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Operational parameters affecting MB/Red-light photosensitized degradation of pharmaceuticals

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ABSTRACT

The methylene blue photosensitization under red light irradiation (MB/Red-light) is a promising and powerful tool for removal of pharmaceuticals from wastewater. To further develop this new technology, the present work aimed at studying the effect of operational parameters on the performance of MB/Red-light pharmaceuticals removal processes. Three pharmaceuticals, *i.e.* diclofenac (DFN), propranolol (PRP), and sulfamethoxazole (SFZ), were used as model compounds, and degradation rate constants and total compound removal were examined. The three operational parameters studied were initial MB concentration (0–5.0 mg/L), initial pharmaceutical concentration (0.1–2.0 mg/L), aeration rate (0–5.0 L/min), and for DFN also the pH. The results show that degradation of pharmaceuticals was promoted with increasing initial MB concentration at values of [MB] below 0.5 mg/L, and leveled off to constant values at [MB] values higher than 2.0 mg/L. Initial pharmaceutical concentration and aeration rate were found to have no significant impact. Moreover, rapid degradation of pharmaceuticals can take place even at low initial dissolved oxygen concentrations (2.0 mg/L, i.e. situations without aeration). In order to better understand the effect of pH on the MB/Red-light pharmaceutical degradation processes, DFN was chosen for more detailed investigation, with identification of the degradation products formed under neutral and alkaline conditions identified by LC–MS/MS. The pH was found to play an important role on the transformation pathways and formation of degradation products.

1. Introduction

In recent decades, pharmaceuticals have been found present at various concentration levels in the aqueous environment [1–3]. As reported by Klavarioti et al. [4], pharmaceuticals were detected in not only ground and surface water but also drinking water according to a broad range of studies [3,5–10]. Due to lack of effective regulation on acceptable emissions of the pharmaceutical compounds to natural water systems, as well as growing evidence of the associated potential hazardous impacts on the environment and human health, concerns are growing rapidly. Studies have indicated that the presence of pharmaceuticals in the environment imposes hazards to aquatic life at different levels, from algae to fish, even at low concentrations [1]. The presence of pharmaceuticals in surface, ground, and drinking water reveals the low efficacy of conventional wastewater treatment processes and drinking water production processes, *e.g.* biological processes, sedimentation, filtration, coagulation/flocculation, in removing the micropollutants [4,11]. Therefore, to cope with the problem associated with pharmaceuticals in water, more advanced treatment processes are required.

In our recent work [12], we addressed the feasibility of using red-light induced methylene blue photosensitization (MB/Red-light) to degrade diclofenac (DFN), sulfamethoxazole (SFZ) and propranolol (PRP) in aqueous solutions, where the primary oxidizing species is singlet oxygen ($^1O_2$). The MB/Red-light photosensitization resulted in rapid elimination of DFN and PRP within 2 h, with total removal of 99.7% and 83.4% respectively; the degradation of SFZ under identical conditions was much slower with lower total removal (21.8%). The MB/Red-light photosensitized degradation of pharmaceuticals has several advantages: (1) unlike the solid photosensitizers, MB is well dissolved in water, therefore the photosensitized produced $^1O_2$ has a better chance to react with pharmaceuticals in water phase; (2) the methylene blue is degraded during the process; (3) the "inner filter effect", which means absorption of light by natural organic matters (NOMs), is

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less because light absorbance by NOMs in the red light range is much less than that in the UV and near UV range [13].

For realizing the implementation of the MB/Red-light process, there is a need to optimize the MB/Red-light process to judge the feasibility and facilitate its real life applications. Although in our recent study, the authors reported that neutral and alkaline pH could favor the MB/Red-light pharmaceuticals removal processes [12]. However, the effect of other operational parameters on the MB/Red-light pharmaceutical compounds degradation process has not been studied yet. Therefore, the objective of the present work was to investigate the effect of various operational parameters, *i.e.* initial MB concentration, initial pharmaceutical concentration, and aeration rate on the MB/Red-light pharmaceutical removal process, in terms of degradation rate constants and total removal. Moreover, in order to better understand the effect of pH on the MB/Red-light pharmaceutical degradation processes, DFN was chosen for more detailed investigation, with identification of the degradation products formed under neutral and alkaline conditions identified by LC–MS/MS.

2. Materials and methods

2.1. Materials

Diclofenac (DFN), sulfamethoxazole (SFZ), metoprolol (MTP), and propranolol (PRP) were purchased from Sigma-Aldrich (Germany) and were used as received. Stock solutions of each pharmaceutical compound were prepared at concentrations of 200 mg/L for each compound. The photosensitizer methylene blue was purchased from Boom BV (The Netherlands), and a MB stock solution at 200 mg/L was prepared. Sodium dihydrogen phosphate and di-sodium hydrogen phosphate dehydrate (≥99.5%, purchased from Boom BV, The Netherlands) were used to prepare the buffer solutions. All stock solutions and reaction solutions were prepared using ultrapure water from a Milli-Q Advantage A10 system (Merck Millipore, Darmstadt, Germany).

2.2. Experimental procedures

Photosensitized experiments were conducted in a set-up which has been described in details elsewhere [12]. In each run, 500 mL reaction solutions were prepared with designated initial MB concentration, initial pharmaceutical concentration, and pH. For the experiments studying the effect of pH, 50 mM phosphate buffer was used to maintain the designated pH value, while all other experiments were conducted in natural pH (circum-neutral) and no buffer was used. Aeration rate was set to designated values. The red-LED (type LZ4-00R200 from LED-ENGIN) was mounted onto a cooling plate under the bottom of the reactor. The red light LED has an emission spectral between 600 nm to 700 nm with a maximum emission at 660 nm. The red-light LED was placed under the bottom of the reactor. The radiant power density entering the reactor was measured to be 1.77 W, by using a THORLABS S120C photodiode power sensor (THORLABS, USA). Under the applied irradiation conditions, the photon flux was calculated to be around 9.77 μmol/s. During the experiments, samples were taken at designated times and the total irradiation time of each run was 120 min. All experiments were carried out in ultrapure water (MilliPore MilliQ), and in duplicates.

2.3. Sample analysis

The MB concentration was measured with a UV/Vis spectrophotometer (Shimadzu UV-1800) at 664.5 nm. Pharmaceutical concentrations were analyzed using an Agilent LC–MS/MS system consisting of Agilent infinity 1260 LC-system (degasser, binary pump, auto sampler with cooled tray and column oven) and Agilent 6420 triple Quadrupole Mass Spectrometer with Electrospray ion source. The compounds were separated using a Phenomenex Gemini Phenyl-Hexyl column (150 × 3 mm, particle size 5 μm) and a gradient of acetonitrile (5 to 90%) and AmmoniumFormate buffer in water. The compounds were detected and quantified on the 6420-QQQ-MS using compound specific multiple Dynamic MRM transitions. Detailed information of the analytical method used can be found in literature [14].

3. Results and discussion

3.1. Effect of initial MB concentration

To investigate the influence of the initial MB concentration on the degradation rate and total removal of pharmaceuticals, experiments were carried out with varied initial MB concentrations. The initial pharmaceuticals concentrations were kept at around 1.0 mg/L, the pH was unadjusted, and the experiments were carried out under air equilibrated conditions.

To avoid the interference of produced transformation products on the kinetics, data of the first 15 min were used to calculate the pseudo-first-order apparent rate constants (k_{app}) according to the equation described in literature [15]. Moreover, considering the fact that the formation of intermediates may influence the degradation rate, total removal values of pharmaceuticals after 120 min was calculated as an indication of efficacy within the time frame of treatment in the tested systems. The results are shown in Fig. 1a. In general, a certain initial MB concentration was needed to initiate the degradation of pharmaceuticals. With initial MB concentration lower than 0.01 mg/L, none of the tested pharmaceuticals had noticeable degradation. With initial MB concentration of 0.1 mg/L, degradation of DFN and PRP was obtained but at rather low degradation rate, while no degradation of SFZ was observed. By increasing initial MB concentration from 0.1 mg/L to 0.5 mg/L, a significant increase in pharmaceuticals degradation was obtained. SFZ experienced slow degradation when initial MB concentration was higher than 0.5 mg/L, and the degradation of SFZ did not change significantly, when the initial MB concentration changed from 0.5 mg/L to 5.0 mg/L. PRP degradation took place when initial MB concentration was higher than 0.1 mg/L. With increased initial MB concentration till 1.0 mg/L, PRP degradation experienced a significant increase. However, with further increased initial MB concentration, from 1.0 mg/L to 5.0 mg/L, no significant increase in PRP degradation rate constant was obtained. The DFN degradation was obtained when initial MB concentration was higher than 0.1 mg/L. The DFN did not degrade significantly at initial MB concentrations lower than 0.1 mg/L, and degraded rapidly when initial MB concentration was higher than 1 mg/L. DFN degradation rate constant increased significantly with increased initial MB concentration till 1.5 mg/L. With further increased initial MB concentration from 1.5 mg/L to 5.0 mg/L, the DFN degradation rate constant was nearly constant.

For the pharmaceuticals total removal after 120 min treatment, initial MB concentration also influenced, as shown in Fig. 1b. In general, the total removal of pharmaceuticals increased by increasing initial MB concentration at low range. Like the degradation kinetics, the influence of initial MB concentration on the total removal is also compound-specific. The total removal of SFZ was negligible when initial MB concentration was lower than 0.1 mg/L. With increased initial MB concentration from 0.1 mg/L to 0.5 mg/L, the total removal of SFZ was significantly increased; while further increased initial MB concentration higher than 0.5 mg/L did not cause significant change in SFZ total removal. For PRP, no removal was obtained with initial MB concentration lower than 0.1 mg/L. By increasing the initial MB concentration