Photochemical Degradation of Fluocinolone Acetonidin Drug in Aqueous Solutions Using Nanophotocatalyst ZnO Doped by C, N, and S

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ABSTRACT: *It has been shown that the photocatalytic activity of doped semiconductor with some nonmetals is higher than pure semiconductor. Hence, with an attempt to achieve higher photocatalytic activity, doped ZnO with C, N, and S was prepared by a sedimentary process and used for the photocatalytic degradation of Fluocinolone Acetonidin as a drug in aqueus solutions. X-Ray Diffraction (XRD), Energy Dispersion X-ray (EDX), X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM) were used to characterize the microstructure and morphology of the precursor and the products. The photocatalytic degradation of drug was investigated using supported ZnO/C, N, and S photocatalyst under UV light irradiation. We also studied the influence of the basic photocatalytic parameters as well as irradiation time, initial concentration of drug, pH of solution, amount of nanoparticles and addition of oxidant on the reaction. The optimum conditions of degradation were obtained accordingly: concentration of Fluocinolone Acetonidin, 20 ppm; amount of photocatalyst, 7 mg; oxidant ($K_2S_2O_8$), 5 mM; irradiation time, 6 h in pH=9. Kinetic analysis demonstrated that the amount of Fluocinolone Acetonidin photocatalytic degradation can be fitted by a pseudo- first- order model.*

KEYWORDS: *Photocatalytic degradation; ZnO/C, N; S photocatalyst; Fluocinolone Acetonidin; UV light irradiation.*

INTRODUCTION

Environmental pollution is one of the most crucial areas of concern and it is highly required to pay more attention to it. In recent years, there has been a growing interest on the presence of pharmaceutical substances in aquatic environment [1]. These molecules are often excreted via urine or feces since they are non-metabolized, entering the wastewater and eventually reaching drinking water if they are not biodegraded or

eliminated during sewage treatments [2]. Recent studies have shown that heterogeneous semiconductor photocatalysis can be an alternative to conventional methods for removal of drug pollutants from water [3-5]. When semiconductors are illuminated with an appropriate radiation source, electron/hole pairs will be produced with electrons promoted to the conduction band leaving behind positive holes in the valence band. The generated electron/hole pairs induce a complex series of reactions that can result in complete degradation of the organic pollutants including drug adsorbed on the semiconductor surface.

Zinc oxide is a potential photocatalyst which has received great attention in researches and industries recently owing to its powerful oxidation capability, nontoxicity, chemical stability and low cost [6-8]. However, the photocatalytic activity of ZnO is limited to irradiation wavelengths in the UV region because ZnO semiconductor has a wide band-gap of about 3.3 eV and is only capable of absorbing UV light with wavelengths below 387 nm [9]. The fast recombination rate of the photogenerated electron-hole pairs also hinders the industrial application of this semiconductor [10]. Considerable efforts have been made to modify ZnO nanoparticles in order to improve its catalytic efficiency in the visible-light region. There are diverse advantages of photocatalysts modifications as well as causing delay in electron–hole recombination, broadening the absorption spectrum and facilitating some specific reactions on the surface of catalysts [9]. A possible strategy to extend zinc oxide photo-absorption of visible light may be modification of its valance band position by nonmetals doping such as nitrogen, carbon, sulfur, etc. Among the nonmetals, N is widely acceptable owing to its compatible size to O and the fact that it has the smallest ionization energy. The doped nonmetal in ZnO may cause its band gap narrowing thus shifting to the photo absorption edge of zinc oxide in visible region. Doping of such transition metals also will reduce the electron-hole recombination [11].

In this paper, we have synthesized doped ZnO with C, N, and S nanocrystals in the presence of different additives. Then the obtained nanocrystals were characterized by Scanning Electron Microscopy (SEM), X-Ray Powder Diffraction (XRD), X-Ray Photoelectron Spectroscopy (XPS) and Energy Dispersion X-ray (EDX).

The particle sizes were calculated from their absorption edge and compared with the sizes estimated from XRD analysis using the Debye–Scherrer formula. The photocatalytic properties of ZnO/C, N, and S nanoparticles were evaluated through the degradation of Fluocinolone Acetonidin solutions initiated by UV radiation.

EXPERIMENTAL SECTION
Preparation of C, N, and S doped ZnO

N, S, C-ZnO powders were prepared using a precipitation method. Thiourea was mixed with zinc sulfate in 250 mL distillated water to form a 0.25 M aqueous solution. The solution was then stirred for 3 h to complete dissolution. The mixture was treated with an ammonia solution (28%) until the pH reached 7. The resulting solution was stirred for another 2 h. Precipitated products were separated from the solution by centrifugation and dried at 100 °C for 24 h. The obtained products were ground and calcined at an elevated temperature for 3 h with a heating rate of 5 °C/min. The T/Z ratio indicated the molar ratio of thiourea to zinc sulfate [12].

Evaluation of photocatalytic activity

Photodegradation studies were carried out with a high pressure mercury vapor lamp (400 W) as the light source. The experiment was performed by mixing 7 mg/L C, N and S-doped ZnO and 5 mM of $K_2S_2O_8$, in 25 mL of the Fluocinolone Acetonidin solution with an initial concentration range of 10-50 mg/L. The pH was chemically controlled at 9. The mixtures were mixed by stirring at 80 rpm for 5 h under UV irradiation. The temperature was kept constant at (25±2) °C. Suspended solids were then separated out and concentration of drug measured using (Jenway 6405 UV-VIS) spectrophotometer at λ_{max}=240 nm. The degree of photodegradation (X) as a function of time is given by: X= $(C_0-C)/C_0$ where C_0 is the initial concentration of drug, and C the concentration of drug at time t.

Characterization of C, N, and S doped ZnO

Fig.1 shows XRD patterns of the C, N and S-doped ZnO fabricated nanoparticles. ZnO usually grows along the (002) direction due to the low surface free energy of (002) plane. The distinguished peaks of the hexagonal

Wurtzite ZnO structure with the angles of $2\theta = 28^0$ (direction of (100)), $2\theta = 32^0$ (preferable direction of (002)), and $2\theta = 35^0$ (direction of (101)) can be observed in this figure. It is noticeable that the preferable direction is elongation with 30 degree axis based on spectra diffraction. Some of the other peaks are suspected to mainly result from S- and OH-containing compounds like $Zn_2(OH)_2SO_4$. Average particle size was determined using Debye-Scherrer formula with Full-Width at Half Maximum (FWHM). The sizes were found to be 12.62 nm using equation (1).

$$D = \frac{k\lambda}{\beta\cos\theta} \quad , \quad k \approx 0.9, \quad \lambda = 1.78\,A^\circ, \quad \beta = FWHM \quad (1)$$

Where D is crystallite size, λ is the X-ray wavelength used, β is the angular line width of half maximum intensity, θ is Bragg's diffraction angle and *k* is a constant.

Morphology of C, N and S-doped ZnO nanoparticles was evaluated by SEM. The SEM images of nano C, N and S-doped ZnO prepared are illustrated in Fig. 2. The surface of sample consists of compact masses with about 300 nm that distributed equally. At a glance, it is different from the SEM illustration and the result of XRD for which the size of grain is about 12.62 nm. The SEM micrographs show strong dependency on doping elements. It should be noted that the electronic microscope illustrates the nanoparticles grew up in the surface by agglomeration gathering.

From X-ray Photoelectron Spectroscopy (XPS) the elements of C, N, S, Zn, and O are recognized. The atomic percentages of the recognized elements in the surface of sample are shown in Fig. 3. There is always oxygen and carbon in non-neutral and non-vacuum state. Therefore, the percentage of these elements in the nanopowder components is noticeable.

The EDX spectrum of the sample ZnO/C, N, S confirms the presence of elements, such as C, N, S, O together with their atomic and weight percent (Fig. 4). The weight percent of elements in EDX spectra for Zn, C, S, N are 61.8, 9.04, 14.07, 1.14, respectively. They are according to the weights of solution (25.38, 14.03, 24.96, and 10.91). The difference among quantities can be related to the vaporizable materials, the formation of dimer and trimmer structures. The noticeable quantities of the percent weights are related to the Zn (61, 81) rather
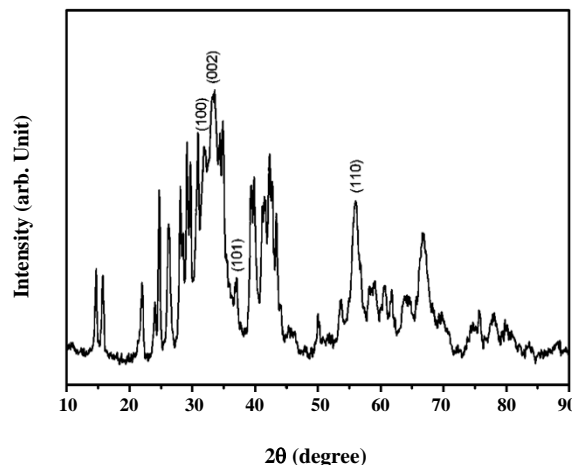

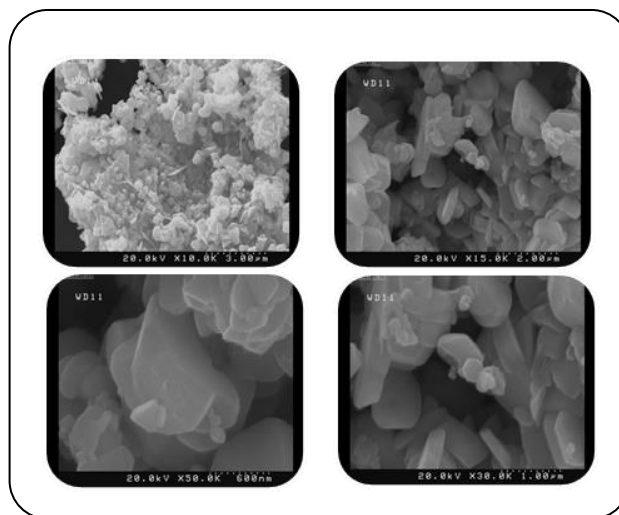*Fig. 1: XRD image of ZnO doped by C, N and S.*
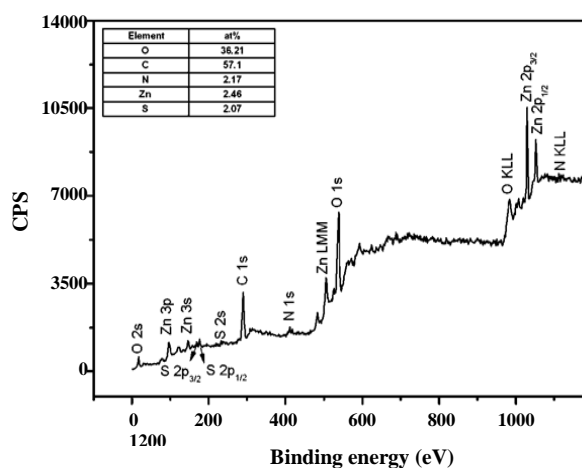

Fig. 2: SEM image of ZnO doped by C, N and S.

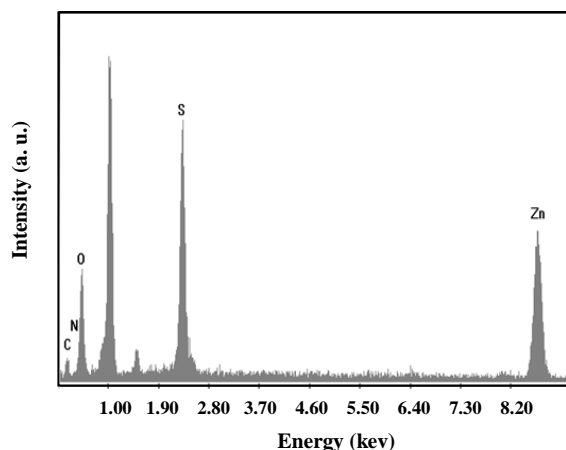*Fig. 3: XPS pattern of heat treated (800 ºC) of ZnO doped C, N, S.*
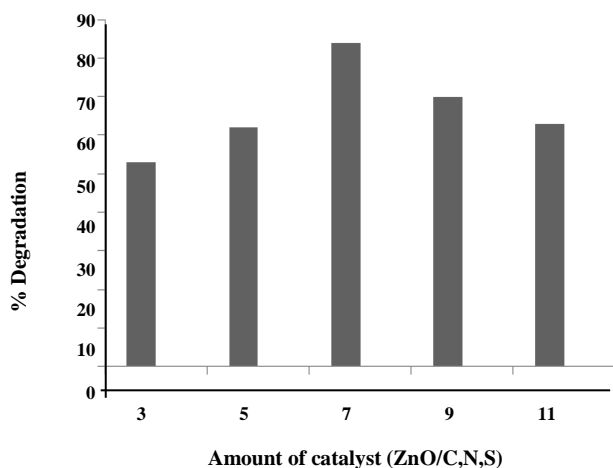
Fig. 4: EDX image of the sample ZnO/C, N, S.

Fig. 5: Effect of the amount of ZnO on the photodegrdation efficiency. Conditions: irradiation time= 6 h, drug concentration = 20 ppm, $K_2S_2O_8$= 5 mM, pH = 9.
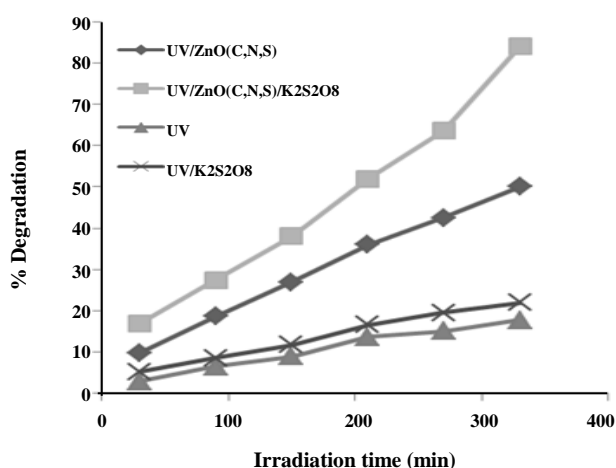

Fig. 6: Effect of UV, C, N and S-doped ZnO and $S_2O_8^{2-}$ on the degradation of Fluocinolone Acetonidin.

than other elements. It can be shown that large amount of zinc element penetrates into the surface without relating to oxygen. It could also be observed by atomic percent of Zn and O and the lots of peaks related to different components of Zn in the diffraction of X-ray.

Material

The Fluocinolone Acetonidin powder (formula: $C_{24}H_{30}F_2O_6$ (anhydrous), Molar mass: 452.49 g/mol) was obtained from Merck. The drug showed an adsorption maximum at 240 nm. The thiourea and zinc sulfate are used to produce zinc oxide doped with C, N, and S nanopowder. $K_2S_2O_8$, H_2O_2, $KBrO_3$, KIO_3, Na_2SO_4, $NaNO_2$, Na_2CO_3, NaCl, 2-propanol, were from Merck. The pH of the solution was adjusted to the desired value between 2.0 and 11.0 by using dilute solution of HCl or NaOH.

RESULTS AND DISCUSSION
Effect of the amount of ZnO/C, N, S

A series of experiments were carried out by varying the amount of ZnO/C, N, S (3 to 11 mg/L) to establish the effect of photocatalyst loading and to avoid unnecessary excess photocatalyst. Experiments performed with different concentrations of ZnO/C, N, S is shown in Fig. 5. It was observed that the photodegradation efficiency enhanced by increasing ZnO concentration up to 7 mg/L, and then was decreased. This can be explained in terms of availability of active sites on the catalyst surface and the penetration of UV light into the suspension. The total active surface area increases with increasing catalyst weight. But at the catalyst weight above optimum loading there is a decrease in UV light penetration due to screening effect of excess catalyst particle in the solution. Hence, the rate of photodegradation decreases at the higher catalyst loading [13].

Effect of UV, C, N and S-doped ZnO and $S_2O_8^{2-}$

The effect of sulfate radical ($SO_4^{\cdot-}$) as an oxidant on the degradation of Fluocinolone Acetonidin was investigated and compared with the UV (only), UV/ $S_2O_8^{2-}$, UV/ C, N and S-doped ZnO and UV/ C, N, and S doped ZnO / $S_2O_8^{2-}$ systems. As depicted in Fig. 6, UV irradiation alone in the absence of persulfate radical and C, N, and S doped ZnO was found to have no measurable effect on the degradation of the drug during 300 min
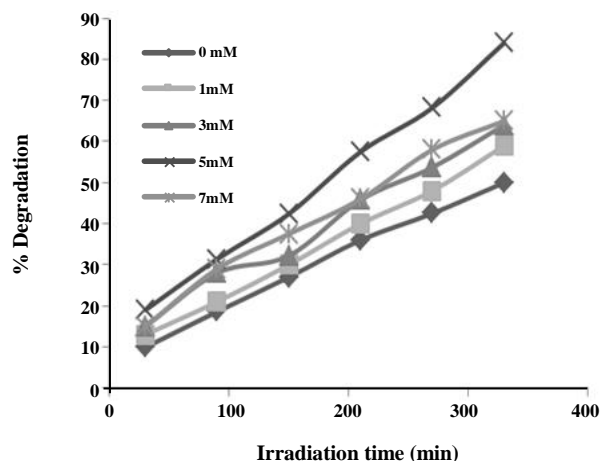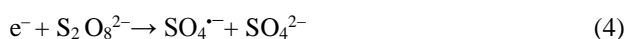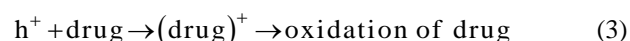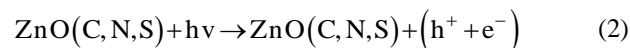
Fig. 7: Effect of $S_2O_8^{2-}$ concentration on the degradation of Fluocinolone Acetonidin. Conditions: irradiation time= 6 h, drug concentration=20 ppm, ZnO/C, N, S = 7 mg, pH= 9.

irradiation time. UV/ C, N, and S doped ZnO system had more significant effect on the degradation of drug than the UV/ $S_2O_8^{2-}$ system. When potassium peroxydisulfate was added to UV/ C, N, and S doped ZnO system drug degradation increased from 50% to 84% after 300 min.

Effect of $K_2S_2O_8$

Acceleration in degradation rate of photocatalytic oxidation on C, N and S-doped ZnO occurs by photogenerated holes. It is well known that oxidation rate increases when recombination process is suppressed. Peroxydisulfate has been shown to be a more reliable and cheaper electron acceptor [14-15]. The effect of peroxydisulfate as an electron acceptor was examined and the result is presented in Fig. 7. The degradation of Fluocinolone Acetonidin was remarkably accelerated by addition of peroxydisulfate: 20 mg/L Fluocinolone Acetonidin and in the presence of 7 mg C-, N-, and S-doped ZnO was completely degraded under irradiation of 0 to 6 hr in the absence and presence of 1-7 mM $K_2S_2O_8$ respectively.

$$ZnO(C,N,S) + h\nu \rightarrow ZnO(C,N,S) + \left(h^+ + e^-\right) \quad (2)$$

$$h^+ + drug \rightarrow (drug)^+ \rightarrow oxidation\ of\ drug \quad (3)$$

$$e^- + S_2O_8^{2-} \rightarrow SO_4^{\bullet-} + SO_4^{2-} \quad (4)$$

The decrease in the mineralization efficiency of drug with increasing SO_4^{2-} concentration is mainly due to scavenging the valuable hydroxyl radicals with SO_4^{2-} ion as shown in equation (6), [16]:

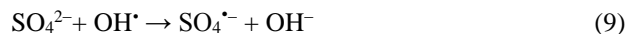$$OH^\bullet + SO_4^{2-} \rightarrow OH^- + SO_4^{\bullet-} \quad (5)$$
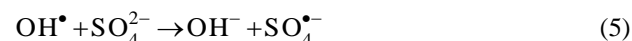
Effect of pH

The photodegradation process is pH depended and the process exhibits different behavior with the chemical character of the drug. The effect of pH on the degradation efficiency of Fluocinolone Acetonidin by $UV/ZnO/S_2O_8^{2-}$ system was studied in the range of 3–11. The degradation of Fluocinolone Acetonidin was more enhanced in pH 9 comparing to the other pH values, i.e. the lower rate of degradation at acidic environment. The interpretation of pH effects on the photocatalytic process is a very difficult task because of its multiple roles such as electrostatic interactions between the semiconductor surface, solvent molecules, substrate and charged radicals formed during the reaction process [17].

Effect of anions

Anions such as NO_2^-, CO_3^{2-}, Cl^-, SO_4^{2-} are often found in wastewater, may influence the photocatalytic reactions for removal of organic pollutants. These substances may compete for the active sites on a ZnO surface or deactivate the photocatalyst and consequently cause a decrease in degradation of targeted surfactant. Generally, anions such as carbonate, nitrite, chloride and sulfate retard the degradation of organic compounds by scavenging the hydroxyl radicals to form the respective anion radicals, according to the following reactions equation (7-10), [18-19].

$$Cl^- + OH^\bullet \rightarrow Cl^\bullet + OH^- \quad (6)$$

$$CO_3^{2-} + OH^\bullet \rightarrow CO_3^{\bullet-} + OH^- \quad (7)$$

$$NO_2^- + OH^\bullet \rightarrow NO_2^\bullet + OH^- \quad (8)$$

$$SO_4^{2-} + OH^\bullet \rightarrow SO_4^{\bullet-} + OH^- \quad (9)$$

To consider how the presence of dissolved inorganic anions affect the photocatalytic degradation rate of Fluocinolone Acetonidin, $NaNO_2$, Na_2SO_4, Na_2CO_3 and NaCl salts were selected. Similar amounts (0.1 M) of these salts were used. Fig. 8 shows the effect of anions on the photocatalytic degradation rate of drug obeying the following order:
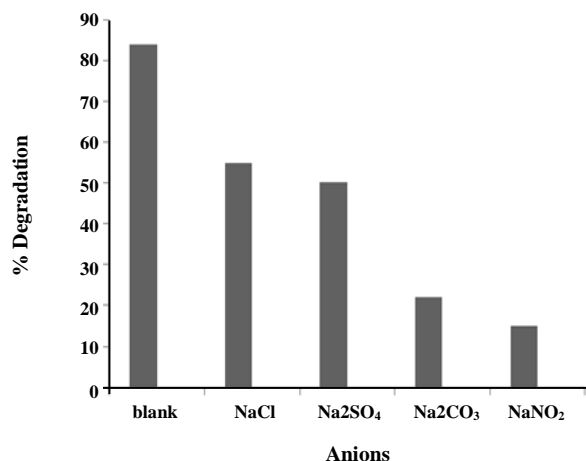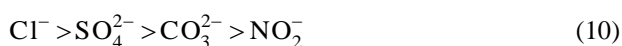
Fig. 8: Effect of anions. Conditions: ZnO/C, N, S=7 mg, K₂S₂O₈=5 mM, pH=9, Irradiation time=6 h.

Fig. 9: Effect of initial drug concentration. Conditions: ZnO/C, N, and S=7 mg/L, K₂S₂O₈=5 mM, PH=9, Irradiation time: 6 h.

$$Cl^- > SO_4^{2-} > CO_3^{2-} > NO_2^- \tag{10}$$

Therefore, these anions should be tried to be eliminated before the catalyst is added in the practical application.

Effect of concentration of drug

The influence of initial drug concentration on degradation was examined in the range of 10–50 mg/L at 7 mg catalyst loading and $K_2S_2O_8$ (5 mM) under UV irradiation. A representative concentration-time profile is shown in Fig. 9. The rate of photodegradation of the drug decreased at higher concentrations. With increasing the amounts of drug, more drug molecules were adsorbed on the surface of the photocatalyst and the active sites of the catalysts were also reduced.

Degradation Kinetics

The results showed that the photocatalytic degradation of the drug in aqueous ZnO/C, N, S can be described by the first order kinetic model as in $(\ln C_0/C) = kt$, where C_0 and C are initial and the concentration at any time [20]. The semi logarithmic plots of the concentration data versus irradiation time gave rise to a straight line. The correlation coefficient and rate constant were calculated as $r^2 = 0.993$ and 0.342 min^{-1} respectively.

CONCLUSIONS

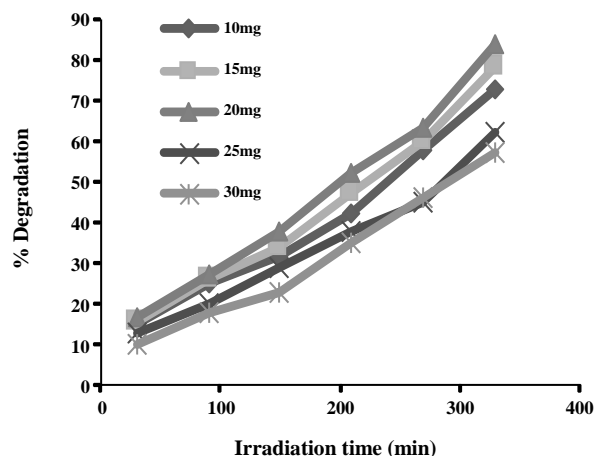In this study the drug Fluocinolone Acetonidin was appropriately mineralized by a photocatalytic reaction using nanoparticles of zinc oxide doped C, N, and S in the form of slurry. The results are summarized as follows:

● The optimum condition for degradation was found to be pH = 9, ZnO/C, N, S = 7 mg, $K_2S_2O_8$ = 5 mM, concentration of Fluocinolone Acetonidin = 20 ppm, irradiation time = 6 hr.

● The results was obtained in taguchi method showed that irradiation time; pH; amount of ZnO; cationic surfactant concentration and dosage of $K_2S_2O_8$ contributed by 4%, 7%, 30%, 18% and 41% respectively.

● The anions SO_4^{2-}, Cl^-, NO_2^- and CO_3^{2-} had an inhibitory effect on the percent of photodegradation of Fluocinolone Acetonidin in the following order:

$Cl^- > SO_4^{2-} > CO_3^{2-} > NO_2^-$
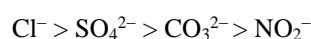
● The kinetic of photocatalytic degradation for Fluocinolone Acetonidin follows a pseudo-first-order equation.

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