Metronidazole in a UV-TiO_2 photocatalytic system: Fate, removal and mineralization

Neghi.N[1] and Mathava Kumar[1*]

[1]Environmental and Water Resources Engineering Division, Department of Civil Engineering, IIT Madras, Chennai- 600 036, India.
(*Corresponding author; E-mail: *mathav@iitm.ac.in; mathavakumar@gmail.com)*

Abstract
In this investigation, metronidazole (MNZ) removal in a batch photocatalytic system was investigated. All experiments were conducted at an initial MNZ concentration of 15 mg L^{-1} at room temperature and without pH control. The effect of UV power (0, 16 and 32 W), the presence of catalyst (0 and 2.5 g L^{-1}) and the type of catalyst (TiO_2 or GAC) were investigated in a double-walled cylindrical reactor. At the end of 120 min, a maximum of 98.1% MNZ removal was observed in the reactor operated under 32W UV power and 2.5 g L^{-1} TiO_2. A decrease in UV power (i.e. from 32 W to 16 W) has resulted a corresponding decline in MNZ removal efficiency (i.e. 94.1%) under similar experimental conditions. The data from kinetic study revealed that MNZ removal followed the pseudo first-order kinetics with a maximum MNZ removal rate constant of 0.026 min^{-1}. In the absence of catalyst, the photolytic systems operated with 32 and 16W power have produced 42% and 24% MNZ removals, respectively, at the end of 120 min. On the other hand, MNZ removal by adsorption on the surface of nano-TiO_2 was negligible, which ensured that MNZ removal in the reactor was mainly by photolysis. The application of GAC as a photocatalyst and adsorbent in the reactor has shown 77.5% and 32.5% of MNZ removal, respectively. These observations indicate that GAC can be used as a catalyst in photocatalytic investigations. Subsequently, the economic analysis (i.e. energy consumed (kWh) and electrical energy per order (E_{EO}, kWh m^{-3} $order^{-1}$)) was performed using the experimental data from photolysis, photocatalysis, and adsorption systems. The E_{EO} calculations pointed out that photocatalytic process (0.077 kWh m^{-3} $order^{-1}$) turns out to be an energy efficient system compared to photolysis (0.141 kWh m^{-3} $order^{-1}$) and adsorption (0.296 kWh m^{-3} $order^{-1}$) for MNZ removal.

Keywords
Antibiotics; Economic analysis; Metronidazole; Photocatalysis; Wastewater treatment.

INTRODUCTION

Pharmaceutically active compounds (PhACs) enter the water bodies through production plants, illegal discharge wastes mainly from hospitals, disposal of human and animal excreta containing PhACs and unethical disposal of unused drugs. Antibiotics, one of the major classes of PhACs, are used in veterinary and human medicines which have detrimental effects to living organisms even at low concentrations (Kummerer, 2009; Mompelat et al., 2009).

Metronidazole (2-(2-Methyl-5-nitroimidazol-1-yl) ethanol, MNZ) is an antibiotic extensively used for treating infections caused by anaerobic bacteria, protozoa and bacteroides. It has been found to be genotoxic to humans, toxic to aquatic organisms and potentially carcinogenic and mutagenic. MNZ has been utilized as an additive in poultry and fish feeds for eliminating parasites. As a result, MNZ has been found in animal tissues, discharged from fishfarm wastewater and effluents from meat processing industries and hospital wastewaters. MNZ is highly soluble in water (9.5 g L^{-1}) and poorly biodegradable, which cause their entry into surface and groundwater sources (Perez et al., 2015). MNZ was detected in the range of 2 to 40 µg L^{-1} and 30 ng L^{-1} in the wastewater influent analyzed at 7 major WWTPs and in river waters of Spain, respectively (Gros et al., 2010). Lindberg et al., 2004 reported the presence of nitroimidazole antibiotics in waters at concentrations of 0.1 to 90.2 µg L^{-1}. There is an alarming concern with the presence of antibiotics including MNZ in treated water from conventional WWTPs. owing to the inadequate removal of emerging micropollutants in the existing sewage treatment facilities (Suarez et al., 2008). On the other hand, advanced oxidation processes (AOPs) such as photolysis and photocatalysis, ozonation, Fenton and photo-Fenton, ultrasound irradiation, sonolysis, electrochemical oxidation and wet air oxidation are useful for the removal of PhACs from water and wastewater (Kanakaraju et al., 2014). Among the AOPs, photocatalysis with TiO_2 has been found to be very effective in the removal of PhACs and biorefractroy compounds owing to the following reasons: (1) scalable to large volumes with necessary technical specifications and also could be operated in a continuous mode (2) TiO_2 is an ideal photocatalyst which is chemically and biologically inert, photoactive, photostable, inexpensive, non-toxic (3) TiO_2 can be excited with visible and near/or UV light (4) the hydroxyl radicals developed in the system is non-selective with the high oxidation potential (E^o = 2.8V/ SHE) (Andreozzi et al., 1999; Friedmann et al., 2010) and also (5) this system which employs UV-C band of light for the treatment will be able to handle antibiotic resistant genes in microbes that are developed due to trace concentrations of antibiotics in water. Therefore, semiconductor-mediated photocatalysis, in particular with TiO_2, has been receiving huge interest among the researchers to take-up the research on antibiotics removal from domestic and industrial wastewaters.

However, the efficiency of UV-TiO_2 system (i.e. mineralization of the target compound) depends on the nature of target compound and the reaction conditions. The economic analysis correlated with the energy consumed and electrical energy per order in the system is really useful to decide upon the applicability of the developed system for the real-time conditions (Vishnuganth et al., 2016). In the past, several investigations were carried out to investigate the feasibility of photocatalysis system for the removal of antibiotics (Hu et al., 2011; Martinez et al., 2013; Jallouli et al., 2014; Asha et al., 2015; Constantin et al., 2015). To our knowledge, this is the first study to investigate the removal of MNZ in a photocatalytic system with TiO_2 and GAC, and also to correlate the results of MNZ removal with the economic analysis. The major objectives of this investigation are to (a) check the feasibility of MET removal by photocatalysis, (b) quantify the roles of catalysts and UV power on MNZ removal and (c) correlate the MNZ removal with economic analysis to identify the best suitable condition for MNZ removal.

MATERIALS AND METHODS

Chemicals

MNZ analytical standard (99%) was purchased from Sigma-Aldrich and used as received. Anatase form TiO_2 (size range of <25 nm, surface area of 45-55 m^2/g and with a density of 3.9 g mL^{-1} at 25°C) was purchased from Sigma-Aldrich and used for experiments. The adsorbent, i.e. GAC, with a particle size fraction of 2-5 mm and with a bulk density of 0.4 kg m^{-3} was supplied by S.D Fine Chemicals Limited, India. The specific surface area (S_{BET}) and total pore volume (V_T) of GAC are as follows: $S_{BET} \sim 1010\ m^2\ g^{-1}$ and $V_T \sim 0.532\ cm^3\ g^{-1}$. Acetonitrile and deionized water were used for HPLC analysis and purchased from Merck, Germany.

Batch photocatalytic reactor setup

A double-walled cylindrical reactor with 1.9 L working volume was fabricated and used for photolytic and photocatalytic experiments. The required UV power was provided by UV lamps (each of 16W power with λ_{max} at 254 nm). A stirring rod was attached to the electronic overhead stirrer as shown in Figure 1 to mix the reactor contents and ensure the catalyst in suspension. In addition, ports were provided to accommodate pH, temperature and ORP probes and to collect samples from the reactor during the course of the reaction (Fig 1).

Experimental methodology

The photolytic and photocatalytic experiments were carried at a fixed initial MNZ concentration of 15 mg L^{-1} and at room temperature (i.e. maintaining constant temperature by recirculating the tap water through the double-walls). Before initiating the catalytic reaction, exactly 2.5 g L^{-1} of catalyst (i.e. TiO_2) was added into the reactor and immediately, the UV power was supplied via the required number of UV lamps. At time intervals of 0, 5, 10, 15, 30, 60 and 120 min, aliquots were withdrawn from each system and analyzed for pH, temperature, oxidation-reduction potential (ORP), chemical oxygen demand (COD), total organic carbon (TOC) and MNZ concentration. In addition, the experiments were repeated only in the presence of catalyst (i.e. with TiO_2 or GAC but without UV power) to estimate the MNZ removal by adsorption. Under similar condition, an additional set of experiments were conducted (a) in the presence of GAC and with UV power to estimate the role of GAC as a catalyst and (b) in the absence of catalyst and with UV power to estimate the MNZ removal by photolysis. The consolidated list of experiments and their conditions are shown in Table 1.

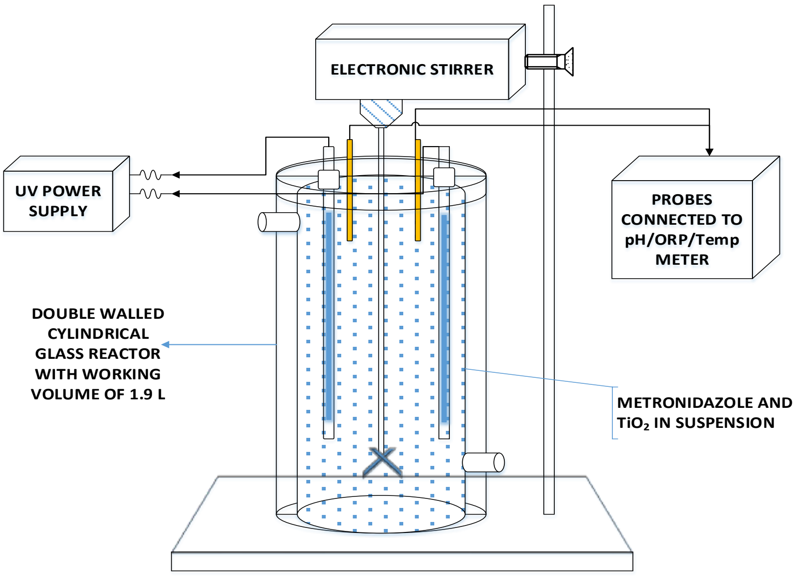


Figure 1. The schematic diagram of double-walled batch photocatalytic reactor

Table 1. List of experiments and their conditions

Run No.	Initial MNZ concentration (mg/L)	UV Power (W)	Catalyst dosage (g/L)	Type of catalyst
Run-1	15	-	-	-
Run-2		16		
Run-3		32		
Run-4	15	-	2.5	TiO_2
Run-5		16		
Run-6		32		
Run-7	15	-	2.5	GAC
Run-8		32		

Analytical techniques

MNZ and its metabolites

MNZ was analyzed using HPLC/UV-Vis (Dionex, Ultimate 3000) using a C_{18} (220 mm (L) × 4.6 mm (I.D) silica based reverse phase column. Acetonitrile and deionized water (Milli-Q) was mixed in the ratio of 60:40, respectively, and used as the mobile phase. The column flow rate was maintained at 1 mL min^{-1} and operated in isocratic-mode. The wavelength of the UV detector was set at 254 nm. Exactly, 20 µL of the sample was injected manually. Under these conditions, the MNZ peak was observed after a retention time of 2.7 min. The metabolites of MNZ were analyzed using a liquid chromatography with a double mass-spectrophotometer (LC-MS-MS) (ThermoElite, USA) operated under positively induced ion scanning-mode and through direct infusion method. The analyzer was maintained at an electro spray voltage of +1.5 kV ion source, heater temperature of 360°C and a capillary temperature of 350°C, and the samples were injected manually.

TOC analysis

Organic carbon constituents of MNZ were analyzed using TOC analyzer (Shimadzu, Japan) equipped with NDIR analyzer. The results are obtained as total carbon and inorganic portion of the carbon present in the sample.

SEM analysis

The surface morphology of TiO_2 was characterized by field emission scanning electron microscopy (SEM) at an accelerating voltage of 30 kV (Genisis 2000, Emcrafts). The elemental composition of the samples was quantitatively determined using energy dispersive spectroscopy (EDS, Genisis 2000). The samples were dried and coated with gold prior to scanning.

Other analytical techniques

The pH, ORP and temperature of the reactor contents were measured using a bench top multi-parameter analyzer (OAKTON, India). COD analysis was performed as per The Standard Methods (APHA, 2002).

Data Analysis

Using the residual COD and MNZ concentration observed in the systems, the percentage removals of MNZ and COD were calculated using the Eq. (1).

$$\eta = \frac{C_0 - C_f}{C_0} \times 100 \qquad (1)$$

Many recent researchers have reported that the photocatalytic degradation of aqueous pollutants in the presence of TiO_2 followed the Langmuir-Hinshelwood (L-H) kinetic model (Perez et al., 2015; Safari et al., 2015; Prados-Joya et al., 2011; Hapeshi et al., 2010). The model is expressed by Eq. (2).

$$r_1 = -\frac{dc}{dt} = \frac{K_1 K_2 C}{1 + K_2 K_o} = k_1 C \qquad (2)$$

Where C_0 is the initial concentration of MNZ (mg/L) and C is the MNZ concentration at time (t, min).The parameters k_1, K_1 and K_2 are pseudo first-order rate constant, surface reaction rate constant (mg/L-min) and L-H adsorption equilibrium constant (L/mg), respectively. When the solution is highly diluted (i.e. C (mol L^{-1}) < 10^{-3}), the term K_2C becomes less than 1 and the denominator of Eq. (2) can be neglected. As a result, the reaction would essentially be reduce to an apparent first-order reaction. Therefore, Eq. (2) can be simplified to a first-order equation by integration as shown in Eq. (3) when C_0 is very small.

$$\ln \frac{C}{C_0} = -k_1 t \qquad (3)$$

A plot between $\ln(C/C_0)$ and t was prepared and the value of k_1 was found out from the slope of straight line. The validation of the results was carried out by analyzing r^2 value of the plot. On the other hand, the electrical energy required for UV-TiO_2 photocatalytic treatment accounts for a major fraction of operating cost and it was calculated as per Eq. (4).

$$\text{Energy consumed per mg of MNZ removal} = \frac{\text{Energy used (W)} \cdot \text{Reaction time (min)}}{1000 \times 60} \qquad (4)$$

Moreover, the energy required to reduce the contaminant concentration by one order of magnitude in addition to the energy consumed by the whole system (E_{EO} as shown in Eq. 5) was used to identify the effectiveness and scale-up of the system for field-scale applications (Vishnuganth et al., 2016).

$$E_{EO} = \frac{P \times t \times 1000}{V \times 60 \times \log \frac{C_0}{C_f}} \qquad (5)$$

In Eq. (5), the parameters P and V denote the power consumed in the system (in Watt) and volume of the reactor in litres (i.e. 1.9 L), respectively. C_0 is the initial MNZ concentration and C_f represents the final MNZ concentration.

RESULTS AND DISCUSSION

MNZ removal by photolysis

After UV irradiation of 120 min, the degradation of MNZ reached 23.9% and 42.4% when supplied with UV power of 16W and 32W, respectively. The corresponding COD reduction was found to be 17.5% and 31.1%, which indicated that complete mineralization of MNZ was not achieved in the photolytic system. This is due to the fact that under direct photolysis only limited number of OH· radicals are formed in the bulk solution and presumably, the degradation was due to oxidation under irradiation or hydrolysis of the antibiotic in water. Prados- Joya et al. showed similar trend in the degradation of nitroimidazoles under direct photolysis carried out with 15W UV lamps (Prados-Joya et al., 2011). Several other researchers also reported similar results for the degradation of tetracycline, amoxicillin, sulfamethaxazole and ofloxacin antibiotics using UV process (Safari et al., 2015; Gao et al., 2012; Hapeshi et al., 2010). The results of different experimental runs are summarized in Table 2.

Table 2. Analysis of different experimental runs

Run No.	Removal (%) after 60 min		Removal (%) after 120 min		Rate constant 'k$_1$' (min^{-1})	Energy Consumed* (KWh)	E_{EO} (KWh m^{-3} order^{-1})
	MNZ	COD	MNZ	COD			
Run-1	1.4	4.0	1.4	4.0	0.000	0.000	0.000
Run-2	23.6	15.3	23.9	17.5	0.002	0.032	0.144
Run-3	33.8	16.9	42.4	31.1	0.004	0.064	0.141
Run-4	15.6	48.8	18.7	61.2	0.001	0.150	0.877
Run-5	61.1	56.3	94.1	72.2	0.022	0.172	0.077
Run-6	62.4	60.0	98.1	80.7	0.026	0.204	0.080
Run-7	21.7	-	32.5	-	0.002	0.096	0.296
Run-8	52.9	-	77.5	-	0.012	0.214	0.129

***** Energy consumed by (a) electronic overhead stirrer - 70/42 W (I/O), (b) UV Lamps - 16 W each, and (c) orbital shaker for adsorption studies - 48 W were included for energy consumption analysis.

MNZ removal by photocatalysis

In the presence of TiO_2, much higher degradation of MNZ was observed, i.e. 98.1% with 32 W and 94.1% with 16 W UV power, after 120 min of reaction. In the similar time frame, the COD reduction has reached up to 80.7% with 32W and 72.2% with 16W. The ORP data of the experimental runs indicate that all the experiments were under the high oxidation state; however, it was higher in the photocatalysis runs conducted with 32 W UV power with TiO_2 (Fig. 2a). As a result, higher rate constant values were observed in this system (Table 2). However, the COD removal data point out that complete mineralization of MNZ was not occurred in any of the experimental runs. However, it could be proposed the formation of one or more degradation intermediates of MNZ with partial mineralization. The samples collected from the photocatalysis experiment (with TiO_2 and 32 W UV Power) was injected in the LC-MS and from the results, it was observed that MNZ was transformed via two major acidic heterocyclic compounds at the end of the treatment (results not shown). However, the determination of complete oxidative pathway of MNZ mediated by hydroxyl radicals is under progress. Conversely, a decline in pH of the experimental system towards acidic range (from pH 8 to pH 5 after 120 min) was noticed during the course of the experiment (Fig. 2b), which could be due to the dissolution of carbon-dioxide (CO_2) produced as a result of partial mineralization. This observation supports the finding/identification of two acidic heterocyclic compounds in the LC-MS analysis.

On the other hand, the MNZ removal was only 77.5% under the condition of 32 W UV power and 2.5 g GAC Catalyst (Table 2). The removal observed was 21% lesser than the efficiency observed in photocatalytic system with TiO_2 as a catalyst. However, the removal efficiency in the GAC photocatalytic system (Run-8) was 82.8% higher than the efficiency observed in photolytic system (Run-3). Comparing Run-7 and Run-8, the improvement in MNZ removal efficiency was nearly 135.6% in GAC photocatalytic system compared with GAC adsorption system. These observations indicate that GAC has the catalytic property apart from its sorption property. Moreover, the photochemical quantum yield of several activated carbons was higher than that of photolysis under similar conditions; however, the nature of degradation intermediates was also modified in the presence of the carbon materials (Velasco et al., 2012).

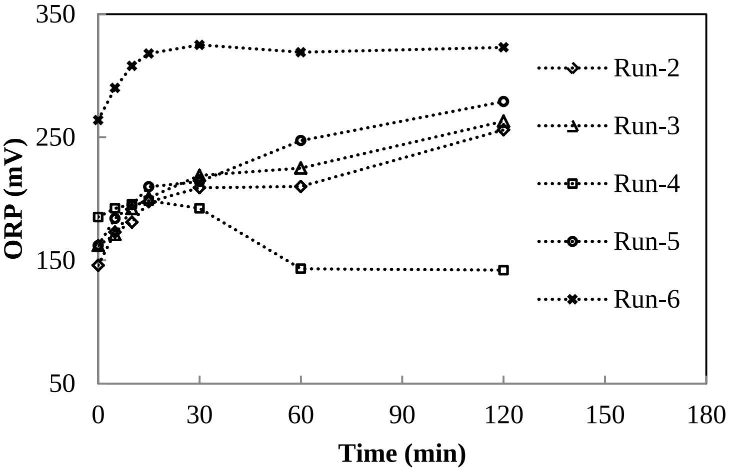


Figure 2(a). Profile of ORP in the photolysis and photocatalysis experimental runs

MNZ removal by adsorption

The MNZ removal by adsorption in the presence of TiO_2 (Run-4) and GAC (Run-7) was quantified using batch experiments and the presence of MNZ molecules on the surface of the adsorbents was observed/identified using SEM/EDS analysis. The MNZ removal in Run-7 was higher than in Run-4 (i.e.73.8%) indicating that GAC has better capability for MNZ adsorption compared to TiO_2 (Fig 3 & Fig 4). Considering the neutrality of MNZ (pKa = 2.5) in the pH range of 6 to 7, the adsorption could be mainly by the physical forces/phenomenon. Therefore, the chance of MNZ desorption from the adsorbed surface is more likely due to the weak association between MNZ and the adsorbent molecules.

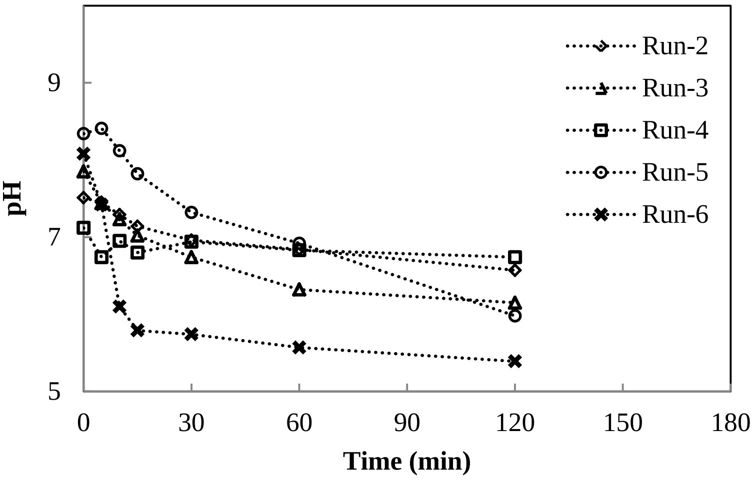
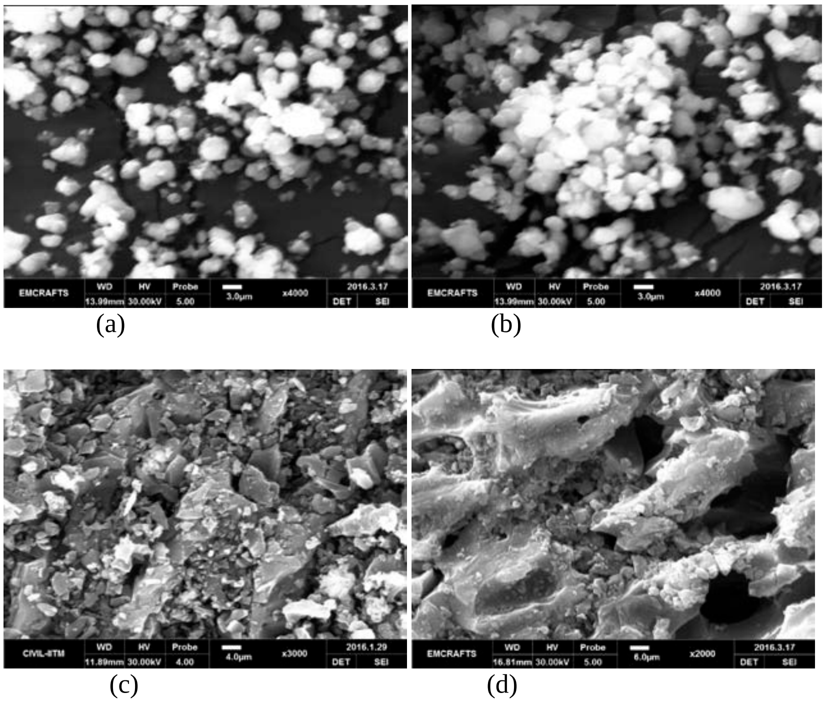


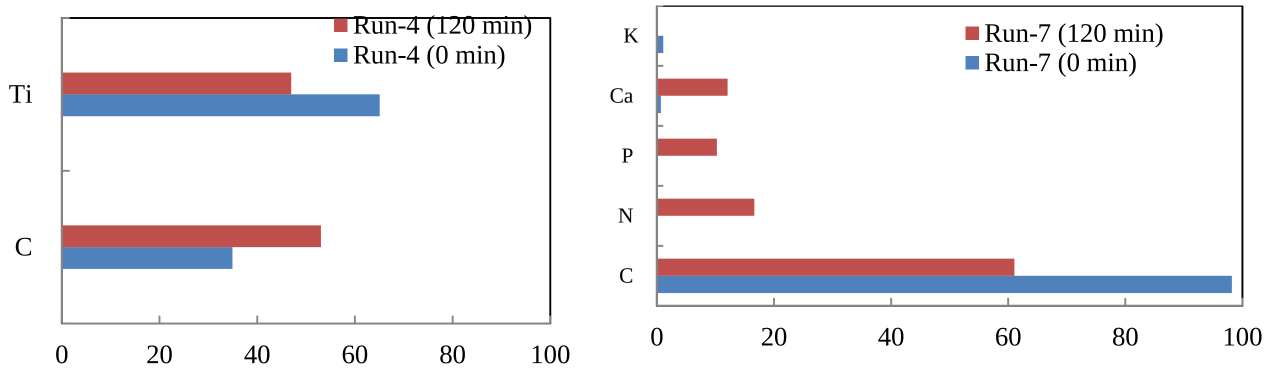
Figure 2(b). Profile of pH in the photolysis and photocatalysis experimental runs



(a) (b)

(c) (d)

Figure 3. SEM images of (a) TiO_2 before treatment, (b) TiO_2 after treatment, (c) GAC before treatment and (d) GAC after treatment (without UV illumination) in Run-4 and Run-7



(a) (b)

Figure 4. EDS analysis showing the elemental composition (in compound %) of (a) TiO_2 and (b) GAC samples before and after treatment (without UV illumination) in Run-4 and Run-7

Comparison of MNZ removal by photolysis, photocatalysis and adsorption

The profiles of MNZ and COD remaining under different experimental conditions specified in Table 2 are shown in Figs. 5 and 6, respectively. It can be seen in the figures that the adsorption and photolysis process have a fairly equal contribution in MNZ removal. However, the adsorption of MNZ on GAC is solely compound dependent. The GAC photocatalysis would be the treatment of choice next to TiO_2 photocatalysis. The cost evaluation of different processes was assessed from the values of energy consumed and E_{EO} (Table 2). By comparing the values of E_{EO}, it is evident that photocatalytic process is highly energy efficient even though it seems to be a high energy consuming system. The GAC photocatalysis system seems to be an energy efficient system for MNZ removal than the photolysis and adsorption systems.

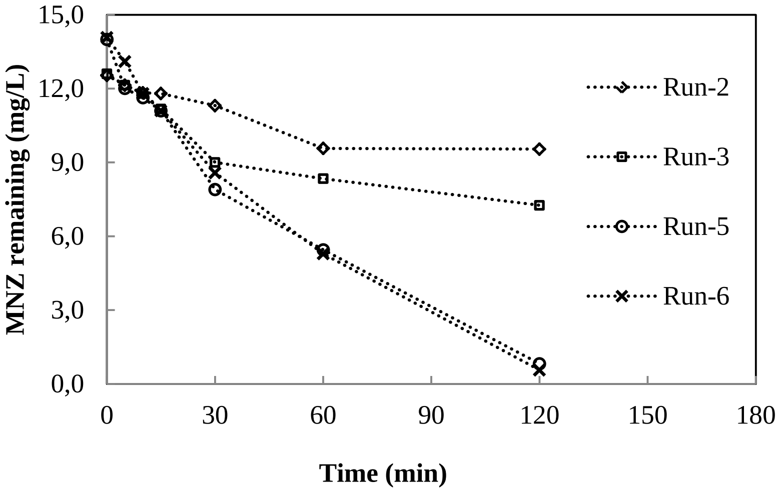


Figure 5. Profile of MNZ remaining in photolysis and photocatalysis experimental runs

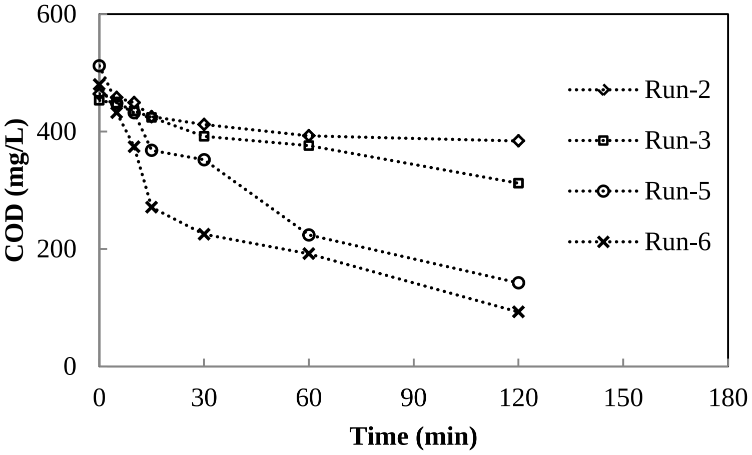


Figure 6. Profile of COD remaining in photolysis and photocatalysis experimental runs

Confirmation of MNZ degradation/mineralization

The samples collected from Run-6 (the experimental combination which has shown the maximum MNZ removal) was taken for TOC analysis and the results are shown in Table 3. The results show that considerable quantity of carbon molecules present in MNZ was removed from the system as CO_2 gas due to the photocatalytic oxidation of MNZ. The percentage removal of total carbon in the system was 56.4%; however, it confirms the partial mineralization of MNZ and formation of MNZ by-products.

Table 3. Outcomes of TOC analysis

Run No	MNZ concentration (mg L^{-1})	Time (min)	TOC (mg L^{-1})	Total Carbon (mg L^{-1})	Inorganic carbon (mg L^{-1})
Run-6	15	0	25.2	29.8	4.6
		120	8.5	13.0	4.5

CONCLUSIONS

The removal of MNZ from aqueous system by UV/TiO_2/GAC photocatalysis, adsorption and photolysis was investigated. The highest MNZ removal was observed in the photocatalytic system operated with 32 W UV power and 2.5 g L^{-1} TiO_2 in 120 min. Removal of MNZ using GAC as a photocatalyst was remarkably higher that of GAC used as an adsorbent. The MNZ decay obeyed pseudo first-order kinetics with a maximum rate constant of 0.026 min^{-1}. TOC and LC-MS analysis confirmed the formation of by-products of MNZ. The efficiency of the system was also analyzed following the concept of electrical energy consumed per order, i.e. E_{EO}. The E_{EO} concept was found to be one of the ideal parameters for the economic analysis.

ACKNOWLEDGEMENT

The authors acknowledge the financial support from Centre for Industrial Consultancy and Sponsored Research (ICSR), IIT Madras to execute this research work (Grant No: CIE/14-15/832/NFIG/SMAT and CIE/14-15/650/NFSC/SMAT).

REFERENCES

Asha, C.R., Kumar, M. 2015 Sulfamethoxazole in poultry wastewater: Identification, treatability and degradation pathway determination in a membrane-photocatalytic slurry reactor. *Journal of Environmental Science and Health Part-A* **50**, 1011-9.

Andreozzi, R., Caprio, V., Insola, A., Marotta, R. 1999 Advanced oxidation processes for water purification and recovery. *Catalysis Today* **53**(1), 51-9.

APHA, Standard Methods for the Examination of Water and Wastewater, 22nd ed., American Public Health Association, Washington, DC, 2005

Friedmann, D., Mendive, C., Bahnemann, D. 2010 TiO_2 for water treatment; parameters affecting the kinetics and mechanism of photocatalysis. *Applied Catalysis B- Environmental* **99**(3-4), 398-406.

Gao, Y.Q., Gao, N.Y., Deng Y., Yang, Y.Q., Ma, Y. 2012 Ultraviolet (UV) light-activated persulfate oxidation of sulfamethazine in water. *Chemical Engineering Journal* **195**(1), 248-53.

Giri, R.R., Ozaki, H., Ota, S., Takanami, R., Taniguchi.S. 2010 Degradation of common pharmaceuticals and personal care products in mixed solution by advanced oxidation techniques. *International Journal of Environmental Science and Technology* **7**(2), 251-60.

Gros, M., Petrovic, M., Ginebreda, A., Barcelo, D. 2010 Removal of pharmaceuticals during wastewater treatment and environmental risk assessment using hazard indices. *Environment International* **36**, 15-26.

Hapeshi, E., Achilleos, A., Vasquez, M.I., Michael, C., Xekoukoulotakis, N.P., Mantzavinos, D., Kassinos, D. 2010 Drugs degrading photocatalytically: Kinetics and mechanisms of ofloxacin and atenolol removal on titania suspensions. *Water Research* **44**, 1737-46.

Hu.L.H., Flanders, P.M., Miller, P.L., Strathman, T.J. 2007 Oxidation of sulfamethoxazole and related antimicrobial agents by TiO_2 photocatalysis. *Water Research* **41**(12), 2612-6.

Jallouli, N., Elghniji, K., Trabelsi, H., Ksibi, M. 2014 Photocatalytic degradation of paracetamol on TiO_2 nanoparticles and TiO_2/cellulosic fiber under UV and sunlight irradiation. *Arabian Journal of Chemistry* (Article in press).

Kanakaraju, D., Glass, D.B., Oelgemoller, M. 2014 Titanium dioxide photocatalysis for pharmaceutical wastewater treatment. *Environmental Chemistry Letters* **12**, 27-47.

Kim, I., Yamashita, N., Tanaka, H. 2009 Performance of UV and UV/H_2O_2 processes for the removal of pharmaceuticals detected in the secondary effluent of a sewage treatment plant in Japan. *Journal of Hazardous Materials* **166**(2), 1134-40.

Kummerer, K. 2009 The presence of pharmaceuticals in the environment due to human use - present knowledge and future challenges. *Journal for Environmental Management* **90**(8), 2354-66.

Lindberg, R., Jarnheimer,P., Olsen, B., Johansson, M., Tysklind, M. 2004 Determination of antibiotic substances in hospital sewage water using solid phase extraction and liquid chromatography/mass spectrometry and group analogue internal standards. *Chemosphere* **57**, 1479-88.

Martinez, F., Lopez-Munoz, M.J., Aguado, M., Melero, J.A., Arsuaga, J., Sotto, A., Molina, R., Segura, Y., Parinete, M.I., Revilla, A, Cerro, L., Carenas, G. 2013 Coupling membrane separation and photocatalytic oxidation processes for the degradation of pharmaceutical pollutants. *Water Research* **47**, 5647-58.

Mompelat, S., Le Bot, B., Thomas, O. 2009 Occurrence and fate of pharmaceutical products and by-products from resource to drinking water. *Environment International* **35**(5), 803-14.

Safari, G.H., Hoseini, M., Seyedsalehi, M., Kamani, H., Jaafari, J., Mahvi, A.H. 2015 Photocatalytic degradation of tetracycline using nanoized titanium dioxide in aqueous solution. *International Journal of Environmental Science and Technology* **12**, 603-16.

Suarez, S., Carballa, M., Omil, F., Lema, J.M. 2008 How are pharmaceuticals and personal care products removed from urban wastewaters? *Reviews in Environmental Science and Biotechnology* **7**, 125-38.

Velasco, F.L., Fonseco, M.I., Parra, B.J., Lima, C.J., Ania, O.C. 2012 Photochemical behaviour of activated carbons under UV irradiation. *Carbon* **50**(1), 249-58.

Vishnuganth, M.A., Remya, N., Kumar, M., Selvaraju, N. 2016 Photocatalytic degradation of Carbofuran by TiO_2-coated activated carbon: Model for kinetic, energy per order and economic analysis. *Journal of Environmental Management* **181**, 201-207.