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Treatment of Paracetamol in Water with Different Salinities over Powder and Supported TiO_2 and ZnO Photocatalysts

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ABSTRACT. Paracetamol's (PCT) presence in water bodies poses a risk to both aquatic life and humans. This study aims to examine the effect of salinities on PCT removal in water using powder and supported photocatalysts. ZnO powder is a superior photocatalyst to TiO_2, where the rate constant can be 18 times higher. Salinity boosted the PCT removal up to 2.7 times for TiO_2 at lower concentrations but decreased the PCT removal for TiO_2 and ZnO at higher values. Immobilizing the powder photocatalysts on a nonwoven polyester support (NPS) dropped the photocatalytic activity, especially for ZnO, whose performance was 36 times lower than its powder counterpart. The passivation of the photocatalysts by the silica binder necessary for attaching the photocatalyst to the support can be linked to the decline in the performance of TiO_2 and ZnO composites. The silica and TiO_2 formed homogeneous layers on the NPS, unlike the silica and ZnO layers. High salinity reduced the performance of TiO_2 composites by 20 times but showed no significant effect on ZnO composites. The performance of the ZnO composite was further reduced when real seawater was used as feed.

Keywords: Titanium dioxide, zinc oxide, polyester, paracetamol, salinity.

INTRODUCTION

For the past three decades, pharmaceutical residues have been discovered in almost all environmental matrices on every continent, including surface water such as lakes, rivers, streams, estuaries, and seawater (Patel et al., 2019). Paracetamol (PCT), or acetaminophen, is a common analgesic and antipyretic and is one of the most prescribed and consumed drugs worldwide (Bertolini et al., 2006). PCT is included in the WHO model list of essential medicines (the 22nd list in 2021) (World Health Organization, 2021). Due to the high demand for PCT and in an attempt to reduce imports, in the early years of 2021, the Indonesian government agreed to build a PCT manufacturing facility (Wareza, 2021). Around the same time, a recent report showed the presence of a high concentration of PCT in Jakarta Bay at 420–610 ng/L; the typical concentration of PCT in marine waters is in the range of tens of ng/L (Koagouw et al., 2021). Further studies showed that short-term and long-term exposures of PCT, even at low concentrations, to adult blue mussels have the potential to alter several genes associated with processes occurring in the reproduction systems of blue mussels (Koagouw, 2021; Koagouw, 2020).

Most wastewater treatment plants (WWTPs) could not completely remove pharmaceutical residue such as PCT because they were designed to handle easily and moderately degradable organics in the mg/L range, while pharmaceutical residue that is present can be active at very low (ng/L−µg/L) concentrations, which were then released into nearby rivers and ended up in the sea (Cai, 2018; Hernández, 2019; Patel, 2019). Pharmaceutical residue may affect marine flora and fauna; therefore, studies on the removal of pharmaceuticals from saline water are important. Photocatalysis using TiO_2 and ZnO can degrade pharmaceuticals with high efficiency (Kar, 2021; Majumder, 2020; Patel, 2019; Prieto-Rodriguez, 2012; Varma, 2020). Removal of PCT by UV-based advanced oxidation processes such as TiO_2 photocatalysis and photoelectrocatalysis, including reaction conditions, dominant reactants, intermediates, and reaction mechanisms, has been well documented in the literature (Brillas, 2023; Shaban, 2019; Tan, 2014; Yang, 2008; Yang, 2009;

Zhang, 2008). Photocatalysis can be supplemented as a tertiary advanced treatment in the existing WWTPs to further degrade pharmaceutical residue in wastewater (Durán-Álvarez, 2021; Silva, 2020).

The efficacy of photocatalytic treatment of pharmaceutical residue is affected by the wastewater quality after primary and secondary treatments. One of the key parameters of wastewater quality is salinity. Wastewater originating from agriculture, aquaculture, tannery, petrochemical, and pharmaceutical industries contains a high degree of salinity (Srivastava et al., 2021). The United States Geological Survey classified saline water into four categories: freshwater (0–1,000 ppm), slightly saline water (1,000–3,000 ppm), moderately saline water (3,000–10,000 ppm), and highly saline water (10,000–35,000 ppm). Ocean water contains about 35,000 ppm of salt (Water Science School, 2018). The presence of salinity in wastewater has been reported to severely limit the performance of many wastewater treatment techniques (Srivastava et al., 2021). The roles of halide ions in PCT degradation, including its kinetics, mechanisms, and product analysis, have been reported for the UV/H_2O_2 process (Li et al., 2015). For photocatalytic processes, the influence of salinity on the photodegradation of TiO_2 has been examined for sulfadiazine, sulfamethizole, sulfamethoxazole, and sulfathiazole (Wu et al., 2019), sulfamethoxazole, sulfamonomethoxine, and sulfadimethoxine (C.-C. Yang et al., 2015), phenol (Asencios et al., 2022), and polycyclic aromatic compounds (B. Liu et al., 2016). For ZnO photocatalysts, it has been assessed for phenol (Al-Hasani, 2022; Asencios, 2022) and methylene blue (Mohammed et al., 2021). The effect of salinity on the photodegradation of PCT has been limitedly explored.

TiO_2 and ZnO photocatalysts were considered safe for humans and the environment. Hence, they were widely studied as photocatalysts. Despite being effective for PCT removal, the TiO_2 and ZnO require separation after the completion of the photocatalytic process (Chekir et al., 2020). Immobilizing the powder onto inert support, such as nonwoven polyester support, is pivotal for its use in fixed-bed photocatalytic reactors (Chekir et al., 2020). TiO_2 (Chen, 2019; Han, 2012; Park, 2008) and ZnO (Sudrajat, 2018) have been immobilized onto nonwoven polymeric support using different techniques such as dip-coating (Park and Na, 2008), spray coating (Han et al., 2012), immersion-padding-drying-baking (Chen et al., 2019), and immersion-drying (Sudrajat, 2018), and tested for removal of toluene (Park & Na, 2008), formaldehyde (Han et al., 2012), sulfaquinoxaline and thiamethoxam (Chen et al., 2019), and methylene blue (Sudrajat, 2018). The spray-coating technique uses pressurized air to deposit photocatalyst particles on a support. It offers a simple, economical, and effective method for immobilizing photocatalyst particles onto a polyester fiber at low temperatures (Han et al., 2012). To improve the attachment of the powder photocatalyst onto the support, the binder was added (Chekir, 2020; Han, 2012). A binder is a compound required to help attach the photocatalyst particles to the support. Without a binder, the photocatalyst particles will be loosely bound and easily washed off.

This study has two objectives: Firstly, to examine the effect of salinities on the photocatalytic degradation of PCT at different salinities in the presence of powder TiO_2 or ZnO photocatalysts. Secondly, to immobilize the TiO_2 and ZnO photocatalysts on a polymeric substrate using a spray-coating technique and test their performance to photodegrade PCT in water at different salinities and real seawater.

EXPERIMENTAL SECTION

Materials

Titanium(IV) oxide (21 nm primary particle size, ≥99.5% trace metal basis), zinc(II) oxide (p.a.), sodium chloride (p.a.), and LUDOX-AS-40 colloidal silica were purchased from Sigma-Aldrich. Non-fusible nonwoven polyester interlining support (NPS, area density (ρA) $=35$ g/m^2, thickness (t)$=0.198$ mm) was obtained from a local manufacturer and used as received. Paracetamol (PCT, 1000 mg/100 mL) infusions were obtained from PT Novell Pharmaceutical Laboratories and used as stock solutions. MiliQ water was used for preparing all solutions and rinsing glassware before usage.

Removal of PCT in Water with Different Salinities Using TiO_2 and ZnO Powder

1 L of PCT standard solutions of 20 ppm were prepared by diluting the stock solutions with miliQ water containing NaCl. The mass of NaCl added was varied to obtain PCT solution at different salinities, namely, freshwater (FW, 0 g/L), slightly saline water (SS, 2 g/L), medium saline water (MS, 6.5 g/L), and highly saline water (HS, 22.5 g/L).

50 mg of TiO_2 or ZnO was dispersed in 10 mL of miliQ water and ultrasonicated for 10 min. The dispersion was mixed with 40 mL of PCT (20 ppm) in a saline solution in a 300 mL crystallizing dish with a diameter of 9.5 cm. The crystallizing dish was stirred using a magnetic stirrer inside a $59.5\times49.5\times50$ cm^3 UV chamber equipped with a 15 W Philips TUV 15W/G15 T8 lamp generating a UV-C irradiation (254 nm) or a 15 W Sankyo Denki F15T8BLB lamp generating a UV-A irradiation (352 nm) at a 12.5 cm distance from the lamp. The interior of the UV chamber was layered with reflective material to allow maximum UV irradiation. At certain durations (10, 20, 30, 45, and 60 min), 1000 µL of the suspension was taken, centrifuged at 7000 rpm for at least 10 min, and filtered using a 0.22 µm regenerated cellulose membrane. The absorbance of the clear solution was measured using a Cary 60 UV-Vis spectrophotometer using a 2 mm pathlength quartz cuvette at a wavelength of 243 nm. The percentage of PCT

removal is calculated as the difference between the absorbance of the solution after UV irradiation (A_t) and the absorbance of the reference solution without UV irradiation (A_0) according to Eq.1.

$$\text{PCT removal (\%)} = ((A_0 - A_t)/A_0) \times 100\% \quad (1)$$

To obtain a more quantitative data representation, the data was fitted into first-order kinetics following previous studies on the kinetics of paracetamol removal (Brillas, 2023; Chekir, 2020; Jallouli, 2017; Shaban, 2019; Tan, 2014; Zhang, 2008) following Eq. 2 where $[\text{PCT}]_t$ and $[\text{PCT}]_0$ is the concentration of PCT at t and zero time whereas k_1 is the first-order rate constant obtained from the slope of the graph of ln([PCT]t/[PCT]0) versus time.

$$\ln([\text{PCT}]_t/[\text{PCT}]_0) = -k_1 t \quad (2)$$

Fabrication and Characterization of TiO_2-NPS and ZnO-NPS Composites

1 g of TiO_2 or ZnO powder was added to a plastic beaker containing 100 mL of MiliQ water and stirred. After 1 hour, 2.5 g of Ludox AS-40 (40 wt.% SiO_2) colloidal silica was added under continuous stirring. This recipe makes a TiO_2 or ZnO suspension at a concentration of 0.01 g/mL. The NPS was cut into a 27×12 cm^2 strip and mounted atop the vertically held metal mesh. The spray coating (SC) was done using a set-up consisting of a Tekiro AT-AB1993 airbrush with a 0.3 mm nozzle diameter that was connected to a 2.5 HP air compressor. The air pressure during the SC was set at 5 bars. The NPS was separated from the airbrush at a distance of 12 cm. The SC was done on one side of the NPS, and the NPS was blow-dried before applying the subsequent coating. After SC, the sample was further dried in an oven set at 120 °C for 1 hour.

The fabricated composite was characterized for its morphology using a JEOL JIB-4610F (FESEM). The elemental distribution in the samples was measured using the EDX attachment of the FESEM. The sample was mounted atop an SEM stub using carbon tape and sputter-coated with gold before the FESEM measurement.

Removal of PCT in Water with Different Salinities and Seawater Using TiO_2-NPS and ZnO-NPS Composites

A simple reactor set-up as shown in **Figure 1** consisting of a 250-mL graduated cylinder (h = 30 cm, D = 4 cm), a single-open quartz tube (h = 29.5 cm, D = 2 cm), and a silicone cork were assembled to form an annular-type reactor held by the silicone cork. Two holes were made through the cork to allow recirculation of the solution inside the graduated cylinder via a silicone tube connected to a peristaltic pump. A 27×12 cm^2 TiO_2 or ZnO-coated NPS was slid into the graduated cylinder, with the side coated with TiO_2 or ZnO facing the lamp. The graduated cylinder was filled with 200 mL of a solution containing PCT at different salinities. An 8 W Sankyo Genki UV-A (352 nm) lamp was connected to a power supply and inserted into the quartz tube. The cylinder was covered with aluminum foil to maximize UV irradiation. After the lamp was switched on, sampling was done every 20 minutes for a total of 360 minutes of irradiation, and the percentage of removal was calculated using Equation 1. Surface seawater in Ancol Bay at -6.120405,106.845603 coordinates were collected on May 22, 2023, at 10:53 AM. The seawater was centrifuged at 5000 rpm for 10 minutes to remove debris. The clear seawater was spiked with PCT stock solutions to obtain a 20 ppm PCT solution in the seawater. The seawater was used as feed for the photocatalytic degradation of PCT, following the method mentioned above.

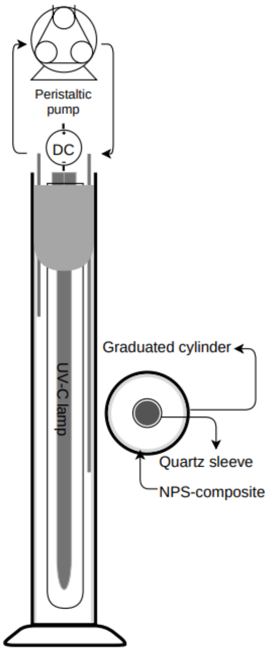

Figure 1 Schematic diagram of the reactor set-up used to test the performance of the TiO_2-NPS and ZnO-NPS composites for paracetamol removal.

RESULTS AND DISCUSSION

Effect of Salinity on the Removal of PCT over TiO_2 and ZnO Powder under UV-A and UV-C Irradiations

Figure 2 (top panel) shows the PCT removal in water with different salinities using TiO_2 and ZnO powder. The PCT removal was slow when TiO_2 was used; the PCT removal reached a maximum of 40% after 60 minutes of UV-A exposure. The PCT removal increased when there was a slight salinity present, but further increased salinity reduced the PCT removal. The PCT removal took place much faster when ZnO was utilized, and the PCT removal reached 89% after 60 minutes of UV-A irradiation. Unlike TiO_2, PCT removal slightly decreased with increasing salinity when ZnO was used. The first-order kinetic rate constant obtained from the PCT removal is tabulated in **Table 1**. The rate constant for PCT removal in freshwater by ZnO powder ($43.20\times10^{-3}min^{-1}$) was 18 times the rate constant obtained using TiO_2 powder as a photocatalyst ($2.40\times10^{-3}min^{-1}$). The rate constant for ZnO decreased to $39.80\times10^{-3}min^{-1}$ with increasing salinity. The rate constant for TiO_2 powder, however, increased initially to $6.50\times10^{-3}min^{-1}$ at low salinity and then reduced to $1.6\times10^{-3}min^{-1}$ at high salinity. The trend observed for PCT removal under UV-A irradiation was reiterated under UV-C irradiation, as shown in **Figure 2** (bottom panel). ZnO powder was a better photocatalyst for PCT removal than TiO_2 powder. Salinity slightly reduced the ZnO performance. The higher the salinity, the higher the reduction. For TiO_2, salinity increased PCT removal at low concentrations but reduced PCT removal at high concentrations.

Although it has been widely reported that salinity is detrimental to pollutant degradation, literature studies show that salinity can have a negative, positive, or no effect. Wu et al. (2019) reported that NaCl inhibited both mineralization and photodegradation of sulfadiazine, sulfamethizole, sulfamethoxazole, and sulfathiazole in the UV/TiO_2 system. Similar observations were suggested by Yang et al. (2015) for the photocatalytic degradation of sulfamethoxazole, sulfamonomethoxine, and sulfadimethoxine by TiO_2 in saline water under UV-A irradiation and by Porcar-Santos et al. (2020), who mentioned that sulfamethoxazole degradation by TiO_2 was two times slower in seawater than in deionized water by the determination of their pseudo-first-order rate constants of 0.020 min^{-1} and 0.041 min^{-1}, respectively. Rahim et al. (2022) studied the impact of salts on formic acid decomposition by TiO_2 membranes and reported that the presence of inorganic salts decreased the treatment performance of the TiO_2 membranes by half. Andreozzi et al. (2018) reported that saline-produced water was difficult to treat through photocatalytic technologies due to the very high concentration of chloride ions. The authors also reported that TiO_2 coupled with reduced graphene oxide shows higher activity than bare TiO_2 nanoparticles.

Salinity has been shown to have detrimental effects on ZnO-based photocatalysts as well. For example, Mohammed et al. (2021) reported a decrease in the removal of methylene blue by ZnO nanorods when salinity increased. Abdullah et al. (2020) observed that methylene blue photodegradation by Ce-doped ZnO decreased from 86.7% to 36.7% when the salinity increased from 0 g/L to 40 g/L. de Moraes, et al. (2023) reported that 4-chlorophenol degradation by kraft lignin-based carbon xerogel/ZnO composite under solar light was reduced by approximately 40% when the concentration of NaCl was increased to 60 g/L. The same group also reported a reduction in the salicylic acid removal by solar-based photocatalytic ozonation using ZnO/Cu_2O/CuO/carbon xerogel photocatalyst, where the rate constant reduced from 0.0272 min^{-1} to 0.0158 min^{-1} when the salinity increased from 0 g/L to 30 g/L (de Moraes, et al., 2023).

Al-Hasani et al. (2022) reported that NaCl slightly improved phenol degradation using ZnO nanorods under visible light irradiation but reduced the degradation at higher concentrations. Liu et al. (2016) reported that the increase in ion strength increased the removal rates of polycyclic aromatic compounds with lower molecular weights. In the absence of photocatalysts, salinity showed minimal effects on PCT degradation by UV/H_2O_2 treatment when the concentration was between 0 and 0.1 mol/L, but it enhanced PCT degradation when the concentration was at 0.2 mol/L, as reported by Li et al. (2015). Another researchers reported that salinity increases indirect photodegradation of PCT in simulated coastal waters (Bai et al., 2018), while Asencios et al. (2022) observed that the presence of salts from seawater did not affect the heterogeneous photocatalysis of activated carbon modified with TiO_2 under UV light significantly but was beneficial under visible light illumination.

It is widely accepted that various reactive oxygen species (ROS) such as hydroxyl radicals, superoxide radicals, and singlet oxygen participate in the photocatalytic process in deionized water. In seawater, the photocatalytic mechanisms are believed to involve halogen radicals, originating from the direct oxidation of halide ions by holes. The halogen radicals may lead to the generation of other reactive halogen species (RHS), which are less reactive than hydroxyl radicals but exhibit higher selectivity towards compounds with electron-rich functional groups (Musial et al., 2023). RHS was also reported as the main contributor to sulfamethoxazole degradation in seawater, where its degradation involved halogenation, dimerization, and oxidation pathways involving mainly reactive halogen species (Porcar-Santos et al., 2020).

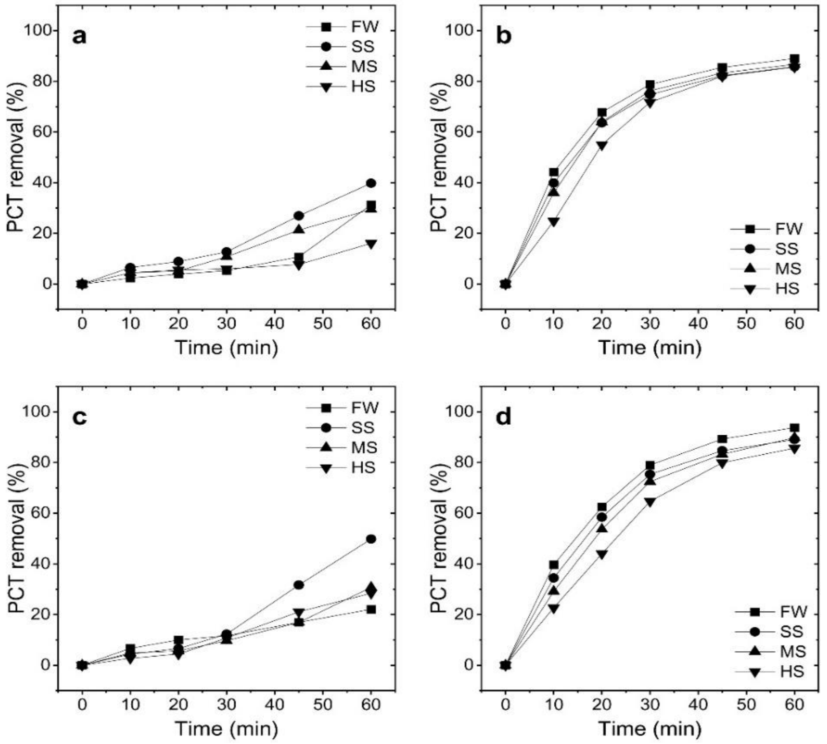

Figure 2 Removal of PCT in water with different salinity in the presence of (**a** and **c**) TiO_2-NPS and (**b** and **d**) ZnO-NPS composites under (**a** and **b**) UV-A and (c and d) UV-C irradiation.

Wu et al. (2019) explained that the inhibitory effect of chloride ions on sulfonamides photodegradation by the UV/TiO_2 system was attributed to the scavenging by chloride ions of hydroxyl radicals (Eq. 3) and holes (Eq. 4) to form less reactive chlorine radicals (Eq. 5), which blocked the active sites of TiO_2. Hence, chloride ions reduced the availability of holes and hydroxyl radicals (Eqs. 3 and 4) (Wu et al., 2019). A similar explanation was given by Mohammed et al. (2021) who studied the effect of salinity on the photodegradation of methylene blue by ZnO nanorods. They explained the hole-scavenging properties of chloride ions, which lead to a reduction in hydroxyl radicals and the formation of chlorine radicals (Eq. 4). The latter converts rapidly to chloride anions (Eq. 6), blocking the surface sites of the photocatalyst from the dye.

$$Cl^- + HO\bullet \rightarrow HOCl\bullet^- \quad (3)$$

$$Cl^- + h^+ \rightarrow Cl\bullet \quad (4)$$

$$HOCl\bullet^- + H^+ \rightarrow Cl\bullet + H_2O \quad (5)$$

$$Cl^- + Cl\bullet \rightarrow Cl_2^{-\bullet} \quad (6)$$

The low PCT removal by TiO_2 found in this study is likely correlated to the high initial PCT concentration used (20 ppm). Previous studies, for example, by Yang et al. (2008) found that the rate constant decreased with increasing initial concentration from 19.5×10^{-3}min^{-1} to 3.7×10^{-3}min^{-1} for initial concentrations of 1.0 µM and 10 µM, respectively. Zhang et al. (2008) reported that the degradation efficiency decreased from 92 to 61% after 40 min of irradiation for PCT initial concentrations of 25 and 100 µM, respectively. Shaban and Fallata, (2019) mentioned that the rate constant for PCT removal by carbon-doped TiO_2 under sunlight decreased from 81.7×10^{-3}min^{-1} to 2.9×10^{-3}min^{-1} when the PCT initial concentration increased from 2 ppm to 10 ppm, respectively. A similar observation was reported for the ZnO system by Al-Gharibi et al. (2021), who prepared Ag-decorated ZnO nanorods and reported that the highest PCT removal for 5 and 20 ppm concentrations was 92 and around 20%, respectively.

The higher activity of ZnO for PCT removal than its TiO_2 counterpart has similarly been reported by Zyoud et al. (2020), where they compared ZnO and TiO_2 nanoparticles for PCT removal under simulated solar light. They reported that the percentage of PCT (50 mL, 20 ppm) degradations by three commercial TiO_2 are lower than two commercial ZnO, where the removal ranges from 13 to 17% for TiO_2 and from 60 to 83% for ZnO after 60 minutes of irradiation. Further, they studied the effect of PCT concentration on the percentage degradation and found that the percentage degradation decreases with increasing PCT concentration, with the lowest (55%) at 40 ppm and the highest (97%) at 10 ppm PCT. The superiority of ZnO over TiO_2 for humic acid degradation has been described due to the higher electron mobility of ZnO (200–300 cm^2/Vs) than TiO_2 (0.1–4.0 cm^2/Vs), leading to higher quantum efficiency, and also because the valence band position of ZnO is lower than the valence band position of TiO_2, leading to a higher oxidation potential for hydroxyl radical generation for ZnO than TiO_2 (Turkten & Bekbolet, 2020).

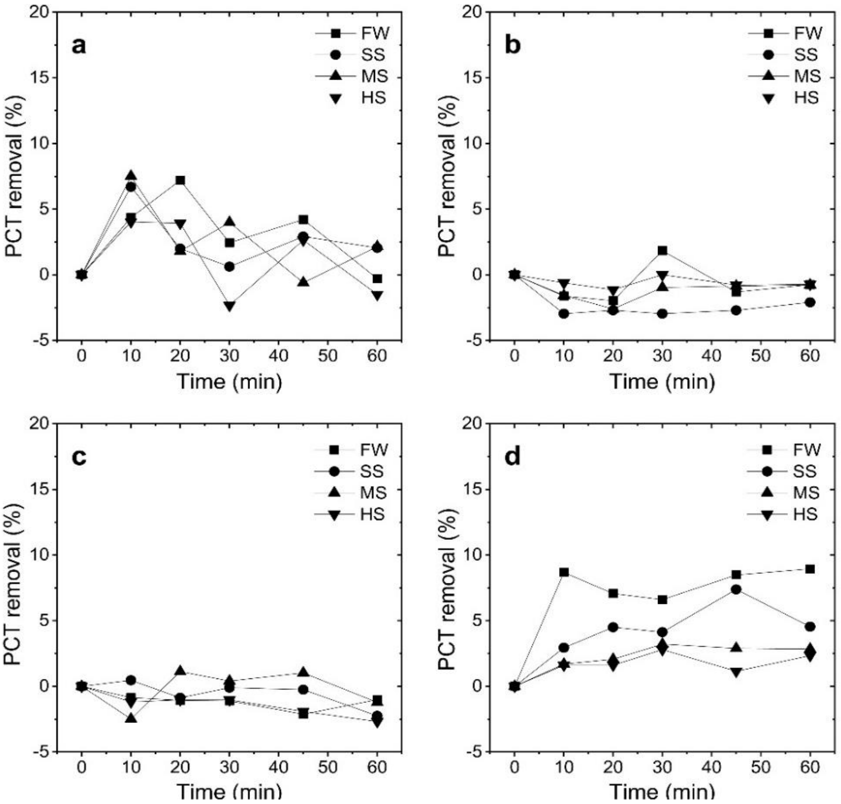

Figure 3 Removal of PCT in water with different salinities due to photolysis under (**a**) UV-A and (**b**) UV-C irradiation and due to adsorption on (**c**) TiO_2 and (**d**) ZnO powder.

Besides photocatalytic degradation, PCT removal can also be due to photolysis and adsorption. **Figure 3** (top panel) shows the PCT removal in water with different salinities due to photolysis under UV-A and UV-C irradiation. The PCT removal due to photolysis was low (less than 7%) for both UV sources, and salinities show no appreciable effect on PCT removal due to photolysis. Yamamoto et al. (2009) reported that PCT was stable against direct photolysis under sunlight, where the first-order rate constant was found to be 0.013−0.020 h^{-1}, while its half-life ranged between 35 and 56 hours. **Figure 3** (bottom panel) shows the PCT removal due to adsorption by the photocatalyst powder. The PCT removal due to adsorption on TiO_2 appeared to be negligible and there was no appreciable effect of salinities on the adsorption. In contrast, the ZnO shows a slightly appreciable PCT adsorption, with a maximum of 9% of PCT in freshwater adsorbed on the ZnO. Salinities clearly affected PCT adsorption on ZnO, where increasing salinity reduced PCT adsorption. Jallouli et al. (2017) reported that PCT adsorption by TiO_2 is affected by the pH of the solution, where the adsorption capacity is around 2 mg/g at pH 5.5–9.0 and less than 1 mg/g at pH = 2.5 or pH = 11.0.

Morphology of TiO_2-NPS and ZnO-NPS Composites

Figure 4 (a and b) show the SEM images of TiO_2-NPS and ZnO-NPS composites. The BSE images provided a stark contrast for heavy elements. In this regard, the TiO_2-NPS composites appeared to be homogeneous, while the ZnO-NPS composites were more heterogeneous, where the ZnO particles appeared whiter than the surroundings. The figure also showed that the silica binder appeared to be nanosized, similar to the TiO_2. This is in line with the manufacturer's description where the TiO_2 has a primary particle size of 21 nm, while the ludox colloidal silica has a particle size of 20-24 nm. Unlike TiO_2, the ZnO appeared to be microsized, thus forming a heterogeneous distribution seen under an electron microscope. Based on analysis of the FESEM images using ImageJ software, the average particle size of ZnO is 0.5 µm. The EDS mapping shown in **Figure 4** (c, d, e, f, g, and h) testifies that the NPS is mainly composed of carbon. The Si atoms from silica and Ti atoms from TiO_2 formed a homogeneous mixture in the TiO_2-NPS composite and the Zn atoms from ZnO attached to the NPS bound by the Si atoms from silica binder.

In this study, TiO_2 and ZnO photocatalysts were immobilized on the polyester using the spray coating technique and colloidal silica as a binder. The method used a TiO_2/SiO_2 mass ratio of 1 following a previous report by Han et al. (2012). However, the NPS used here is thinner (0.198 mm) as compared to 3 mm in Han et al. (2012). A similar composite was reported by Chekir et al. (2020), who used TiO_2 coated on nonwoven natural cellulose using silica as a binder at a TiO_2/SiO_2 ratio of 1. They also used zeolite to increase the adsorption properties of the photocatalyst. Jallouli et al. (2017) also used a similar composite as Chekir et al. (2020) and tested it for PCT removal under solar light. Other than silica, an inorganic binder such as aluminum alkoxide has been used (Park & Na, 2008). Other reports used organic binders such as polymethylmethacrylate (Marandi et al., 2011), polyvinyl alcohol (L. Liu et al., 2012), polyethylene glycol, polyacrylic acid (Sukitpong & Chiarakorn, 2019), chitosan, and PVDF (Abed et al., 2019).

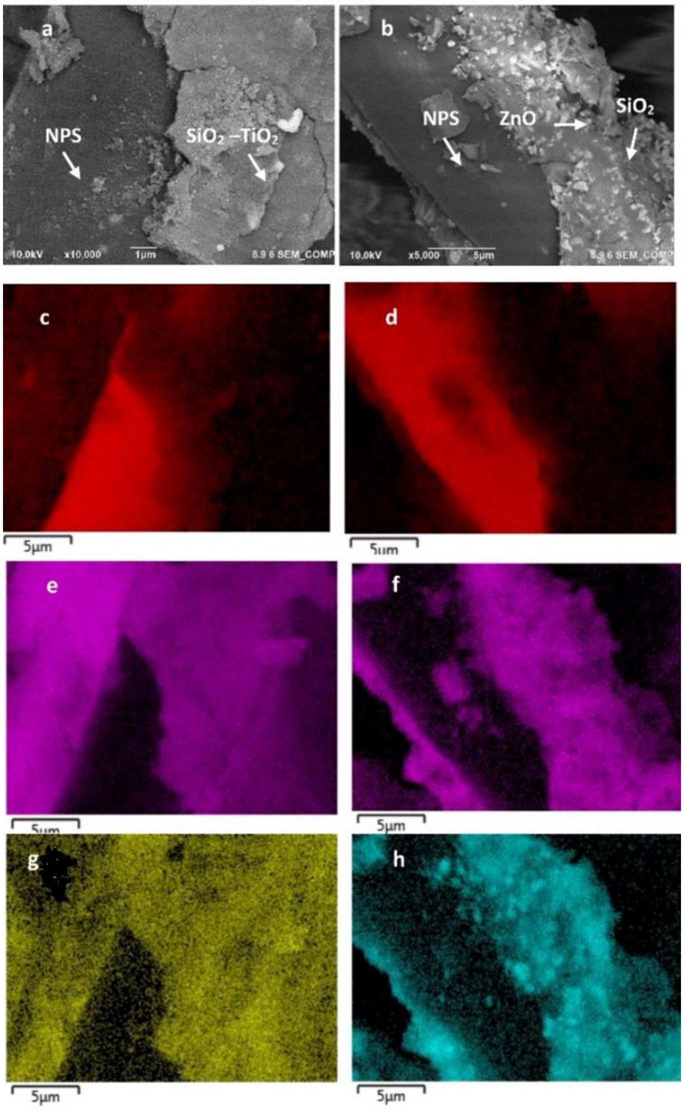

Figure 4 BSE micrographs of (**a**) TiO_2-NPS and (**b**) ZnO-NPS at 10K magnification and elemental distribution of (**c** and **d**) C, (**e** and **f**) Si, (**g**) Ti, and (h) Zn atoms in (**c**, **e**, and **g**) TiO_2-NPS and (**d**, **f**, and **h**) ZnO-NPS composites.

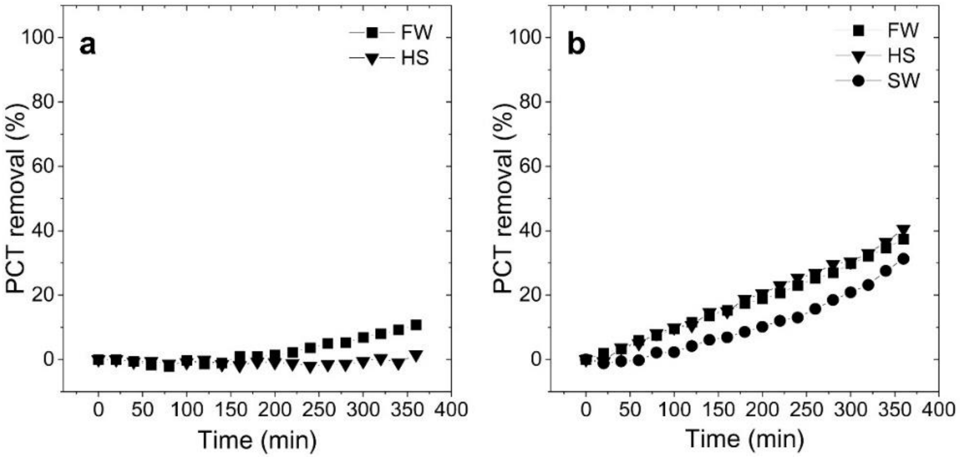

Figure 5 Removal of PCT in water with different salinity in the presence of (**a**)TiO_2-NPS and (**b**) ZnO-NPS composites under UV-A irradiation.

Effect of Salinity on the Removal of PCT over TiO_2 and ZnO Composites under UV-A Irradiation

Figure 5 shows the performance of TiO_2 and ZnO composites for PCT removal in fresh water and water with high salinity under UV-A irradiation. Although TiO_2 powder showed appreciable performance for PCT removal, its composite counterpart showed poor performance. The PCT removal only reached 11% for 360 minutes of UV-A irradiation. The calculated rate constant for PCT removal was $0.40\times10^{-3}min^{-1}$ compared to $2.40\times10^{-3}min^{-1}$ for TiO_2 composite and TiO_2 powder, respectively. High salinity appeared to inhibit PCT removal to an almost negligible degree; the rate constant was $0.03\times10^{-3}min^{-1}$ at high salinity. The PCT removal inhibition due to high salinity was similarly observed for the powder form of the photocatalysts as mentioned earlier. The reduction in the PCT removal by supported photocatalyst was similarly observed for the ZnO photocatalyst, where the PCT removal reached a maximum of 41% for 360 minutes of irradiation. The calculated rate constant was $43.20\times10^{-3}min^{-1}$ for ZnO powder and $1.20\times10^{-3}min^{-1}$ for ZnO composite. Unlike TiO_2 composite, high salinity appeared to give no significant effect on PCT removal using ZnO composite photocatalysts; the rate constant was $1.40\times10^{-3}min^{-1}$ at high salinity. The reason why ZnO composites can withstand higher salinity than TiO_2 composites can be linked to the higher electron mobility and higher oxidation potential for hydroxyl radical generation in ZnO than in TiO_2 (Turkten & Bekbolet, 2020).

Since the ZnO composite showed better performance than the TiO_2 composite, it was tested for PCT removal in real seawater. **Figure 5** shows the performance of the ZnO composite for PCT removal in seawater under UV-A irradiation. The PCT removal is low, with a maximum removal of 31% after 360 minutes of irradiation. This is slightly smaller than the PCT removal in water with high salinity (41%). Although salinities appeared to have no significant effect on PCT removal using ZnO composite. It should be noted that the artificial water with varying salinity used in this study contains only Na^+ and Cl^- ions. Real seawater contains not only Na^+ and Cl^- ions, but also other ions such as SO_4^{2-}, Mg^{2+}, Ca^{2+}, K^+, HCO_3^-, Br^-, BO_3^{3-}, Sr^{2+}, and F^-. Real seawater also contains dissolved organic and inorganic carbon (Anthoni, 2006). The higher salt content in seawater and the complex composition of real seawater may have further reduced the removal to a lower number. The calculated rate constant for PCT removal in real seawater is $1.00\times10^{-3}min^{-1}$ compared to $1.20\times10^{-3}min^{-1}$ in fresh water.

In this investigation, photocatalyst powder outperformed its composite counterpart in terms of PCT elimination. Similar findings were made by Jallouli et al. (2017), who discovered that the TiO_2 suspension/UV system is more efficient than the TiO_2/cellulosic fiber combined with solar light. The use of silica binder may be related to the decline in performance of the photocatalyst composite. Due to its similar size, the TiO_2-SiO_2 mixture produced a uniform mixture on the surface of the nonwoven support, as evidenced by the FESEM picture of the composite. However, because ZnO and SiO_2 had particles with different sizes - microns versus nanometers - on their surfaces, ZnO took on a heterogenous appearance on the surface of polyester. SiO_2 is an inactive photocatalyst; hence, the decrease in performance of the composite can be attributed to the SiO_2 on the NPS, which passivates the active TiO_2. Previous researchers have noted that after combining with SiO_2, TiO_2 loses some of its photocatalytic activity. For example, Temerov et al. (2021) prepared TiO_2/SiO_2 nanoparticles using the liquid flame spray technique and found that the photocatalytic gas phase acetylene oxidation was completely removed by adding 5% of SiO_2, which can be attributed to the formation of a thin passivating SiO_2 layer on top of the TiO_2 nanostructures. A similar observation was reported by King et al. (2008), who coated TiO_2 with a SiO_2 layer using the atomic layer deposition technique and reported that the photocatalytic conversion of isopropanol to acetone of anatase pigment-grade TiO_2 was decreased by 98% after the deposition of 2 nm SiO_2 films. The spray-coating technique used in this research may not have completely covered the TiO_2 nanoparticles with the SiO_2 layer, as the composites still retain certain photocatalytic activity. While the silica binder is required to increase active photocatalyst attachment to the NPS, the ratio between the silica binder and active TiO_2 must be fine-tuned to obtain a mechanically stable and yet still active composite, as it forms a mixture of photocatalytically active and inactive particles on the NPS support.

Table 1. Summary of first-order rate constant ($\times10^{-3}$ min^{-1}) of PCT removal by powder and supported TiO_2 and ZnO photocatalyst under UV-A irradiation.

	Fresh Water		Slightly Saline		Medium Saline		Highly Saline		Real Seawater	
	k_1	r^2	k_1	r^2	k_1	r^2	k_1	r^2	k_1	r^2
Powder										
TiO_2	2.40	0.9539	6.50	0.9235	5.10	0.9227	1.60	0.8426		
ZnO	43.20	0.9691	38.70	0.9705	41.00	0.9733	39.80	0.9895		
Supported										
TiO_2-NPS	0.40	0.9417					0.03	0.1146		
ZnO-NPS	1.20	0.9865					1.40	0.9843	1.10	0.9438

CONCLUSIONS

TiO_2 and ZnO powders, as well as their polyester composite counterparts, have been studied for their ability to remove paracetamol from water with varying salinities. TiO_2 is not nearly as effective as photocatalyst ZnO powder in removing PCT. Salinity increased PCT removal for TiO_2 at low concentrations but decreased PCT removal for TiO_2 and ZnO at high concentrations. The photocatalytic activity decreased when the powder photocatalysts were immobilized on a nonwoven polyester substrate. High salinity drastically decreased the performance of the TiO_2 composite but had no discernible impact on the ZnO composite. When real saltwater was used as the feed, the ZnO composite's performance was further lowered. The passivation caused by the photocatalytically inactive silica binder can be connected to the decreased PCT elimination by the composites.

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