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Photocatalytic degradation of Sulfamethoxazole in water: investigation of the effect of operational parameters

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Abstract : The potential of a common semiconductor, TiO_2, has been explored as an effective catalyst for the photodegradation of Sulfamethoxazole (SMZ) antibiotics from aqueous solution. In this laboratory study, the effects of pH (3-11), nanoparticle dose (0.02-0.16 g/L), reaction time (5-150 min), initial SMZ concentration (20-100 mg/L) and lamp power (15W) were assessed on SMZ removal efficiency in a batch photocatalytic reactor. SMZ concentration in output was measured by the HPLC at the maximum wave length of 267 nm. The optimum obtained pH and TiO_2 nanoparticle dose were 3 and 0.08 g/L respectively. In this study, at the optimum reaction time of 60 min, by increasing the concentration of SMZ the removal efficiency decreased. Under optimal conditions of concentration, the removal efficiency was 96.5%. On the basis of the obtained results, it can be concluded thatTiO_2nanoparticles photocatalytic process can efficiently remove SMZ from aqueous solutions.
Keywords : TiO_2, Photocatalysis, UV–visible light, Sulfamethoxazole.

Introduction:

Water contamination is caused by various sources such as industrial effluents, agricultural runoff and chemical spills[1-3].Industrial effluents contain several non-biodegradable substrates that can be harmful to theenvironment[4, 5].Pharmaceutical antibiotics, which are used extensively worldwide in human therapy and the farming industry, have attracted increasing concern in recent years, because they have been proved to be a class of potent pollutants[6, 7]. Antibiotics discharged from wastewater treatment plants(WWTPs) to the environment have received a growing concern because of their potential toxic effect on the aquatic biota as well ashuman[8-10].

Sulfamethoxazole (SMX) is a sulfonamide antibiotic. It is commonly used to treat urinary tract infections, sinusitis, and toxoplasmosis[11]. SMX is also used to promote livestock growth and has been detected in raw influents. The removal rate of SMX in wastewater treatment facilities is lower as compared to other antibiotics including fluoroquinolone and macrolide groups[12, 13].

These compounds reach waterways mainly through the discharge of wastewaters and effluents[14]. Additional pollution sources are direct emissions from production sites, improper disposal of surplus-drugs in households, medical care, and therapeutic treatment of livestock[15].Pharmaceuticals are often not completely removed in sewage treatment plants and therefore, are emitted into receiving water systems[16-19].Most of the organic compounds are not easily degradable by standard biological methods[20-22]. Methods such as adsorption

on activated carbon, ultrafiltration, reverse osmosis, coagulation, ion exchange and oxidation with peroxide are usually applied efficiently. Nevertheless, they do not destruct the pollutant molecule[23-26].

One difficulty with these methods is that they are not destructive, but only transfer the contamination from one phase to another, therefore, a new and different kind of pollution is faced and further treatments are deemed necessary[27, 28]. In recent years an alternative to conventional methods, is "Advanced Oxidation Processes" (AOPs), based on the generation of very reactive species such as hydroxyl radicals that quickly and nonselectively, oxidizes a broad range of organic pollutants[29,30].The key advantage of this degradation method is that itcan be carried out under ambient conditions and lead to complete mineralization of organic carbon[31,32].

During the past two decades, photocatalytic processes involving TiO_2 semiconductor particles under UV light illumination have been shown to be potentially advantageous and useful in the treatment of wastewaterpollutants[33,34].In the present investigation photocatalytic degradation of SMZ in the presence of TiO_2 with UV light as the illuminant has been reported. The effect of various parameters such as pH, catalyst weight and the initial concentration of SMZ on the degradation of the SMZ has been examined and the results obtained are discussed.

Materials and methods

The Sulfamethoxazole (99%) (CAS Number= 723-46-6; chemical formula: $C_{10}H_{11}N_3O_3S$; molecular weight=253.279 g/mol; maximum wavelength =267 nm) were obtained from Sigma-Aldrich Ltd., USA and SMZ was used as such without further purification. The SMZ shows an absorption maximum at 267 nm and the structure of the antibiotic is shown in Fig. 1.

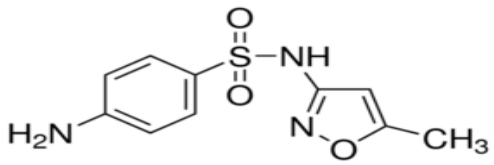

Fig. 1. The chemical structure of Sulfamethoxazole

Titanium oxide (99.8% purity), used as photocatalyst was obtained fromMerck. The BET (Brunauer–Emmett–Teller) surface area of TiO_2 wasdetermined by flow method using Micromeritics pulse chemisorb2700. The surface area of TiO_2 was found to be 34 m^2/g.

All other chemicals were of analytical grade obtained from Merck and used as such.The desired concentrations of the SMZ solutions were prepared using double distilled water. The pH of the solution was adjusted to the desired values between 3 and 11 by using dilute solutions of HCl or NaOH.

The photodegradation studies were carried out in a batch reactor system and provided with a water circulation arrangement in order to maintain the temperature in the range of 25–30°C. The reactor consisted of a rectangular tray of 16 cm ×5 cm × 5 cm made of borosilicate glass, mounted suitably on a magnetic stirrer. The radiation source was a low-pressure mercury vapour lamp (15 W) emitting ultraviolet radiation with a peak wave length of 245 nm. The lamp was fitted on the top of the reactor. The light source used in the photocatalysis experiments was standardized by ferrioxalate actinometry and its intensity was found to be 2.42×10^{19} quanta per second.

The optimum conditions used in the present study was a batch volume of 250 mL, 8 cm distance between UV source and solution with a stirring speed of 100 rpm and 60 min time for adsorption equilibrium. In all the experiments, the SMZ solution of known concentration containing a suspension of known weight of catalyst powder was irradiated with UV light. Samples of 5 mL were withdrawn at regular intervals of time and centrifuged. Absorbance of the supernatant solution was measured and returned to the reactor.SMZ analysis was performed using an Agilent 1200 series HPLC equipped with a C18 column, a UV detector (at wavelength 267 nm), and a methanol/water (50/50 v/v) mobile phase at a flow rate of 0.6 ml/min. The amount of SMZ adsorption at equilibrium q_e (mg/g) was calculated from the following equation[35-37]:

$q_e = (C_0 - C_t)V/W$

Where C_0 and Ce (mg/L) are the liquid-phase concentrations of SMZ at initial and equilibrium, respectively, V (L) the volume of the solution and W (g) is the mass of adsorbent used.

Results and discussion

Effect of the amount of photocatalyst

The effect of the amount of TiO_2on the SMZ removal was studied as shown in Figs 3. The photodegradation efficiency increases with an increase in the amount of photocatalyst, reaches the higher value of catalyst amount (0.08 g/L) and then decreases. The most effective decomposition of SMZ was observed with 50 mg/L of TiO_2. The reason of this observation is thought to be the fact that when all SMZ molecules are adsorbed on TiO_2, the addition of higher quantities of TiO_2would have no effect on the degradation efficiency[38, 39]. Another cause for this is supposedly an increased opacity of the suspension, brought about as a result of excess of TiO_2 particles.

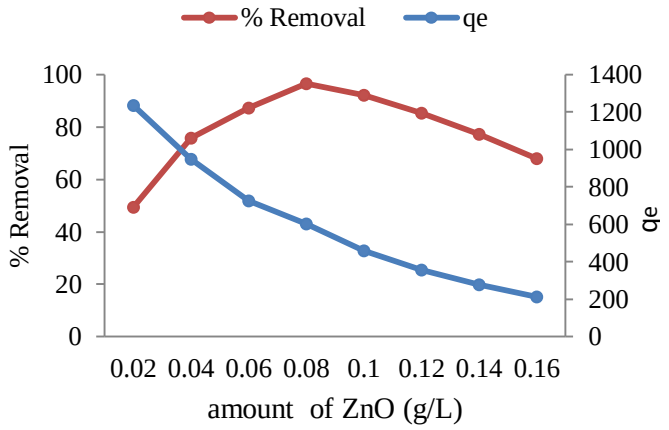

Fig. 3. Effect of ZnO amount on photodegradation efficiency of SMZ

Effect of UV irradiation and TiO_2particles

Fig. 4 shows the effect of UV irradiation and TiO_2 particles on photodegradation of SMZ. It can be seen from the figure that in the presence of both $TiO_2$and light, 96.5% of SMZ was degraded at the irradiation time of 90min. This was contrasted with 29.0% degradation for the same experiment performed in the absence of TiO_2, and the negligible 46%when the UV lamp had been switched off and the reaction was allowed to occur in the darkness. These experiments demonstrated that both UV light and a photocatalyst, such as TiO_2were needed for the effective destruction of SMZ. This is due to the fact that when TiO_2 is illuminated with the light of λ<390 nm, electrons are promoted from the valence band to the conduction band of the semiconducting oxide to give electron–hole pairs[41,42]. The valence band (h_{VB}^{+}) potential is positive enough to generate hydroxyl radicals at the surface and the conduction band (e_{CB}^{-}) potential isnegative enough to reduce molecular oxygen. The hydroxylradical is a powerful oxidizing agent and attacks organicpollutants present at or near the surface of TiO_2. It causes photooxidation of pollutants according to the following reactions (Eq. (2-7).The mechanism is assumed up in Fig. 2.

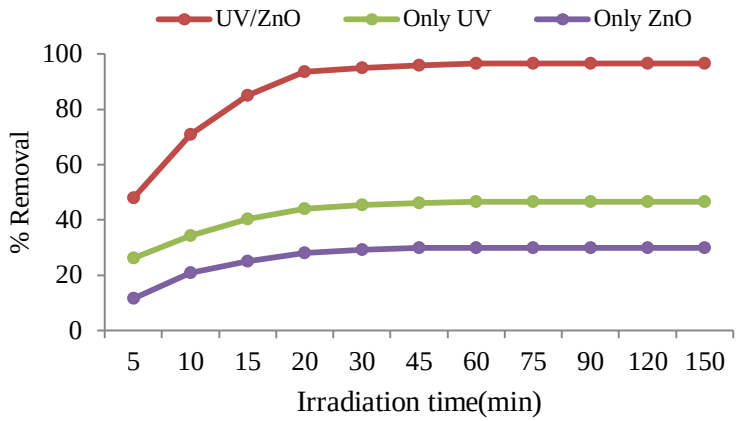

Fig. 4. Effect of UV light and TiO_2 on photocatalytic degradation of SMZ

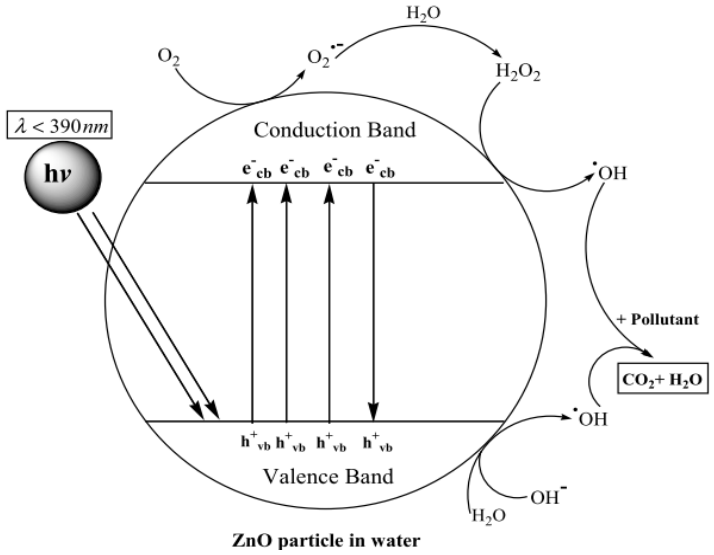

Fig. 2. General mechanism of the photocatalysis

TiO_2 + hv (λ<390 nm) → TiO_2 (e_{CB}^-+ h_{VB}^+) (2)
h_{VB}^++ H_2O (ads) → H^+ + •OH (ads) (3)
h_{VB}^++ OH^-(ads) →•OH (ads) (4)
e_{CB}^-+ O_2 (ads)→•O^{-2}(ads)(5)
•OH (ads) + SMZ → degradation of the SMZ (6)
h_{VB}^++ SMZ → $SMZ^{\bullet+}$→ oxidation of the SMZ (7)

Effect of initial SMZ concentration

The effect of initial SMZ concentration on photodegradation efficiency is shown in Fig. 5. It was observed that the photodegradation conversion of SMZ decreases with an increase in the initial concentration of SMZ. The presumed reason is that when the initial concentration of SMZis increased, more and more SMZ molecules are adsorbed onthe surface of TiO_2. The large amount of adsorbed SMZ is thought to have an inhibitive effect on the reaction of SMZ molecules with photogenerated holes or hydroxyl radicals, because of the lack of any direct contact between them[42,43]. Oncethe concentration of SMZ is increased, it also causes the SMZ molecules to adsorb light and the photons never reach the photocatalyst surface, thus the photodegradation efficiency decreases.

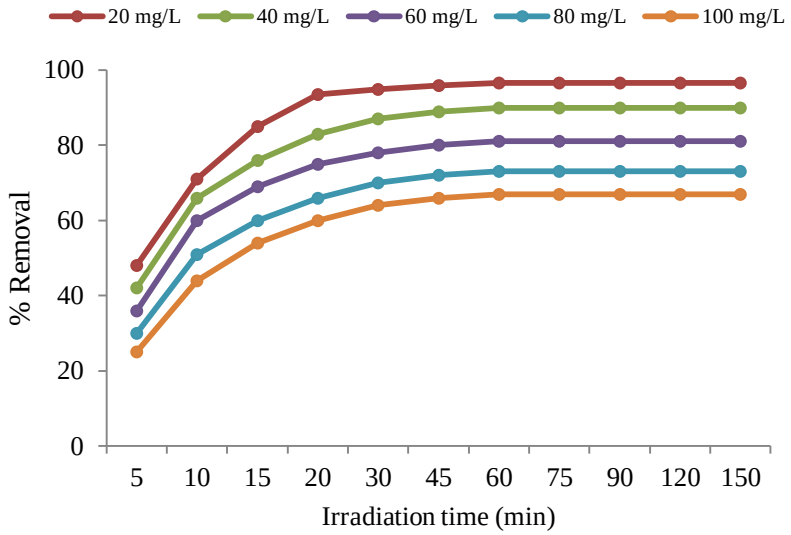

Fig. 5. Effect of initial SMZ concentration on photodegradation efficiency

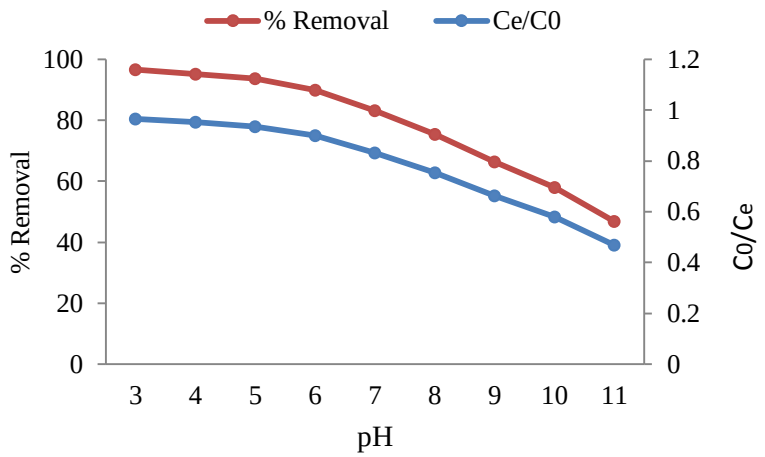

Fig. 6. Effect of pH on photodegradation efficiency of SMZ

Effect of pH

pH value is one of the factors influencing the rate of degradation of some organic compounds in the photocatalytic process. It is also an important operational variable in actual wastewater treatment. Fig. 6 demonstrates the photodegradation of SMZ at different pH from 3 to 11, which clearly shows that the best results were obtained in acidic solution, (pH =3). According to the zero point of charge of TiO_2, its surface is presumably positively charged in acidic solution and negatively charged in alkaline solution. Since the SMZ has a sulfuric group in its structure, which is negatively charged, the acidic solution favors adsorption of SMZ onto photocatalyst surface, thus the photodegradation efficiency increases[39,44]. There is also the photocatalytic degradation of SMZ in acidic solutions, which is probably due tothe formation of $OH^{\bullet}$ as it can be inferred from the following reactions.

$e_{CB}^{-} + O_{2(ads)} \rightarrow {}^{\bullet}O_{2\,(ads)}^{-}$

${}^{\bullet}O_{2\,(ads)}^{-} + H^{+} \rightarrow HO_2^{\bullet}$

$2HO_2^{\bullet} \rightarrow O_2 + H_2O_2$

$H_2O_2 + {}^{\bullet}O_{2\,(ads)}^{-} \rightarrow {}^{\bullet}OH + OH^{-} + O_2$

Conclusions:

The photocatalytic degradation of an SMZ in aqueous solution with TiO_2 as photo catalyst in slurry form have been investigated using solar light and UV. The study of the effect of various photo catalysts TiO_2, on the degradation. The effects of various parameters such as catalyst loading and initial SMZ concentration on degradation have been investigated to find out optimum conditions. The result of this study clearly establish that TiO_2 semiconductor photocatalysis can be efficiently used for the degradation of the SMZ and other antibiotics compounds in effluents. Rate of removal of SMZ is effected by pH, conc. of SMZ solution, amount of semiconductor and contact time. The optimum degradation of neutral SMZ found at pH=3, Concentration of SMZ =20 mg/L and amount of TiO_2= 0.08 g/L and contact time 60 min.

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