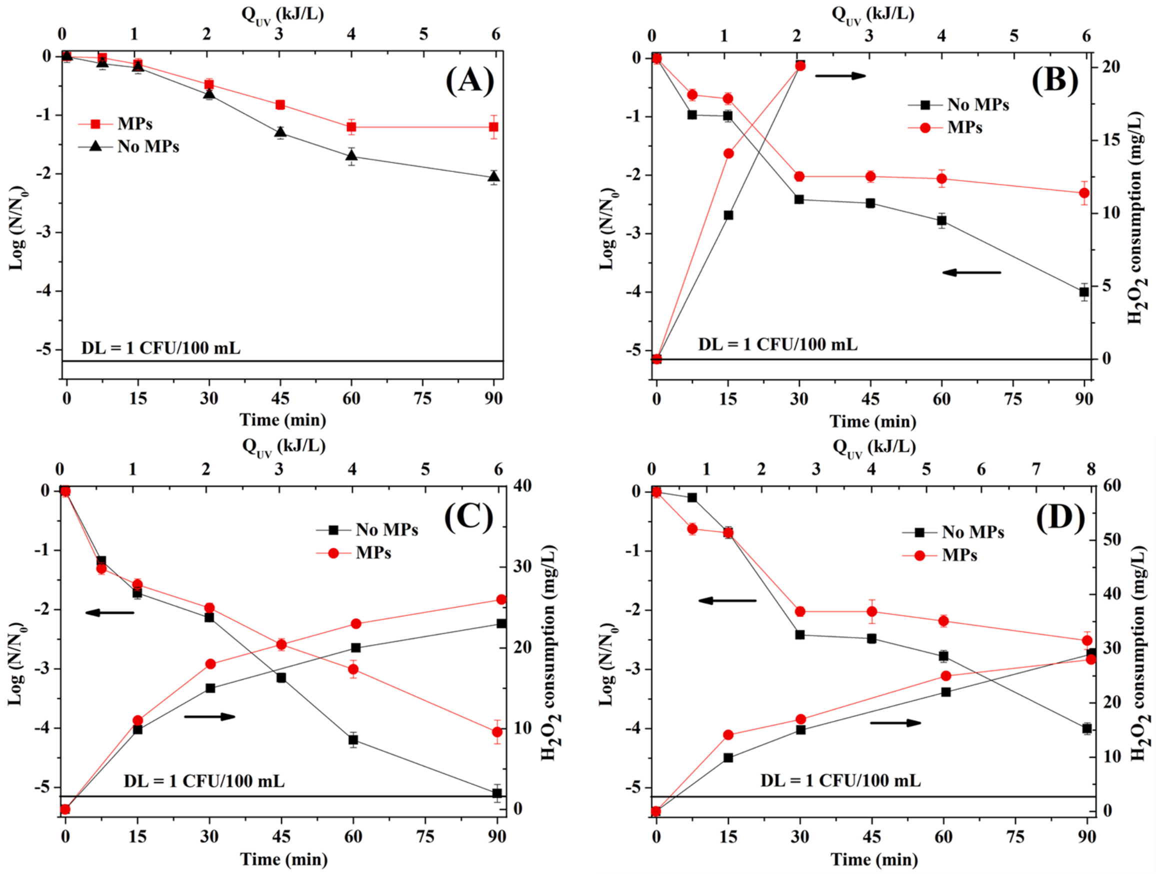

Fig. 2. Inactivation of *E. coli* in real wastewater at varied initial H_2O_2 concentration of (A) 0 mg/L (SODIS), (B) 20 mg/L, (C) 40 mg/L, and (D) 60 mg/L with and without PE-MPs (MPs concentration = 1.0 g/L).

H_2O_2 addition were also performed to better evaluate the effect of MPs on sunlight disinfection as well as the differences with sunlight/H_2O_2 process. Sunlight disinfection efficiency without MPs was twice (Fig. 2**A**) as compared to sunlight tests with MPs. When solar radiation was coupled to H_2O_2 (20 mg/L initial concentration), disinfection efficiency remarkably increased to 2.2 log units and 4.0 log units, with and without MPs, respectively (Fig. 2**B**). Total inactivation of *E. coli* (residual concentration below the DL, 1 CFU/100 mL) being achieved when the concentration of H_2O_2 was increased to 40 mg/L without MPs. A further increase in H_2O_2 concentration to 60 mg/L reduced *E. coli* inactivation to 4.0 log units (without MPs). The low inactivation of bacteria at high H_2O_2 concentration (60 mg/L) could be explained by the scavenging effect of $^{\bullet}OH$ [34]. The photoinactivation mechanism of microorganisms under natural sunlight can be well explained by direct or indirect oxidative damage to the cells due to generation of $^{\bullet}OH$ [35]. UV-A region (315–400 nm) of the sunlight spectrum is absorbed by endogenous chromophores (sensitizers), generating reactive oxygen species (ROS) such as $^{\bullet}OH$ which damage the cell nutrients (proteins and lipids) and cause DNA rupture via indirect oxidation [36]. Whereas UV-B region (290–320 nm) of the sunlight spectrum can directly cause damage to DNA or RNA by forming cyclobutane pyrimidine dimer photoproducts [37]. These dimers are capable to inhibit gene replication, change gene expression and cause genetic mutation [38].

It is worthy to mention that log inactivation of *E. coli* in presence of PE-MPs was lower (1.0–1.8 log units) than without MPs at different H_2O_2 concentrations (0.0–60 mg/L). Low disinfection efficiency of sunlight/H_2O_2 treatment in presence of MPs is attributed to the interference of MPs due to blocking/absorbing or shading effect of solar radiation. In presence of sunlight, inactivation mechanism of bacteria is mediated by intracellular photo-Fenton reactions. Intracellular photo-Fenton reaction is indirectly initiated by the absorbance of UVA and UVB region of the sunlight [39]. In presence of MPs, the direct penetration ability of sunlight in wastewater is reduced. Consequently, intracellular photo-Fenton reactions within the cell are also reduced, eventually decreasing the inactivation rate of bacterial cells. Moreover, consumption profile of H_2O_2 during sunlight/H_2O_2 treatment showed that more than 50% of H_2O_2 was consumed when initial H_2O_2 concentration was 40 mg/L (Fig. 2**C**) and 60 mg/L (Fig. 2**D**). Whereas, no residual H_2O_2 was observed in case of low H_2O_2 concentration (20 mg/L) (Fig. 2**B**). Since complete inactivation of *E. coli* was achieved at H_2O_2 concentration of 40 mg/L, this concentration was chosen for subsequent experiments.

3.2.1.2. Effect of initial MPs concentration. The effect of initial MPs concentration (0.25 g/L, 0.5 g/L and 1.0 g/L) on *E. coli* inactivation by sunlight/H_2O_2 treatment was investigated at an initial H_2O_2 concentration of 40 mg/L (Fig. 3). The results showed no significant difference in the inactivation of studied bacteria at PE MPs concentration of 0.25 g/L and 0.5 g/L after 90 min treatment. Residual concentration of *E. coli* reached the DL (1 CFU/100 mL) after 90 min of sunlight/H_2O_2 treatment. On the contrary, the inactivation of *E. coli* decreased from ~5.2 log units to ~4.1 log units when the concentration of MPs was increased from 0.5 g/L to 1.0 g/L, respectively. These results are consistent with a previous study where concentration of 0.25 g/L and 0.5 g/L of PE MPs did not significantly affect UV disinfection process [5]. However, high concentration of MPs (1.0 g/L) resulted in 2–3 log unit reduction of target bacteria. The negative effect of MPs on the process efficiency of sunlight/H_2O_2 treatment could be due to two possible mechanisms: (1) absorbing/scattering effect of UV light [40] and (2) interaction of microorganisms with MPs [41,42]. Presence of

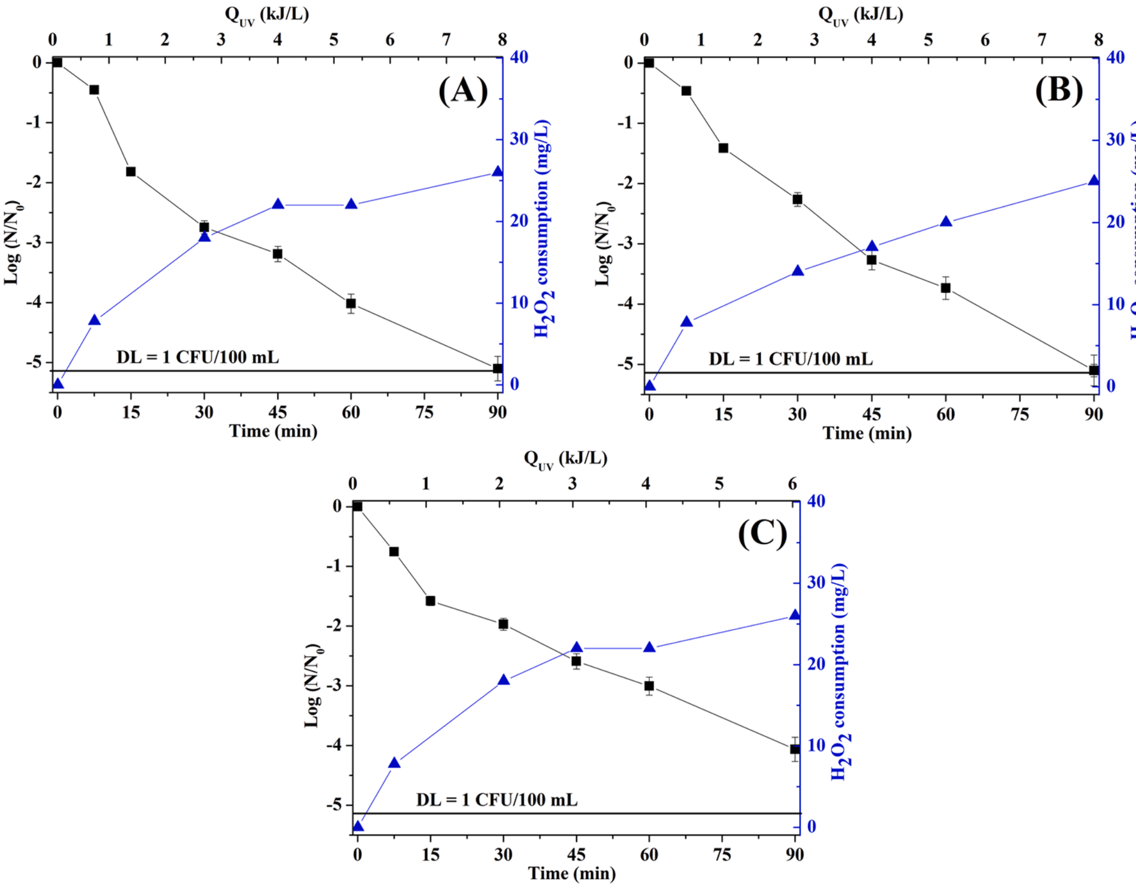

Fig. 3. Inactivation of *E. coli* by sunlight/H_2O_2 at different PE MPs concentrations: (A) 0.25 g/L, (B) 0.5 g/L, and (C) 1.0 g/L (H_2O_2 concentration = 40 mg/L).

suspended solids in wastewater may cause reflection and scattering phenomenon of UV light [16]. Consequently, lack of direct sunlight penetration into the cells shielded microorganisms from inactivation [43]. For instance, it was reported that when the turbidity of wastewater increased to 2 NTU, UV disinfection efficiency decreased by 50% due to low penetration of UV light [40]. The second mechanism founds confirmation in FeSEM analysis. Microplastics-associated bacteria with formation of biofilm on the surface of PE MPs could be easily seen after sunlight/H_2O_2 disinfection (Fig. 1**H** and **S2**), confirming shielding of bacteria from inactivation. Accordingly, PE MPs were found to provide a more favourable substrate for microorganisms' attachment in comparison with PVC, PS, PP and PET MPs [44].

3.2.1.3. Effect of MPs type. The effect of different types of MPs (PE, PS and PVC) on inactivation of *E. coli* by sunlight/H_2O_2 treatment was studied. The concentration of MPs and H_2O_2 dose were kept constant at 0.5 g/L and 40 mg/L, respectively. In case of PE MPs, residual concentration of *E. coli* in wastewater reached the DL (1 CFU/100 mL) after 90 min of sunlight/H_2O_2 treatment (Fig. 4). However, no complete inactivation of *E. coli* was observed with PS and PVC MPs, even after 120 min treatment. The maximum log inactivation of *E. coli* reached to ~4.7 log units with PS and PVC MPs. The lower and slower disinfection efficiency with PS and PVC MPs could be attributed to different characteristics and behaviour of MPs in wastewater, which ultimately affected interaction of bacteria with MPs. Due to smooth surface of PS MPs (Fig. 1**D**), no biofilm formation and microbial attachment was observed after disinfection, while some cracks and surface erosion are evident (Fig S2). Although complete inactivation of *E. coli* was observed in case of PE MPs, rough surface of PE MPs resulted in aggregation of biofilm and microbes (Fig. S2). Similar to PS MPs, no obvious biofilm was noticed on surface of PVC MPs after sunlight/H_2O_2 disinfection, but EPS formation (Fig. S2), which is early indication of biofilm development and microbial attachment. According to previous studies, different MPs have different light absorption capacity in wastewater when exposed to UV light radiation [45,46], finally affecting disinfection process. Pristine PE MPs would not absorb ultraviolet light (λ > 290 nm) due to absence of chromophores group (photo-initiators) in their

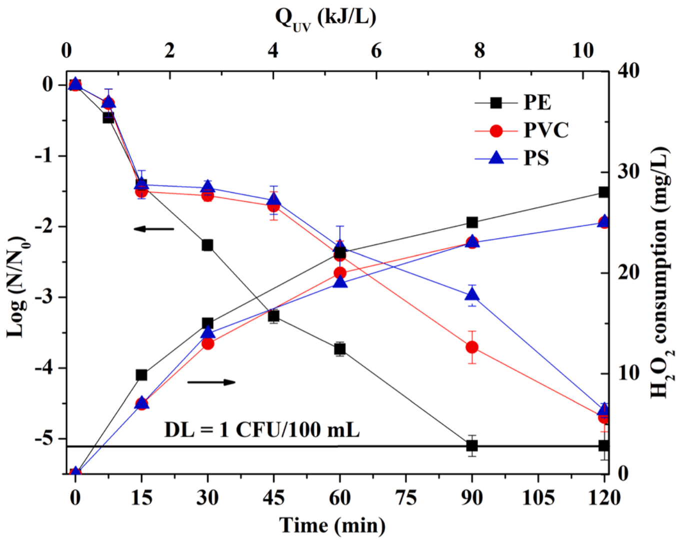

Fig. 4. Effect of MPs type (PE, PVC, and PS) on inactivation of *E. coli* bacteria by UV/H_2O_2 in real wastewater (MPs concentration = 0.5 g/L, H_2O_2 concentration = 40 mg/L).

molecular structure [47]. On the contrary, presence of phenyl group and chlorine group in PS and PVC MPs respectively, could absorb light energy to excite the electron and transfer light energy to their molecules [48]. The light absorption property of PS and PVC MPs could have reduced the amount light energy available for disinfection process. Moreover, high density of PS (1.06 g/cm^3) and PVC (1.38 g/cm^3) MPs compared to PE MPs (0.98 g/cm^3) allow a better mixing of PS and PVC particles in wastewater. Since sunlight radiation reaches the outer surface of the wastewater sample to move towards the inner part, UV light is initially adsorbed by PS and PVC MPs in the external part of the reactor and a decreasing fraction is expected to reach the whole volume.

3.2.1.4. Effect of water matrix. The effect of water matrix on treatment efficiency of sunlight/H_2O_2 in presence of MPs was investigated using DI water and real wastewater. The concentration of PE MPs and H_2O_2 in wastewater were 0.5 g/L and 40 mg/L, respectively. A complete inactivation of *E. coli* was achieved after 60 min in DI water, while 90 min treatment was necessary in real wastewater (Fig. 5**)**. These results indicated that characteristics of wastewater, such as turbidity, organic matter and ionic species can reduce process efficiency. According to scientific literature, presence of ions in wastewater such as bicarbonates (HCO_3^-), carbonates (CO_3^{2-}), chlorides (Cl^-) and NO_3^- could inhibit the inactivation of microorganisms by acting as scavenger of hydroxyl radicals and absorbing UV-A spectrum of sunlight [49-51]. Moreover, presence of organic and inorganic substances in wastewater can also interact with MPs and coat on their surfaces, eventually facilitating microbial attachment [52]. Consequently, microorganisms can survive for longer time on MPs and after resuspension in water matrix could be transported to water environments [16].

3.2.2. Solar photo-Fenton process

3.2.2.1. Effect of Fe:EDDS complex ratio. The effect of Fe:EDDS complex ratio (1:1 and 1:2) on inactivation of *E. coli* by SPF was investigated with and without MPs. The concentration of PE-MPs and H_2O_2 was kept constant at 0.5 g/L and 40 mg/L, respectively. Experimental results revealed that when SPF was operated using low Fe:EDDS complex ratio (1:1) with MPs, the concentration of *E. coli* decreased below the DL (1 CFU/100 mL) after 120 min, (Fig. 6**A)**. On the contrary, inactivation of *E. coli* reached 4.2 log units when SPF test was carried out without addition of MPs. With the increase of EDDS concentration (Fe:EDDS = 1:2), SPF treatment efficiency without MPs decreased and only 2.5 log inactivation units was achieved (Fig. 6**B**). While complete inactivation of *E. coli* was observed in 90 min when SPF was operated with MPs. According to these results, the presence of MPs improved disinfection performance of SPF. The improved disinfection efficiency of SPF in presence of MPs could be attributed to one or more of the following mechanisms. MPs undergo photooxidation by absorbing light energy, resulting in generation of bio-stable free radicals known as “environmental persistent free radicals” (EPFRs) [47] including oxygen, carbon or oxygenated carbon centred radicals [53]. Formation of EPFRs is mediated by transition metals (iron) and organic moieties in two stages. Initially, physisorption of organic molecules and metal occurs via weak bonding, followed by chemisorption process, where electron transferring occurs from adsorbed species to metal, resulting in the formation of EPFRs [54]. In addition, presence of functional groups (hydroxyl, chlorine and oxygen) on MPs surface can also facilitate the formation of stable free radicals [53]. EPFRs have tendency to react with hydrogen peroxide or persulfate under light irradiation to produce ROSs such as singlet oxygen, superoxide and •OH [53]. ROSs formed from photooxidation of MPs could provide additional benefit in bacteria inactivation. For instance, high inactivation of *E. coli* in presence of PE MPs could be attributed to increased ROSs and •OH. Another possible mechanism that supports high bacterial inactivation with PE MPs could be attributed to photochemical reactive components including dissolved organic matter formed due to secondary ROSs [55]. As an essential chromophore in wastewater, DOM in water medium transform to excited triplet state (^{3}DOM*) after sunlight irradiation [47]. After reaching triplet excited state, DOM is converted into hydroxyl radicals and singlet oxygen via transfer of electrons [56]. Therefore, the increased inactivation of *E. coli* by SPF as MPs concentration was increased (Fig. S3), unlike of sunlight/H_2O_2, can be explained by the higher iron concentration, which mediated the formation of EPFRs and later ROS in SPF process.

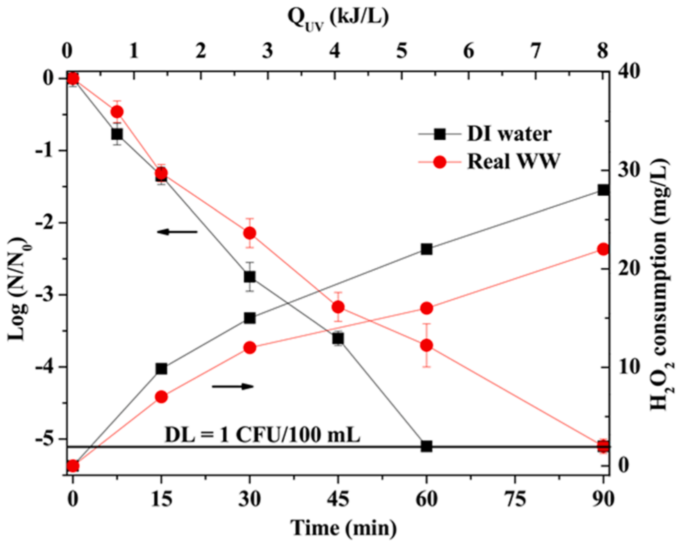

Fig. 5. Effect of wastewater matrix (real wastewater and DI water) on inactivation of *E. coli* bacteria by sunlight/H_2O_2 (MPs concentration = 0.5 g/L, H_2O_2 concentration = 40 mg/L).

Inactivation of bacteria by SPF process involves two simultaneous mechanisms: (1) extracellular attack of hydroxyl radicals on cell membrane, and (2) intracellular photo-Fenton reactions. In SPF process with Fe:EDDS, organic and hydroxyl radicals are generated according to the following reactions (1) and (2) [57]:

$$Fe(III):EDDS + h\nu \rightarrow [Fe(III):EDDS]^* \rightarrow Fe^{+2} + EDDS^{\bullet} \quad (1)$$

$$Fe^{+2} + H_2O_2 \rightarrow Fe(III) + {}^{\bullet}OH + OH^- \quad (2)$$

Furthermore, other ROSs including superoxide radicals ($HO_2^{\bullet}$ and $O_2^{\bullet-}$) can also be generated due to reaction between iron and aminopolycarboxylic acid in presence of oxygen molecules [58]. The generated hydroxyl radicals and ROS could damage microorganisms by attacking the cell membrane of pathogens, while diffusion of Fe and H_2O_2 into the cells can enhance the internal Haber-Weiss reactions [39]. At first, ferric iron inside the cell is reduced to ferrous iron and initiates intracellular Fenton process. In absence of MPs, low inactivation of *E. coli* (2.5 log units) at high Fe:EDDS complex ratio (1:2) could be attributed to the increased DOC content due to high concentration of EDDS, which may act as carbon source for pathogens as well as scavenger of hydroxyl radicals [59]. These results are in agreement with the findings of another study where high concentration of EDDS (0.3 mM) resulted in a decreased log inactivation of pathogenic bacteria because the high DOC in wastewater act as OH radicals scavenging [58]. Therefore, SPF with low Fe:EDDS complex (1:1) was found to be the best condition for the inactivation of *E. coli* in the present study, consistently with the results reported by Bianco et al. [60] in the inactivation of *E. faecalis*.

Inactivation kinetics data of both the treatment processes (sunlight/H_2O_2 and SPF with EDDS) with and without MPs are shown in Table 2. Noteworthy, without MPs, inactivation kinetic of sunlight/H_2O_2 (40 mg/L H_2O_2) treatment was comparatively higher (0.054 1/min) than SPF with EDDS (1:1) (0.032 1/min). On the contrary, in presence of MPs inactivation kinetics by SPF using complex ratio of 1:2 (Fe:EDDS)

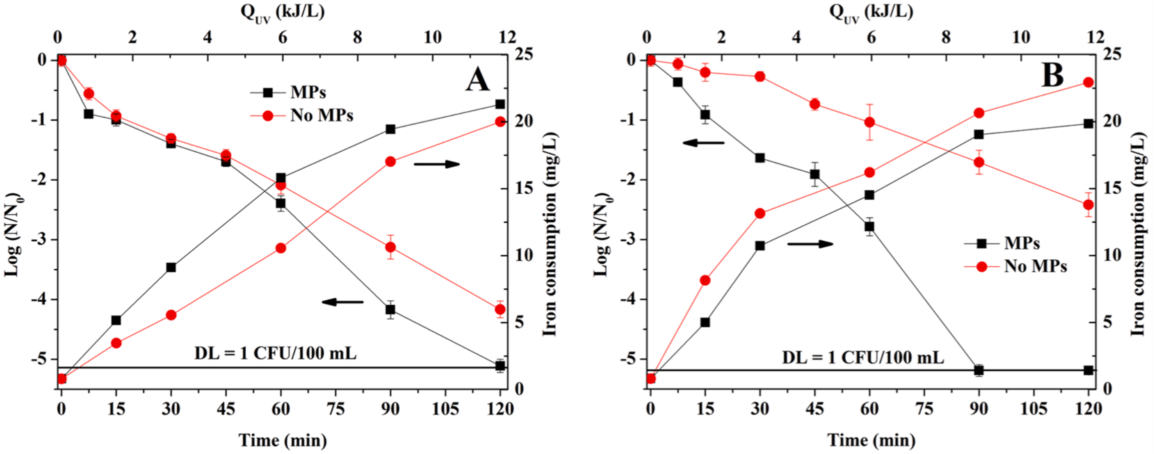

Fig. 6. Effect of Fe:EDDS complex dose (A) 1:1 and (B) 1:2 on *E. coli* inactivation with and without MPs (MPs concentration = 0.5 g/L, H_2O_2 dose = 40 mg/L, MP type = PE).

Table 2
Pseudo-first order kinetic constants *(k)* for *E. coli* inactivation by sunlight/H_2O_2 and SPF with EDDS complex in secondary treated urban wastewater.

Treatment	H_2O_2 dose (mg/L)	MPs dose (g/L)*	Fe:EDDS ratio	k (1/min)	DL
SODIS (MPs)	-	1.0	-	0.015 ± 0.002	NA
SODIS (no MPs)	-	0	-	0.025 ± 0.002	NA
Sunlight/H_2O_2 (MPs)	20	1.0	-	0.024 ± 0.006	NA
Sunlight/H_2O_2 (no MPs)	20	0	-	0.040 ± 0.005	NA
Sunlight/H_2O_2 (MPs)	40	1.0	-	0.039 ± 0.004	NA
Sunlight/H_2O_2 (no MPs)	40	0	-	0.054 ± 0.004	90 min
Sunlight/H_2O_2 (MPs)	60	1.0	-	0.027 ± 0.005	NA
Sunlight/H_2O_2 (no MPs)	60	0	-	0.045 ± 0.006	NA
SPF (MPs)	40	0.5	1:1	0.041 ± 0.002	120 min
SPF (no MPs)	40	0	1:1	0.032 ± 0.001	NA
SPF (MPs)	40	0.5	1:2	0.054 ± 0.004	90 min
SPF (no MPs)	40	0	1:2	0.020 ± 0.001	NA

* PE MPs type

showed faster inactivation kinetic (0.054 1/min) than that of sunlight/H_2O_2 (0.039 1/min) using 40 mg/L H_2O_2. Dissolved iron concentration in both the treatment processes (sunlight/H_2O_2 and SPF with EDDS) decreased by 80% (Fig. 6), possibly due to the degradation of EDDS and iron precipitation. Such high iron precipitation indicated that Fe:EDDS complex was not stable enough for long time during the treatment [61]. The residual concentration of H_2O_2 in case of SPF using Fe:EDDS ratio 1:1 and 1:2 decreased by 38 mg/L after 120 min treatment (Figs. S4 and S5).

3.2.2.2. Effect of microplastic type. The effect of MPs type (PE, PS and PVC) on the inactivation of *E. coli* by SPF was investigated too. *E. coli* concentration in PE MPs test decreased below the DL (1 CFU/100 mL) after 120 min of SPF treatment (Fig. 7). However, total inactivation of *E. coli* was not observed in the tests with PS and PVC MPs (~3.7 and ~2.6 log units reductions after 120 min of SPF treatment, respectively). The lower disinfection performance of SPF in presence of PS and PVC MPs may be due to several mechanisms simultaneously occurring during the treatment, such as light absorption/scattering by MPs [5], quenching of radicals and production of DOC [47]. The possible mechanism of *E. coli* inactivation in presence of MPs (PE, PVC and PS) during SPF treatment is illustrated in Fig. 8. MPs during photo-aging process undergo oxidation and produce ROSs [62]. However, MPs could quench EPFRs and ROSs, and inhibit the treatment performance [63]. According to previous studies, free radicals generated by oxidized PS MPs resulted in turn back attack on MPs, thereby reducing treatment performance [47,63]. PS MPs can release DOC under sunlight irradiation faster than PE MPs [64], thus reducing disinfection efficiency in wastewater containing a sufficiently high PS MPs concentration.

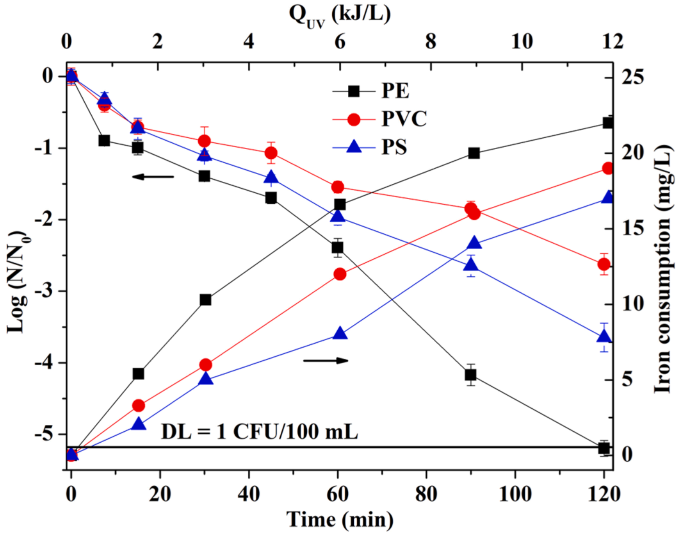

Fig. 7. Effect of MPs type (PE, PVC, and PS) on the inactivation of *E. coli* by SPF (MPs concentration = 0.5 g/L, H_2O_2 concentration = 40 mg/L, Fe:EDDS = 1:1).

3.3. Regrowth of bacteria after disinfection treatment

To the best of authors knowledge, no previous study has been performed on post-treatment regrowth of *E. coli* in presence of MPs either by sunlight/H_2O_2 or SPF with EDDS complex. The regrowth tests were carried out on samples taken in the middle and the end of treatment process (Fig. 9). A limited regrowth of *E. coli* was achieved after sunlight/H_2O_2 treatment (~1.0E+01 CFU/100 mL) in comparison to SPF with EDDS complex (~1.2 E + 02 CFU/100 mL) 48 h after treatment on

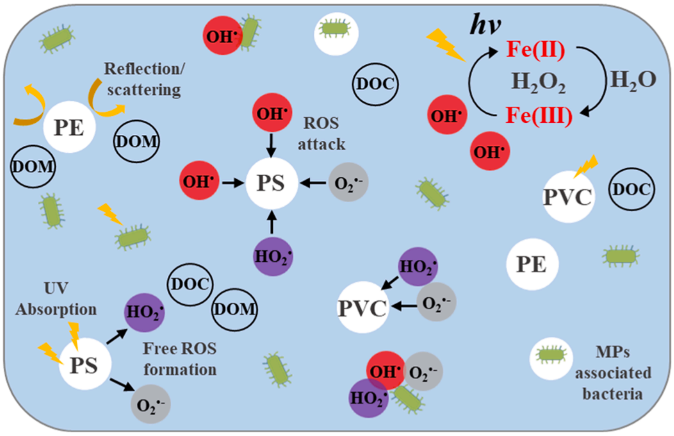

Fig. 8. Schematic representation of *E. coli* inactivation mechanism by SPF process in presence of different types of MPs.

the samples without MPs taken at the end of the process. Regrowth of bacteria without MPs at the mid stage of both treatment processes (sunlight/H_2O_2 and SPF with EDDS complex) was remarkably high (1.0E+01, 2.7E+02) compared to that one with MPs (5.0E+01, 1.7E+02). Unlike sunlight/H_2O_2 treatment (without MPs) which achieved faster inactivation, the lower inactivation of *E. coli* by SPF with EDDS (Fig. 9**B**) and, consequently, the higher residual concentration in the sample taken in the middle of the process, could be the possible reason for the higher bacterial regrowth. These results were in accordance with the findings of a previous study in which regrowth of pathogenic bacteria with sunlight/H_2O_2 treatment was limited in comparison to SPF disinfection process [65]. The damage caused to bacterial cells by SPF with EDDS complex was comparatively lower than that of sunlight/H_2O_2 for the reason explained above. Additionally, the higher concentration of DOC due to the presence of EDDS could have promoted better conditions for bacterial regrowth after disinfection. Higher bacterial regrowth without MPs could be also due to the different mechanisms of the treatment processes and subsequent stress/damage to bacterial cells [65,66]. Moreover, post-treated FeSEM images of PE MPs reveal attachment of biofilm and bacteria on their surfaces (Fig. 1**H and I**). Possibly, bacteria attached on MPs surface might be injured and could not regrowth due to lack of nutrients on MPs. On the opposite, higher bacteria regrowth in MPs free wastewater could possibility due to the higher opportunity of free bacteria to interact with nutrients in wastewater. This result is in agreement with a previous study in which regrowth of *E. coli* by sunlight/H_2O_2 treatment reached 8 CFU/mL after 48 h of incubation [33].

4. Conclusions

In this study the effects of PE, PS and PVC MPs on disinfection performance by sunlight/H_2O_2 and Fe:EDDS SPF processes and possible implications in wastewater reuse for crop irrigation were investigated. Disinfection efficiency of sunlight/H_2O_2 decreased as the initial concentration of MPs was increased. On the contrary, SPF disinfection was positively affected by MPs, *E. coli* inactivation increasing as the MPs concentration was increased, possibly due to the contribution of MPs to the formation of ROS. Compared to PE MPs, PS and PVC MPs exhibited higher interference to *E. coli* inactivation by both the treatment processes. Attachment of bacteria and biofilm formation on surface of on PE and PVC MPs confirmed by FeSEM analysis, support the interference of MPs with solar driven AOPs. Although the disinfection efficiency of SPF increased as MPs concentration was increased, it was less effective in controlling regrowth of *E. coli* (~120 CFU/100 mL) in comparison with sunlight/H_2O_2 process (~10 CFU/100 mL) 48 h after the treatment. Wastewater reuse for crop irrigation can from one side result in MPs accumulation in soil and their uptake by plants, with phytotoxicity effects, and from the other side result in a reduced bacterial regrowth due to MPs occurrence. The findings from this study suggest that sunlight/H_2O_2 and SPF with EDDS can effectively mitigate the risk associated with reuse of wastewater even in presence of MPs.

Environmental Implication

Microplastics (MPs) are considered contaminants of emerging concern due to their toxic effects on the aquatic and terrestrial environments. Recently, their occurrence in urban wastewater is attracting the interest of the scientific community not only for the impact on the environment but also for their possible interference with treatment processes. In this work the interference of three types of MPs on the inactivation of Escherichia coli by sunlight/H2O2 and solar photo-Fenton at neutral pH in real secondary treated urban wastewater, was investigated for the first time to also evaluate the possible impact on wastewater reuse.

CRediT authorship contribution statement

Mister Adeel: Methodology, Investigation, Formal analysis, Writing – original draft. **Veronica Granata:** Formal analysis, Methodology, Supervision, Writing – review & editing. **Giovanni Carapella:** Formal analysis, Methodology. **Luigi Rizzo:** Conceptualization, Methodology, Supervision, Writing – review & editing, Funding acquisition.

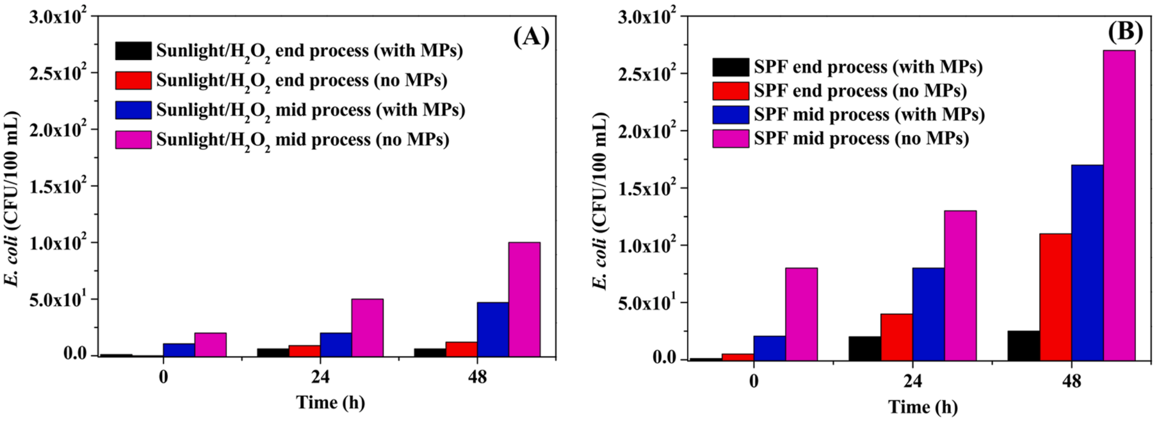

Fig. 9. Regrowth of *E. coli* with and without MPs after (A) sunlight/H_2O_2 treatment and (B) SPF with EDDS complex (1:1) (H_2O_2 concentration = 40 mg/L, PE MPs concentration = 0.5 g/L).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2023.133102.

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