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Ag-TiO₂ nanoparticles for photocatalytic degradation of sparfloxacin

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Abstract

Liquid Impregnation (LI) technique was developed to prepare 1% and 2% Ag doped Titania nanoparticles. The characterization of the prepared nanoparticles was achieved by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Analysis (EDX) and Transmission Electron Microscopy (TEM). The crystallite size was obtained by Scherrer equation analysis of XRD main peak of doped and undoped nanoparticles. It was observed that crystallite size of bare TiO2 was 17.00 nm, whilst the crystallite size of 1% Ag doped titania and 2% Ag doped titania was 13.07 nm to 14.17 nm. TEM images ascertained that particle size of Ag-TiO₂ nanoparticles were in the range 40-45 nm in length and 10-15 nm in width. The pH of the solution exerted a negative effect on photodegradation rate of sparfloxacin. The masking effect on the degradation of sparfloxacin was observed at higher catalyst dosages. The increase in UV intensity linearly enhanced the degradation rate of sparfloxacin and the influence of initial sparfloxacin concentration on the degradation rate was investigated and discussed. Copyright © 2018 VBRI Press.

Keywords: Photocatalysis, degradation, sparfloxacin, TiO₂, doping.

Introduction

Contamination of ground water and surface water due to industrial organic contaminant creates several threats to flora and fauna in the ecosystem [1]. The existence of such contaminants in the ecosystem increases the environmental pollution. Deprivation of such pollutants becomes the necessary to minimize the pollution. Now-a-day's use of semiconductor photocatalysts activated by UV-light or visible light has gathered attention as they potentially degrade the number of organic contaminants in water [2-5]. The important characteristic of photocatalytic degradation is it can work at ambient conditions, without producing any byproducts [6].

Advanced oxidation processes (AOPs) are most widely used technique for the treatment of harmful organic contaminants present in water system. The conventional and biological treatment methods are not effective in the treatment of organic contaminants and may produce hazardous byproducts. AOPs follows in-situ generation of very active free-radical species such as hydroxyl (OH·) that degrade a variety of organic contaminants without being the use [7-8] using chemical or light energy. The AOPs usually involve a semiconductor photocatalyst activated by UV or Visible light resulting in complete or Incomplete mineralization of the organic contaminants [9]. Many reports demonstrated the suitability of titania in the photo degradation of pharmaceutical compounds [10].

Titania (TiO₂), a semiconductor nanoparticle is one of the widely used photocatalysts. This is because of its inertness, bio-compatibility, high efficacy, inexpensive, good optical and electrical properties [11-12]. Optical energy gap of Anatase TiO₂ is 3.2 eV, which indicates that it absorbs light in the UV- region. Absorption of UV light promotes the valence electrons into the conduction band creating holes in the valance band [13]. However, the high rate of electron-hole recombination in TiO₂, reduces the photocatalyst efficiency. The recombination process can be minimized to certain extent, by doping TiO₂ with nobel metals [14]. The doping Ag on TiO₂ helps in improve the charge separation and thus increasing the photocatalytic efficiency of TiO₂. In addition, the antibacterial action of silver, particularly in the colloidal form, is also well stated in literature [15].

Sparfloxacin (SPF) belongs to fluoroquinolone class of antibacterials. It is potent antibiotic widely used for the treatment of bacterial infections such as corneal ulcer in case of eye infection. It is active towards broad range of Gram +Ve and Gram –Ve microbes like Streptococcus pneumoniae, Staphylococcus aureus.
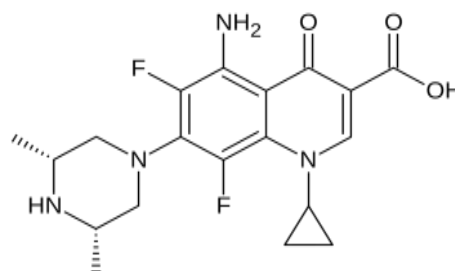
Structure of Sparfloxacin

In the present study, to enhance the photocatalytic efficiency of TiO_2. Liquid Impregnation (L.I.) technique was used to prepare Ag-TiO2 nanoparticles. The characterization of the prepared nanoparticles was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Energy dispersive X-ray Analysis (EDX) and Transmission Electron Microscopy (TEM). Photo-catalytic efficiency of these prepared nanoparticles was studied on SPF in water environment investigating different parameters such as initial substrate concentration, pH, catalyst dosage and intensity of UV light.

Experimental

Materials

Analytical grade Sparfloxacin was purchased from Sigm-aldrich and a stock solution of sparfloxacin prepared by known amount of sample is dissolved in double distilled water. The Anatase TiO_2 sample was procured from SRL, Mumbai, India. During experiment all other chemicals and reagents were used are analytical grade.

Synthesis of photocatalyst

Liquid Impregnation Method (LI)

1% and 2% Ag doped TiO_2 nanoparticles were prepared by Liquid Imprignation technique. 1% and 2% mole ratio of AgNO3 was added to 1g of TiO_2 dispersion in deionized water. The slurry was placed in a magnetic stirrer and stirred for 3 hours. The slurry was kept overnight for liquid impregnation dried at 100^oC for 10 hours. Finally, the dried nanoparticles were calcined at 450^oC in a muffle furnace [**16**].

The photo degradation process

The photo degradation process was carried out in a photoreactor fixed with 8 W ultra-violet lamps (UVC Phillips λmax at 254 nm). At regular interval of 15 minutes the reaction mixture was taken out and centrifuged at 2000 rpm for 5 min. The [SPF] was recorded at 292 nm (ε = 21913 l mol^{-1} cm^{-1}) using a UV-Visible Spectrophotometer (Varian BV, The Netherlands) and the degradation efficiency was studied.

Results and discussion

Influence of silver doping

Silver doping on anatase TiO_2 decreases the crystallite size. Smaller crystallite size greater will be the surface area. Greater level silver doping favors charge separation effectively, preventing the recombination of electron-hole pairs, and thus increasing the photocatalytic efficiency [**9**]. The rates of photocatalytic degradation of SPF by UV, UV/TiO_2, UV/ 1% Ag-TiO2 and UV/2% Ag-TiO2 were studied and compared. It was found that UV/2% Ag-TiO2 exhibited higher degradation efficiency compared to

UV, UV/TiO_2 and UV/1% Ag-TiO2. The degradation efficiency of SPF was found to be 43%, 58%, 75% and 90% with UV, UV/TiO_2, UV/1% Ag-TiO2 and UV/(2%) Ag-TiO2 respectively within 100 minute as shown in supplementary Fig 1. Further studies were carried out with 2% Ag-TiO2 as it showed the maximum efficience.

Characterization of TiO_2 and Ag-TiO2

The XRD patterns were collected with the help of Siemens AXS D5005 system using copper K_α source (**Fig. 1**). The diffraction peaks can be assigned to all the lattice planes of anatase TiO_2. The average crystallite size of Ag-TiO2 nanoparticles was obtained from the broadening of the anatase main intense peak (101), using Scherrer equation, The crystal size of TiO_2 is of 17 nm whilst the crystallite size of 1% Ag-TiO2 is 14.17 nm, 2% Ag-TiO2 13.07. This is in line with reported work [16], where 15 nm to 37 nm of Ag-TiO2 nanoparticles were reported.
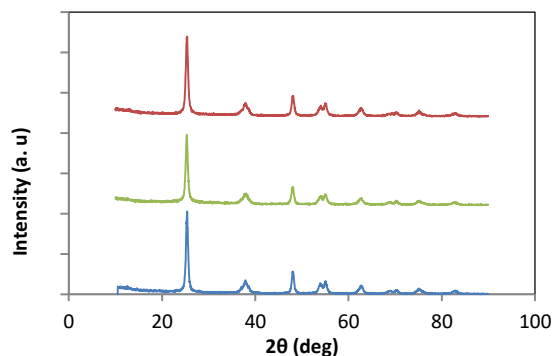

Fig. 1. XRD patterns of (a) Undoped TiO_2, (b) 1% Ag - TiO2 and (c) 2% Ag - TiO2

Scanning electron microscope

SEM morphology (Supplementary Fig. 2.) shows the non-uniform agglomerates of the Ag-TiO2 nanoparticles, which leads to high surface area. High surface area leads to greater efficiency of prepared Ag-TiO2 nanoparticles [**16**].

Transmission electron microscope

TEM topography **(Fig. 2 (a) and Fig. 2 (b))** confirms the non-uniform distribution of agglomerates of cylindrical Ag-TiO2 nanoparticles. Spreading of small dark spots detected were recognized as Ag particles on TiO_2 nanoparticles with a particle size of roughly 10-15nm in width and 40-45 nm in length.
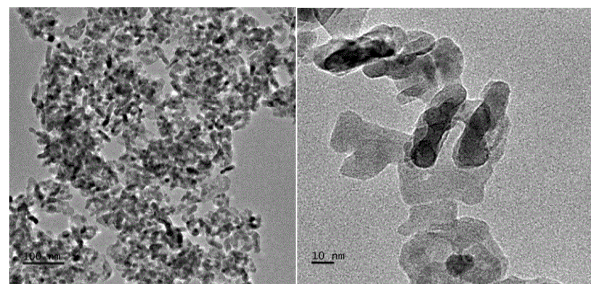

Fig. 2. TEM micrographs of (a & b) 2% Ag/TiO_2

Electron dispersive X-ray spectroscopy

EDX examination provides information on elemental analysis of samples. The EDX analysis discloses the presence of Ti, O and Ag at 4.508, 0.525 and 2.983 keV respectively. The atomic % of Ti, O and Ag is 77.51, 20.49 and 2.0 respectively. This composition of Ti, O and trace amount of Ag, results in better photocatalytic efficiency.

Influence of photocatalyst dosage

It was observed that the rate of photodegradation rises up to 0.25 g l^{-1}, beyond 0.25 g l^{-1} the rate of reaction almost remains constant as shown in **Fig 3**. This behavior is due to the fact that as the Ag-TiO$_2$ dosage was increased in the initial state, the active sites of the Ag-TiO$_2$ also increases but after this limiting value (0.25 g l^{-1}) any increase in the Ag-TiO$_2$ dosage increases the turbidity of the solution and thus masks photocatalyst from UV light for the reaction to proceed, and hence the degradation efficiency decreases [**13**].
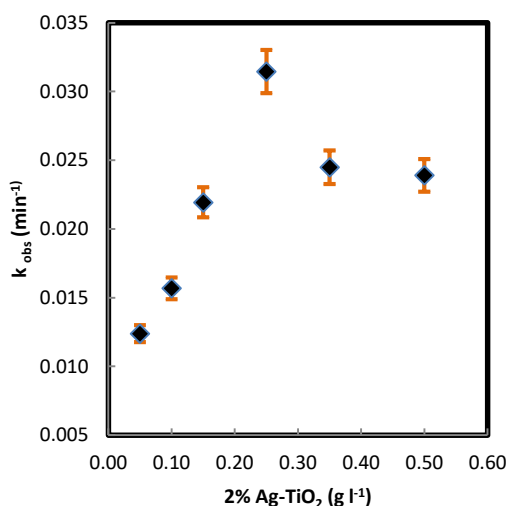

Fig. 3. Effect of different amount of 2% Ag-TiO$_2$ photocatalyst on the degradation of SPF at 25 ^{0}C, [SPF] = 0.875 x10^{-5} mol dm^{-3}, at pH = 5, light intensity = 4 mW/ cm^2.

Influence of [SPF]

The effect of variation of SPF concentration was studied by taking different concentration of SPF from 0.35 x 10^{-5} to 3.5 x 10^{-5} mol dm^{-3} by maintaining other parameters constant. In the beginning, increase in the concentration of SPF, enhances the rate of photocatalytic degradation, reaching maximum value [SPF] = 0.875 x 10^{-5} mol dm^{-3}. Further increase in [SPF] leads to decrease in the rate of photocatalytic degradation as shown in **Fig 4**. This may be due to the fact that, as the [SPF] increases, more number of SPF molecules are available for degradation, hence the enhancement in rate of degradation. Exceeding [SPF] 0.875 x 10^{-5} mol dm^{-3} the SPF turns as a filter for the incident light, thus reduces the rate of photocatalytic degradation [14].
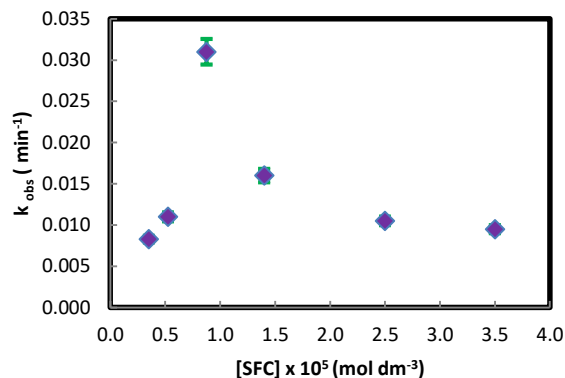

Fig. 4. Effect of [SPF] on photocatalytic rate constants with 2% Ag-TiO$_2$ at 25 ºC, [Ag-TiO$_2$] = 0.2 g l^{-1}, at pH=4, light intensity = 4 mW/ cm^2.

Influence of pH

The influence of pH on the photodegradation efficiency of SPF was studied for pH values between 5.0-9.0, whilst maintaining other parameters constant. High rate of photocatalytic degradation of SPF was observed at pH 5.0 and lower in the pH range 6.0-9.0 as shown **Fig. 5**. This enhancement in the rate of photocatalytic degradation may be due to the fact that in acidic medium the photocatalytic surface is +vely charged and it adsorbs more -vely charged SPF ions leading to effective interaction between drug and catalyst. Hence, the rate of degradation is maximum observed at pH 5.

On the contrary in alkaline medium the OH$^-$ ions collect on the surface of photocatalyst creating a negatively charge and SPF is also -vely charged in alkaline medium. Hence, the repulsion between SPF anion and photocatalyst takes place leading to reduction in rate of photodegradation at pH 6 to 9. This is in line with the reported work [**17**].
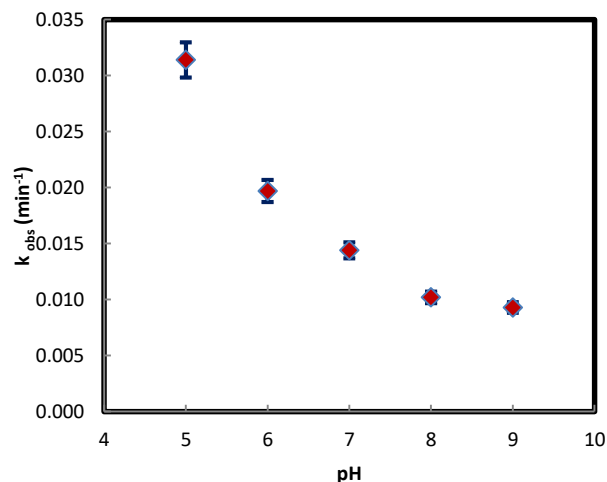

Fig. 5. Effect of pH on the rate constant of photo catalytic degradation of SPF with 2% Ag-TiO$_2$ at 25ºC, [Ag-TiO$_2$] = 0.2 g l^{-1}, [SPF] = 0.875 x 10^{-5} mol dm^{-3}, light intensity = 4 mW/cm^2.

Influence of UV lamp distance

Influence of UV light intensity on the Photodegradation of SPF was investigated by varying the lamp distance from the reaction site. The results are shown in **Fig. 6.** It is observed, that, an increase in light intensity increased the rate of photocatalytic degradation. This can be attributed to the fact that increase in UV light intensity excites more number of Ag-TiO$_2$ nanoparticles and generate more number of electron hole pairs. The holes take up the electrons from SPF molecules adsorbed on the surface of Ag-TiO$_2$ particles and decompose them [**16**].
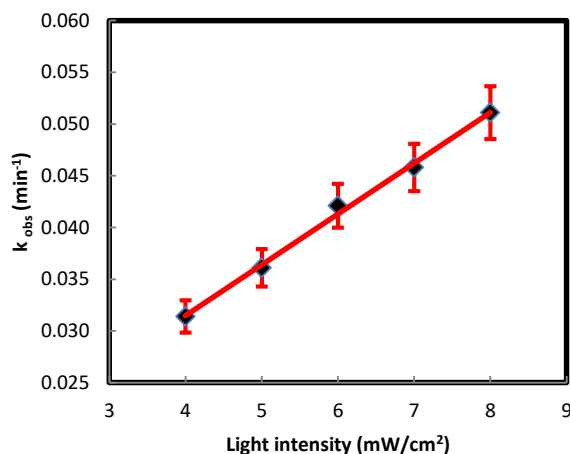

Fig. 6. SPF degradation under different UV intensities SPF with 2% Ag-TiO$_2$ at 25 ºC, [Ag-TiO$_2$] = 0.2 g l^{-1}, [SPF] = 0.875 x 10^{-5} mol dm^{-3}, at pH=5. light intensity = 4 mW/cm^2.

Conclusion

LI method was used to prepare 1% and 2% Ag-TiO$_2$ nanoparticles. The resulting Ag-TiO$_2$ (17 to 13.07 nm) nanoparticles having better potential towards the mineralization of SPF in acidic medium (pH 4). The XRD analysis shows that the prepared Ag doped TiO$_2$ nanoparticles were anatase in crystal phase. TEM and EDX analysis shows that the presence of Ag in TiO$_2$. Under optimal conditions, over 90% photocatalytic degradation of SPF was achieved in 100 min using 2% Ag-TiO$_2$ photocatalyst.

Author's contributions

Conceived the plan: RMK; Performed the expeiriments: RMK,RSM, MSH; Data analysis: RMK, RSM; Wrote the paper: RMK, RSM, MSH. Authors have no competing financial interests.

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