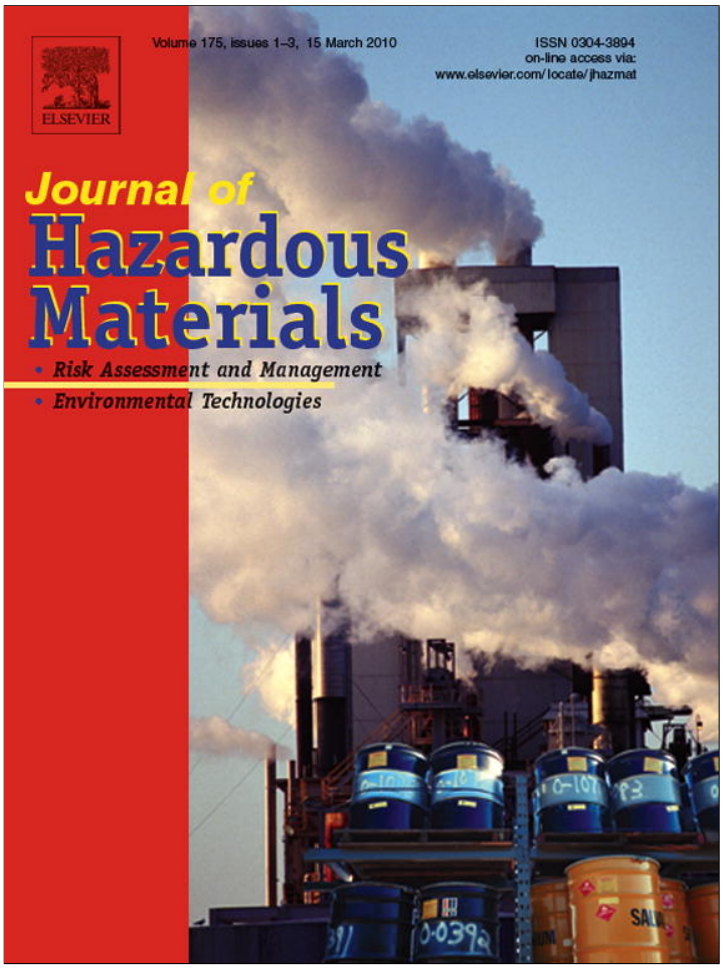

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pH induced polychromatic UV treatment for the removal of a mixture of SMX, OTC and CIP from water

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ABSTRACT

Water and wastewater effluents contain a vast range of chemicals in mixtures that have different chemical structures and characteristics. This study presents a treatment technology for the removal of mixtures of antibiotic residues (sulfamethoxazole (SMX), oxtetracycline (OTC) and ciprofloxacin (CIP)) from contaminated water. The treatment combines pH modification of the water to an optimal value, followed by a photolytic treatment using direct polychromatic ultraviolet (UV) irradiation by medium pressure UV lamp. The pH adjustment of the treated water leads to structural modifications of the pollutant's molecule thus may enhance direct photolysis by UV light. Results showed that an increase of water pH from 5 to 7 leads to a decrease in degradation rate of SMX and an increase in degradation rate of OTC and CIP, when studied separately and not in a mixture. Thus, the optimal pH values for UV photodegradation in a mixture, involve initial photolysis at pH 5 and then gradually changing the pH from 5 to 7 during the UV exposure. For example, this resulted in 99% degradation of SMX at pH 5 and enhanced degradation of OTC and CIP from 54% and 26% to 91% and 96% respectively when pH was increased from 5 to 7. Thus the pH induced photolytic treatment has a potential in improving treatment of antibiotics in mixtures.

1. Introduction

Growing awareness of the long term effects of chemical releases into the aquatic environment has increased over the last decades. Pharmaceuticals are among those emerging organic micro-contaminants due to their extensive use and their increasing occurrence in the aquatic environment. The potential sources for pharmaceutical pollution include chemical manufacture facilities, medical facilities and those who receive them and use them (humans/animals/plants). While current water treatment technologies produce water that satisfies current regulatory standards, the list of pollutants that are not regulated in drinking water is extensive, thus low concentrations of pollutants are "legally" discharged from point and non-point sources to receiving waters [1]. The potential health effects and acute toxicities of those pollutants in the environment are not well known [2]. For example, some of the major concerns of antibiotic residues (a main subset product of the pharmaceutical industry) in the environment involve the development of multiple drug resistant bacteria that will flourish and make its way into the food chain and may even severely affect human health [3,4]. Ultimately a portion of the pharmaceuticals disposed will reach domestic wastewater treatment plants (WWTPs), which do not sufficiently remove these contaminants. As a result, some of those micropollutants will be discharged to the receiving body of water or used for irrigation and may result in ground water pollution [5].

Several studies conducted throughout Europe and the USA, have confirmed the occurrence of pharmaceutical residues (e.g., antiphologistic, blood lipid regulators, anti-inflammatory drugs and antibiotics) in surface and ground water [6–8]. For example, frequently used pharmaceuticals (the anti-epileptic carbamazepine), analgesic anti-flammatory drugs (ibuprofen, diclofenac, ketoprofen and naproxen) were detected in lakes, rivers and WWTP effluents in Switzerland at concentrations ranging between 5 and 3500 ng/L [9]. More than 20 individual pharmaceuticals belonging to different therapeutic classes were found in WWTP effluents in four European countries (Italy, France, Greece and Sweden) [10]. Skadsen et al. [11] investigated the occurrence and fate of 22 compounds including pharmaceuticals, personal care products and endocrine disrupting compounds (PPCPs and EDCs), at various locations within the City of Ann Arbor's (Ann Arbor, MI, USA) water use cycle. Laboratory analysis indicated that over the four sampling cites, 17 compounds were detected in wastewater influent, 15 compounds were detected in treated wastewater effluent, 10 compounds were detected in source water (Huron River), and 4 compounds were detected in drinking water.

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The examples above show the occurrence of pharmaceutical residues in various environments and especially it emphasizes that these compounds occur as a mixture of pollutants at the source. A study by Cokgor et al. [12] demonstrated that observing the fate of individual organic compounds, while ideally desirable, proves in most cases not meaningful and sometimes misleading due to their natural occurrence in mixtures. Several studies have already showed the toxic additive effect of pharmaceuticals in a mixture, at environmental exposure levels [13–15]. Thus, more research should be conducted on mixtures of pharmaceuticals rather than a single compound.

To meet increasingly rigorous drinking water quality standards, it will be necessary to develop and adopt advanced treatment technologies for water and wastewater treatment plants. The selection of the treatment technology depends on the target pollutant, the nature of the water source and the intended use of the treated water. In most cases a combination or sequence of methods will be needed to treat mixtures of pharmaceuticals in water.

Ultraviolet (UV) treatment (as a type of 'direct' photolysis) of water is being increasingly used for disinfection of wastewater and drinking water in North America, Europe, and numerous other countries around the world. Photolysis is defined as the process by which a chemical species undergoes a chemical change as the result of the absorption of photons [16]. If a molecule absorbs a photon, it is then in an excited state and can more readily transform. For most chemicals, direct UV photolysis alone is not a practical process for degradation, however, numerous chemical contaminants of concern absorb UV at wavelengths below 300 nm; hence can potentially undergo direct photolysis [17].

Wu et al. [18] investigated the photodegradation of a widely used herbicide, metolachlor, applying monochromatic (254 nm) UV light. Approximately half of the metolachlor was degraded at UV fluence of 1000 mJ/cm^2 (at pH 7.5) which is 25 times higher than typical UV dose at water treatment plants (WTPs) required for disinfection. Shemer et al. [17], found that UV photolysis rate of 3,5,6-trichloro-2-pyridinol (a degradation product of the insecticide chlorpyrifos), increased with solution pH up to a constant maximum value of 6.40×10^{-3} cm^2/mJ at pH 5, thus was highly pH dependant within the pH range 2.5–5. Other researchers showed the influence of pH on the photodegradation kinetics of the antibiotics tetracycline [19,20], sulfadimethoxine [21] and the pesticides atrazine and bensulfuron methyl [22]. Obviously, pH impacts the degradation kinetics of many pharmaceuticals.

However, none of the previous studies have suggested the combination of direct UV photolysis together with an artificial pH modification of the treated water during the treatment itself, as a potential water treatment, aimed at removing a mixture of target pollutants at the optimum pH for each compound separately. Therefore, the goals of this study is to (a) determine the photodegradation kinetics of sulfamethoxazole (SMX), oxytetracycline (OTC) and ciprofloxacin (CIP), separately and within a mixture, using direct UV light and pH adjustment and (b) suggest a treatment solution based on pH induced polychromatic UV treatment for the optimal removal of pharmaceuticals in mixtures.

2. Materials and methods

2.1. Chemicals

SMX, OTC and CIP standards (99.9% purity) were obtained from Sigma–Aldrich, HPLC grade acetonitrile, formic acid (FA), sodium hydroxide and water purchased from Bio-Lab Ltd. (Jerusalem, Israel). All chemicals were used as obtained and working solutions were prepared with deionized (DI) water (Direct-Q3 UV system, Millipore).

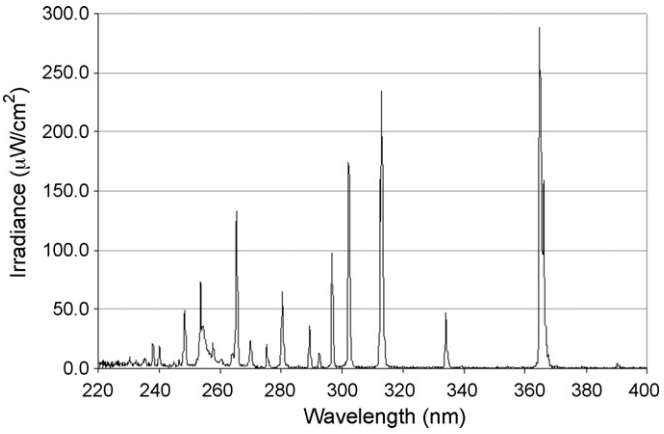

Fig. 1. Relative spectral emittance of the medium pressure mercury UV lamp.

2.2. Photolysis experimental set-up

Photolysis was carried out using a 0.45 kW polychromatic (200–300 nm) medium pressure (MP) Hg vapor lamp (Ace-Hanovia Lamp Cat. No. 7830-61, from Ace Glass Inc.), housed in a quasi-collimated beam apparatus. A 150 mL of deionized (DI) water sample was spiked with SMX, OTC or CIP to achieve a starting concentration of 1 μg/mL of each compound, separately and in a mixture. The pH of the solution was modified to the required pH value using FA or sodium hydroxide. The solution was irradiated under gentle stirring in a 85 mm × 50 mm crystallization dish (56.8 cm^2 surface area, solution depth approximately 2.7 cm) open to the atmosphere. Samples of 0.5 mL were withdrawn at appropriate intervals for chromatography analysis in an HPLC/MS apparatus. Exposure times necessary to achieve UV fluences from 0 to about 6000 mJ/cm^2 were determined from the average irradiance between 200 and 300 nm. The average irradiance was calculated using the solution spectral absorbance, the spectral incident irradiance obtained from a calibrated spectroradiometer (with spectral range at 200–390 nm and resolution of 0.45 nm FWHM; USB4000, Ocean Optics, FL, USA) placed in the same position as the center of the crystallization dish, the reflection at the sample surface and the measured petri-factor for the dish [23]. The UV fluence was calculated by multiplying the average irradiance with exposure time. UV absorption coefficient of the antibiotics solutions at different pH was measured via UV–vis spectrophotometer (Varian, Cary 100BIO, Victoria, Australia) and the molar (decadic) absorption coefficients for the antibiotics were further determined. Emission spectra of the UV lamp are shown in Fig. 1.

2.3. HPLC–MS analysis gradient conditions

The antibiotics were separated, detected and quantified by HPLC-UV Agilent, model 1100 (ACE-RP C18 column 2.5 mm × 250 mm) and an MS detector (Finnigan LCQ). The HPLC consist of a binary pump, a microvacuum degasser, a diode array detector and a thermostatic column compartment. The column temperature was set to 28 °C, the flow rate was 0.5 mL/min and the volume injected was 100 μL. UV absorption of SMX was recorded at 260 and 280 nm, OTC was recorded at 270 and 360 nm and CIP was recorded at 270 nm. HPLC mobile phase consisting of water (A) and acetonitrile (B) adjusted to pH 3 by the addition of formic acid. The eluent gradient started with 85% of eluent A followed by a 2.5-min linear gradient to 30% of eluent A, 3.5-min isocratic elution and a 2 min linear gradient back to 85% of eluent A, which was maintained for 17 min to equilibrate the column. The mass spectrometer was used in positive electro-spray ionization (ESI)

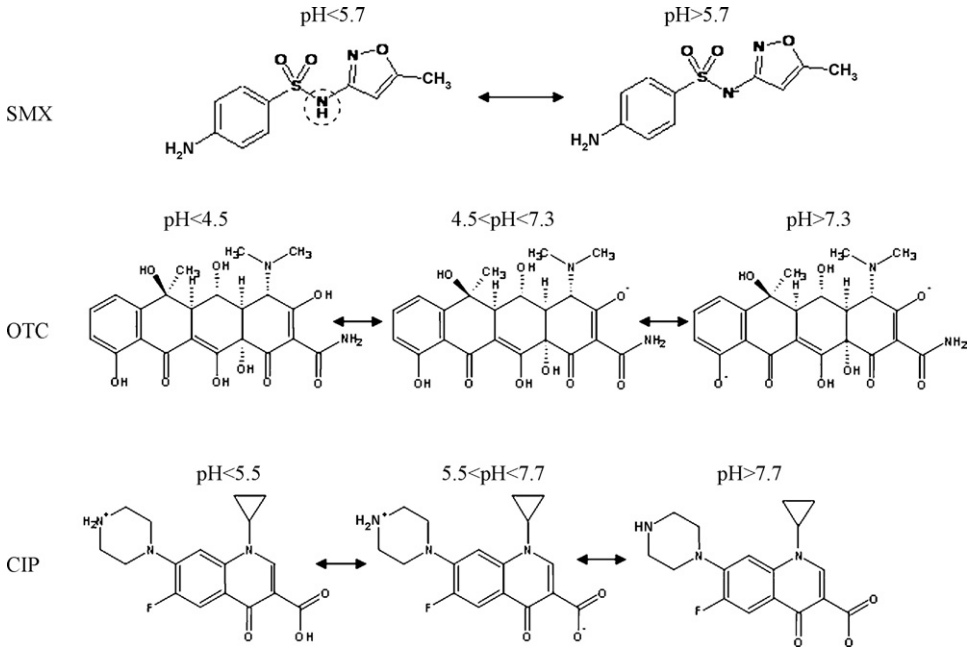

Fig. 2. Acid–base speciation of the antibiotic SMX, OTC and CIP.

mode and the probe temperature was set to 220 °C. The flow from the HPLC was passed through a split connector with 60 μL/min of effluent introduced into the MS interface. Ions were registered in the single ion monitoring mode (SIM). The sheath gas flow was 60 (arbitrary units), auxiliary flow was 11 (arbitrary units) and capillary temperature was set at 200 °C. The spray voltage was set to 4.5 kV. Instrument control, data acquisition and evaluation were performed with Xcalibur software.

2.4. The selected antibiotics

The selected antibiotics represent main antibiotic groups which were detected in the environment. SMX is a sulfonamide antibiotic, commonly used in human and veterinary medicine in food-producing animals as growth promoters and as therapeutic and prophylactic drugs for a variety of bacterial and protozoan infections [24]. OTC is a tetracycline antibiotic, used mainly in veterinary medicine and in animal feeds to maintain health and improve growth efficiency [24,25]. CIP, from the fluoroquinolones antibiotics (FQs), is an entirely man-made non-steroidal antibiotic. In its hydrochloride form, CIP is one of the most popular FQs used in human medicine [26,27]. The acid–base speciation of SMX, OTC and CIP is presented in Fig. 2.

3. Results and discussion

3.1. Photodegradation kinetic of SMX, OTC and CIP (separately)

The aim of this study was to determine feasibility of pH adjustment of water (by using an inorganic acid or base) to an optimal pH value, which depends on the micropollutant's chemical characteristics (and related to its pK_a's values). The pH modification can influence the 'electronic' (molecular/atomic) structure (e.g., extent or degree of double bond conjugation) of the target water contaminant, the absorbance, and hence the potential for photolytic degradation when irradiated at the relevant wavelength. Thus there may be a relationship between the pH, molecule structure to its absorbance.

Several researchers have correlated between the molar absorption coefficient and photolysis quantum yield (QY) of different pharmaceutical compounds and the pH of the irradiated solution. For example, Sortino et al. [28] showed that for pH values both lower and higher than 7.4, enoxacin (a fluoroquinolones antibiotic) absorption peak at 261 nm shifted towards the red and increased in intensity, while its absorption peak at 380 nm has broadened. The enoxacin photodegradation QY was also found to be highly pH dependent with maximum at pH 7.4. Fasani et al. [29] have confirmed the pH dependence of the photodegradation QY for different fluoroquinolones antibiotics, namely: norfloxacin, enoxacin and lomefloxacin. Other anti-bacterial agents such as triclosan [29–31], sulfamethoxazole and trimethoprim [32] all showed different degrees of pH dependence of their molar absorption coefficients and QY, with apparent relation to their differently charge species.

Fig. 3 illustrates the molar (decadic) absorption coefficients of the antibiotics SMX, OTC and CIP in water at initial pH of 5 and 7. All three antibiotics absorb light within the UV range. OTC has a smoother molar absorption coefficient throughout the entire UV range, while SMX and CIP show high peaks at various wavelengths. Moreover, the general trends in the molar absorption coefficients

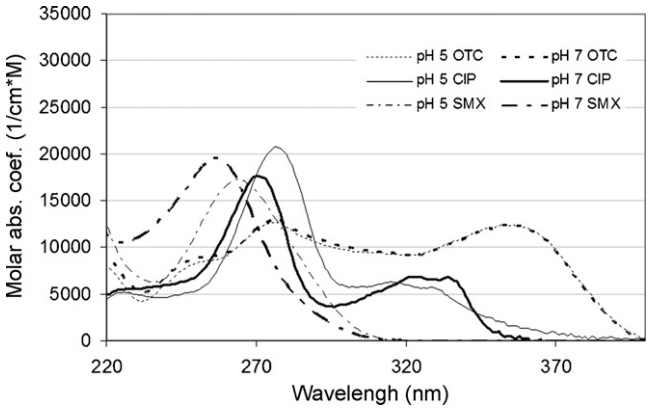

Fig. 3. SMX, OTC and CIP molar absorption coefficients at pH 5 and 7.

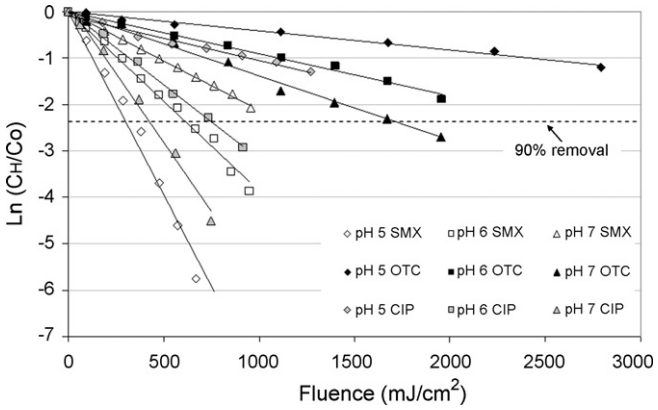

Fig. 4. UV direct photolytic degradation of 1 μg/mL SMX, OTC and CIP studied separately in deionized (DI) water, as a function of (UV) fluence at different initial pH values (5, 6 and 7) using MP collimated beam apparatus. The dashed line represents 90% degradation.

between pH 5 and 7 are similar for all antibiotics. For SMX the absorbance peak at 264 nm for pH 5 shifted to the left and peaked at 256 nm for pH 7. Moreover, the peak of SMX at pH 7 is higher at a value of 19,600 l/cm M compared to 17,200 l/cm M at pH 5. For CIP the absorbance peak at 277 nm for pH 5 shifted to the left and peaked at 270 nm for pH 7. Moreover, the peak of CIP at pH 7 is lower at a value of 17,600 l/cm M compared to 20,700 l/cm M at pH 5. Similarly to other studies, these compounds also showed different degrees of pH dependence of their molar absorption coefficients.

Fig. 4 illustrates the impact of UV photolysis of SMX, OTC and CIP studied separately in DI water using a MP lamp (200–400 nm) at pH 5, 6 and 7 to study the impact of acid–base properties on degradation of these compounds and possibly suggest conditions for enhanced removal. The degradation of the antibiotics was plotted by the natural logarithm of $[C]_H/[C]_0$ as a function of UV fluence (mJ/cm^2), where $[C]_0$ and $[C]_H$ are the initial antibiotic concentration and the concentration after UV fluence respectively. The fluence H, (the UV dose), was calculated as average fluence rate (mW/cm^2) multiplied by the exposure time (s). In all cases, the reaction kinetics between $\ln(C_H/C_0)$ and fluence were fitted using a linear regression (with $R^2 > 0.9$) resulted in pseudo-first order reaction kinetics which reflects the difference in degradation rate between the antibiotics. Linear regression analysis was used to fit the curve to the following equation:

$$\ln \frac{[C_H]}{[C_0]} = k \times H \quad (1)$$

where k is the pseudo-first-order fluence-based decay rate constant (cm^2/mJ).

Fig. 4 clearly indicates that pH highly influence the antibiotics direct photolysis rate. For example, lowering the pH of the UV treated water from pH values that exceed SMX pK_a (Fig. 2a) to values that are below it, thus from pH 7 to 5, results in a significant increase in the antibiotics degradation rate. Possibly slight shift in the absorption coefficients between pH 5 and 7 can be related to differences in photodegradation kinetics of these antibiotics. However, the key parameters to evaluate the rate of a photochemical reaction are both the quantum yield (QY) and the overlap between the emission spectra of the UV lamp and molar absorption coefficients of the compound, which quantifies the light absorbance of a compound at each wavelength. Thus, a detailed study is needed to understand the potential mechanisms of UV photodegradation with pH, molar absorption coefficients and QY which is not the aim of the current study.

Plotting the rate constant (obtained in Fig. 4) as a function of pH will allow clearly observing the trends. Fig. 5 illustrates the

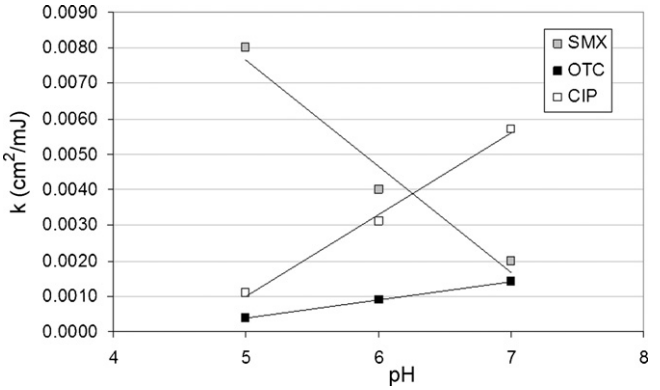

Fig. 5. Degradation rate constant [k (cm^2/mJ)] of SMX, OTC and CIP studied singly (i.e., separately), in deionized (DI) water, as a function of pH values (5–7); based on the empirical data illustrated in Fig. 4.

photodegradation rate constant of SMX, OTC and CIP as separate compounds in water as a function of pH. All compounds photolysis rate showed high pH dependency, however, while for CIP and OTC increasing pH increased photolysis rate, for SMX the opposite trend was observed. It is clear that a gradual increase of water pH from 5 to 7 leads to a decrease in degradation rate of SMX and an increase in degradation rate of OTC and CIP, thus the optimal pH values for UV photodegradation is 5 for SMX and 7 for OTC and CIP.

3.2. Photodegradation kinetic of SMX, OTC and CIP in a mixture

Initially, when studying a mixture of antibiotics compounds, the first step is to develop an analytical protocol for obtaining the full separation of these compounds. Fig. 6 illustrates a mass spectrum chromatographic separation as determined by relative abundance and MS detection of a mixed standard solution including three antibiotics: (a) SMX, (b) CIP and (c) OTC. The separation was achieved by developing an LCMS method using a gradient. The different retention times (RT) of each compound in the mixture indicates that full separation was achieved.

The aim of this part of the study is to determine the UV photodegradation of mixtures of pharmaceuticals rather than a single

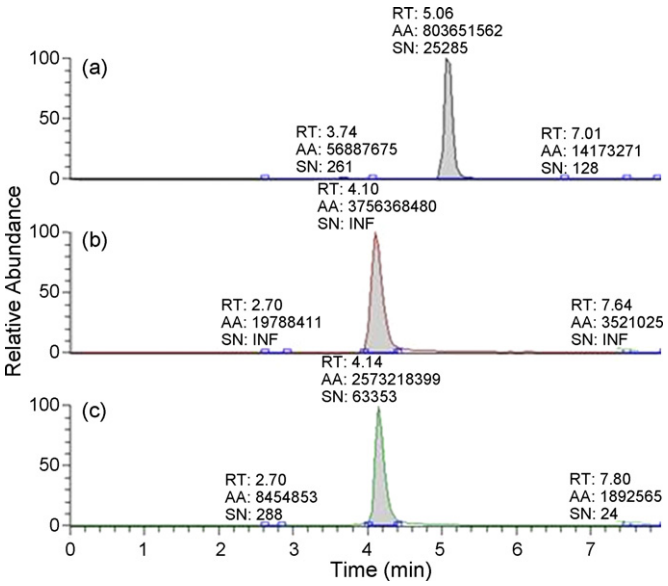

Fig. 6. MS chromatographic separation as determined by relative abundance and MS detection of a mixed standard solution including three antibiotics: (a) SMX, (b) CIP and (c) OTC. RT is retention time, AA is peak area and SN is signal to noise ratio.

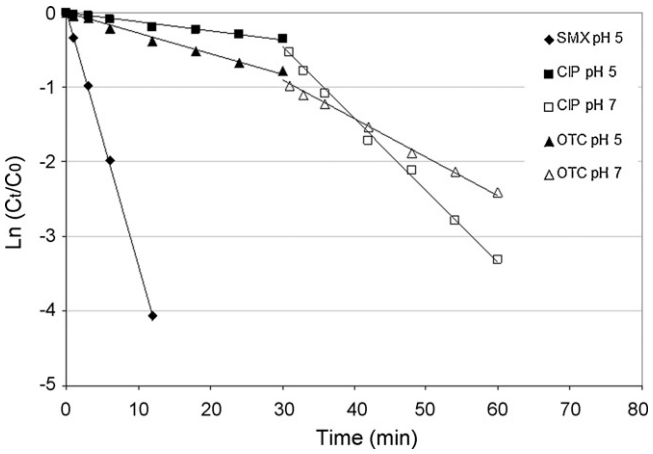

Fig. 7. Time-based photodegradation of SMX, OTC and CIP studied in a mixture, in deionized (DI) water at different pH values (5 and 7).

compound, as they naturally occur in the environment. It is essential to recall as a reference that at pH 5, SMX is mostly in its neutral form, OTC is negatively charged and CIP is positively charged; and at pH 7, SMX and OTC are mostly negatively charged and CIP is in its neutral form. Due to essential differences in optimal pH values for UV photodegradation of the examined antibiotics, the experiments of water containing all compounds in a mixture of SMX, OTC and CIP were conducted under the following conditions:

(a) Irradiation of mixed solution at pH 5 for 30 min. The goal herein is to maximize the degradation of SMX and
(b) Change the water pH to 7 following irradiation for an additional 30 min. The goal herein is to accelerate the degradation of OTC and CIP.

Fig. 7 illustrates the photodegradation of SMX, OTC and CIP studied in a mixture, in DI water at pH values of 5 and 7.

As expected, during the first irradiation time (at pH 5) the degradation of SMX was almost complete (98.4%, below detection limit), while OTC was degraded by 54% and CIP degraded by 26%. However, changing the water pH from 5 to 7 with additional 30 min of exposure resulted in a significant improvement of OTC degradation to 91% and CIP degradation to 96%. Without pH change, OTC would have been degraded 81% and CIP only 53% after 60 min of UV exposure.

The photodegradation time-based rate constants (k) for SMX, OTC and CIP, studied separately, at pH 5 was 0.7421, 0.055 and 0.0382 l/min respectively. While in a mixture, the time-based rate constants at pH 5 were 0.3368, 0.0125 and 0.0276 l/min respectively. This suggest that although these compounds are at trace concentrations, still the overall impact on the solution absorbance of a mixture reduced the rate constant of the specific compounds when in mixture compared to a compound studied separately. Nevertheless, this impact is not significant compared to the benefit of pH modification of water for enhanced photolysis.

3.3. Sequential pH optimization

Treating water contaminated with multiple contaminants (more than one) requires determining the optimal pH values for each contaminant or group of contaminants.

Sequential pH optimization (Fig. 8), can be used for an optimized photolytic treatment of water contaminated with more than one antibiotic and may include several steps as follows: (a) first pH modification of the water to optimize the degradation of one contaminant type, UV irradiation of the water and (b) a second pH modification to optimize the degradation of the second contaminant type and a second exposure to UV radiation. Fig. 8 is a schematic diagram illustrating a 'series' type exemplary specific system for treating a mixture of contaminants in water via pH optimized direct photolysis.

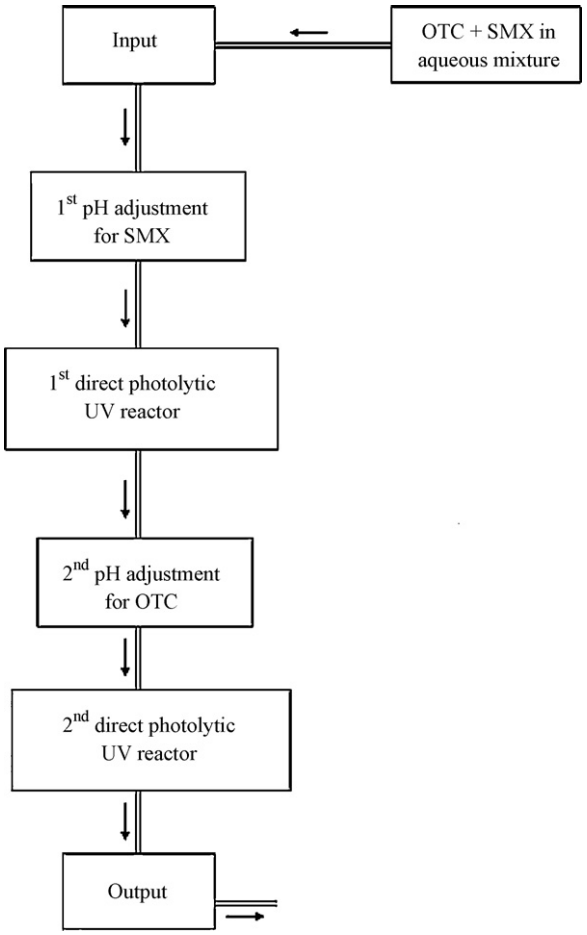

Fig. 8. Sequential pH optimization.

3.4. Practical considerations

The outcomes from this research can be applied to actual practices of UV photolysis of antibiotics. Practical outcome of this study can contribute to actual UV oxidation practices and to design of a pH modified UV based photolytic treatment. A simple calculation was conducted to determine the reduction in UV dose which can be translated to energy consumption in a plant.

Degradation of 90% of the antibiotics was chosen to emphasize the reduction in UV dose due to pH modification and improvement in energy consumption. A UV dose needed for 90% degradation of the antibiotics was calculated by inserting the adequate numbers into Eq. (2):

$$\ln \frac{[10]}{[100]} = -2.3 = k \times H \tag{2}$$

For example, in the case of SMX degradation at pH 5, degradation rate constant was 0.0079 cm^2/mJ (from Fig. 4), thus:

$$\ln \frac{[10]}{[100]} = -2.3 = -0.0079 \times H_{90\%} \Rightarrow H_{90\%} = 291\ \text{mJ/cm}^2 \tag{3}$$

Table 1
UV dose required to achieve 90% removal for OTC and SMX, at different pH values in the environmental range.

Compound	Family	Relevant pK_a (5–7)	UV dose for 90% removal (mJ/cm^2)			Reduction in UV dose (%)
			pH 5	pH 6	pH 7	
SMX	Antibiotics-sulfonamides	5.7	291	590	1095	73.4
OTC	Antibiotics-tetracyclines	3.3, 7.7, 9.7	5750	2556	1643	71.4
CIP	Antibiotics-fluoroquinolones	5.5, 7.7	2091	742	404	80.7

The reduction in UV dose (absolute value) is presented in Eq. (4):

$$\%\,\text{reduction} = \frac{H_{\text{pH 1}} - H_{\text{pH 2}}}{H_{\text{pH 1}}} \times 100 \quad (4)$$

where $H_{\text{pH 1}}$ and $H_{\text{pH 2}}$ are the maximal and minimal UV dose for 90% degradation respectively as presented in Table 1:

$$\text{For SMX}: \%\,\text{reduction} = \frac{1095 - 291}{1095} \times 100 = 73.4\%$$

Table 1 shows the UV dose required to achieve 90% removal for OTC, CIP and SMX, at different pH values and the achieved reduction in UV dose. 90% degradation of SMX at pH 5 occurred at a UV fluence of less than 300 mJ/cm^2 (approximately 4 min of UV exposure), while 90% degradation at pH 7 was achieved only after UV dose of more than 1000 mJ/cm^2 (approximately 12 min). Moreover, the absolute photodegradation rate improvement of the compounds at different pH values was as high as 81% for CIP, in other words, changing pH value from 5 to 7 for CIP improved its photolysis rate by more than 5-fold and the energy consumption as well.

3.5. Technological application

In the natural environment, pharmaceuticals and antibiotics will appear as a mixture of contaminates. For example, researchers showed the presence of numerous antibiotics (e.g., ciprofloxacin, erythromycin, ofloxacin, sulfamethoxazole, trimethoprim, metronidazole, and doxycycline) in several hospitals effluents in Germany, Sweden, Spain [33–35] and Vietnam [36]. Thus it is apparent that for the same water source these compounds are in mixtures, although most research studies present the break-down or removal of these compounds separately. Moreover, regulation of all chemicals (and pharmaceuticals in particular) that enters our water sources is nearly impossible as only a minor fraction is studied and regulated as a separate compound without considering the impact of these mixtures on human health. As a consequence, treatment technologies that can be used to treat a variety of compounds in mixtures with slight operational modifications should be designed.

The main target of the proposed treatment is defined as Pollution Prevention at Source, which is treatment of local streams contaminated by a mixture of organic micropollutants before entering the environment or reaching the central water or wastewater treatment plant, such as industrial water (food, beverage and pharmacology) and hospital wastewater. It should be emphasized that using this type of technology will require pretreatment of the water source, in order to achieve efficient removal of pollutants. However, applying the proposed treatment for "End of Pipe" use such as tertiary treatment at municipal water and wastewater treatment plants should not be overlooked.

3.6. Summary and conclusions

All pharmaceuticals investigated showed a high pH dependency. However, some compounds degrade rapidly at pH values above their pK_a and some at pH values below their pK_a; thus, pH influenced the pollutant molecules photodegradation kinetic in a variety of mechanisms. Results showed that an increase of water pH from 5 to 7 leads to a decrease in degradation rate of SMX and an increase in degradation rate of OTC and CIP, when studied separately and not in a mixture. Therefore the optimal pH values for UV photodegradation in a mixture, involves initial photolysis at pH 5 and then gradually changing the pH from 5 to 7 during the UV exposure. For better understanding the pH variation and its influence on the photolysis rate of pharmaceuticals, additional photodegradation tests should be conducted on various micropollutants and their mixtures, representing important classes of pharmaceuticals and at mixtures that represent their natural occurrence.

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