

**Removal of betamethasone sodium phosphate from wastewater
using zinc oxide nanoparticles**

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ABSTRACT

The photocatalytic degradation of betamethasone sodium phosphate was investigated in aqueous suspensions of zinc oxide nanoparticular with diameter size 20 nm under a variety of conditions. Different parameters such as irradiation time, the amount catalyst ($0.12\text{--}0.8\text{ g L}^{-1}$), initial concentration of drug ($10\text{--}50\text{ mgL}^{-1}$) and initial pH values (ranging from 3 to 11) were investigated in the presence of various electron acceptors. It was observed that 0.44 gL^{-1} of photocatalyst is the optimum value for photocatalyst dosage. In the most favorite conditions, the degradation efficiency was obtained 30gL^{-1} for betamethasone sodium phosphate. Finally, the kinetics process was studied and the photodegradation rate of betamethasone sodium phosphate was found to obey pseudo-first-order kinetics equation represented by the Langmuir-Hinshelwood model.

Keywords: photocatalytic degradation, betamethasone sodium phosphate, wastewater, zinc oxide nanoparticles

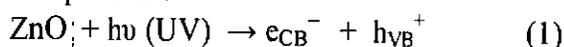
INTRODUCTION

Polluted water has always been a serious problem to the environment. Besides, various water pollutants including pesticides, dyes and surfactants, pharmaceuticals are emerging classes of aquatic contaminants. Both human and veterinary pharmaceuticals have been increasingly detected in sewage, natural, surface and ground water [1-5]. The reason why they may be dangerous for the environment is that these substances, generally developed with the aim to perform a biological effect on human beings, may also affect other living organisms in a non-predictable way. These compounds enter the aquatic environment after their ingestion and subsequent excretion either without modifications or in the form of non-metabolized parent compounds [6].

Most chemical and physical processes are not destructive but they only transfer the contaminants from one form to another. These processes include chemical precipitation methods and separation of pollutants, coagulation, electro coagulation and elimination by adsorption on activated carbon. Therefore, a new and different kind of pollution problem is being faced which in turn calls for further treatment [7-9]. An alternative method different from the conventional procedures has been introduced in recent years. The process, called advanced oxidation process (AOP), is based on the generation of very reactive oxygen species such as hydroxyl radicals that oxidize a broad range of organic pollutants quickly and non-selectively [10, 11]. The photocatalytic oxidation of organic

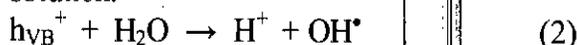
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pollutants (advanced oxidation process) has also received much attention during recent years. This is an attractive method for removal of toxic, recalcitrant aliphatic and aromatic pollutants, from wastewater. The degradation technique, which uses suitable semiconductor, irradiated by a light source with an energy higher than, or at least equal to, their band gap is also a novel method. Advanced oxidation processes like photocatalysis system including a combination of semiconductors such as TiO_2 , ZnO , CdS , Fe_2O_3 and ZnS together with UV light [12]. Among the semiconductors whose photocatalytic properties have been studied, TiO_2 is the most commonly used. It is proven to be an effective, stable, harmless, and inexpensive semiconductor [13]. However, another semiconducting oxide, ZnO , has recently been receiving attention from researchers. ZnO is well known to semiconductor under solar irradiation, and its photocatalytic mechanism has been proven to be similar to that of TiO_2 , although it shows less vigorous oxidation states [14]. ZnO has sometimes been reported to be more efficient than TiO_2 . The biggest advantage of ZnO is that it absorbs over a larger fraction of the solar spectrum than TiO_2 [15]. For this reason, ZnO is the most suitable photocatalyst for removal in the presence of sunlight [16]. The mechanism constituting heterogeneous photocatalytic oxidation processes has been discussed extensively in the literature [17, 18]. When zinc oxide is illuminated with light of band gap energy (3.2 eV), electrons in conduction band (e_{CB}^-) and holes in valence band (h_{VB}^+) are produced according to equation 1:



These charge can recombine, or the holes can be scavenged by oxidizing species (for example, H_2O , OH^-), and electron by reducible species (for example, O_2) in the

solution.



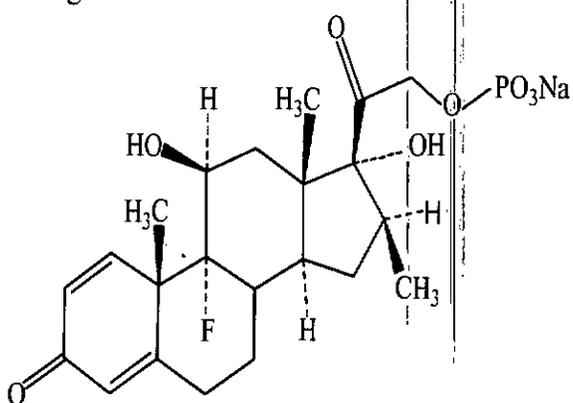
The hydroxyl radical (like OH^{\bullet}) is a highly reactive oxidizing reagent and can decompose most organic contaminants.

Betamethasone sodium phosphate is a potent glucocorticoid steroid with anti-inflammatory properties. Steroidal anti-inflammatory drugs (corticosteroid) are a special group of widely available pharmaceuticals that are often found in wastewaters.

In the present research, photodegradation of betamethasone sodium phosphate in the presence of ZnO nanoparticles and electron acceptors using UV light as illuminator has been reported.

EXPERIMENTAL

The Betamethasone sodium phosphate powder (formula: $\text{C}_{22}\text{H}_{28}\text{FN}_2\text{O}_8$, Molar mass: 516.4 g/mol) was obtained from Behdasht Kar™. The structure of betamethasone sodium phosphate is shown in Fig. 1.



9-Fluoro-11 β , 17-dihydroxy- 16 β -methyl-3,20-dioxopregna-1,4-diene-21-yl disodium phosphate

Fig. 1. Chemical structure of betamethasone sodium phosphate.

The Zinc oxide nano powder (particle size, Ca. 20nm; BET area, 50 m^2/g ; 99.5%)

was obtained from Nanoamor (USA) and $K_2S_2O_8$, H_2O_2 , from Merck. The pH of the solution was adjusted to the desired value between 2.0 and 11.0 by using dilute solutions of HCl or NaOH.

Photocatalytic Reaction

The photo degradation studies were carried out in a batch reactor system. All experiments were done in a rectangular tray of (90×60×40cm) made of MDF. The slurry was composed of drug solution and catalyst, kept in a reactor (a cylindrical Pyrex vessel of 2cm diameter with capacity of 50ml) and placed on a magnetic stirrer. The radiation source was a high pressure mercury vapor lamp (400w), fitted on the top of reactor. An exhaust fan was fitted on the side wall of the chamber to maintain a constant temperature.

Procedure

In a 50ml flask, 25ml of the drug solution of an appropriate concentration (indicate concentration) was placed and its pH value measured. A known amount (indicate) of ZnO nano powder was added to the drug/oxidant and the mixture was irradiated with the UV lamp. The aqueous suspension was magnetically stirred (speed of 80 rpm) all throughout the experiment. 5ml samples were withdrawn on regular intervals and centrifuged. Absorbance of the supernatant solution was measured and returned to the reactor. The quantitative estimation of the drug was carried out using a UV-Vis spectrophotometer (Model Jenway 6405) at $\lambda_{max} = 241nm$. 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 .

RESULTS AND DISCUSSION

Effect of ZnO concentration

A series of experiments were carried out by varying the amount of ZnO (0.12 to 0.8 g/l)

in order to establish the effect of photocatalyst loading and to avoid unnecessary excess of photocatalyst. Experiments performed with different concentrations of ZnO as presented in Fig. 2. It can be seen that the photodegradation efficiency increases with an increase in ZnO concentration up to 0.44g/l, and is then decreased. This type of behavior 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. However, 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.

Effect of initial concentration

The influence of initial drug concentration on degradation was examined in the range of 10–50mg/l at 0.44 g/l catalyst loading and $K_2S_2O_8$ (1mM) under UV irradiation and the representative concentration-time profiles are shown in Fig. 3. It was observed that the rate of photodegradation of the drug decreased at higher concentrations. With increasing the amounts of betamethasone sodium phosphate, more drug molecules will be adsorbed on the surface of the photocatalyst and the active sites of the catalysts will be reduced. Therefore, with increasing occupied space of catalyst surface, the generation of hydroxyl radicals will be decreased. Also, increasing concentration of drug can lead to decreasing the number of photons that is arrived to the surface of catalysts. More light is adsorbed by molecules of drug and the excitation of photocatalyst particles by photons will be reduced. Thus, photodegradation efficiency will also be diminished [19].

Effect of pH

Photodegradation of drug was studied in amplitude pH of 3.0 –11 in the presence of ZnO catalyst (0.44 g/l) and $K_2S_2O_8$ (1mM). The results for irradiation time of 180 min are shown in Fig. 4. In all cases, the maximum degradation efficiency was obtained in alkaline pH 9.0 for betamethasone sodium phosphate. In

presence of ZnO and in pH 9.0, degradation efficiency 98% is obtained. The interpretation of pH effects on the photocatalytic process is a very difficult task due to its multiple roles such as electrostatic interactions between the semiconductor surface, solvent molecules, substrate and charged radicals formed during the reaction [20].

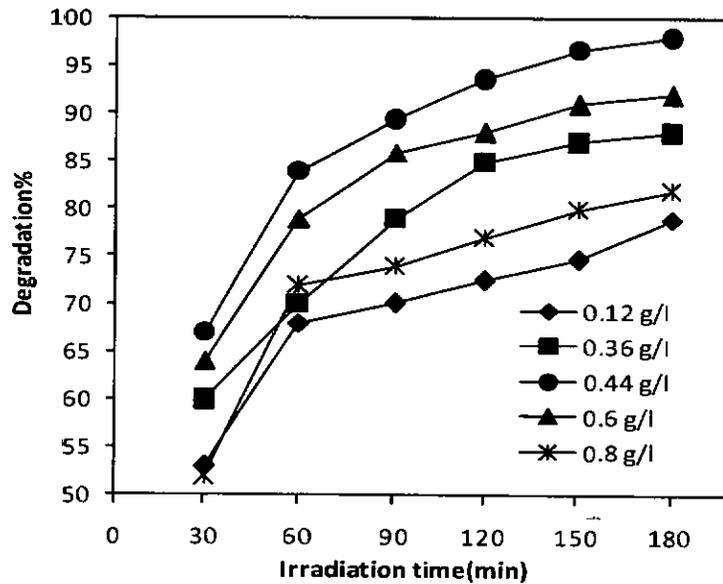


Fig. 2. Effect of ZnO concentration the photodegradation efficiency. Irradiation time 180 min, drug concentration 30mg/l, $K_2S_2O_8$ 1mM, pH 9.0 and V=25ml.

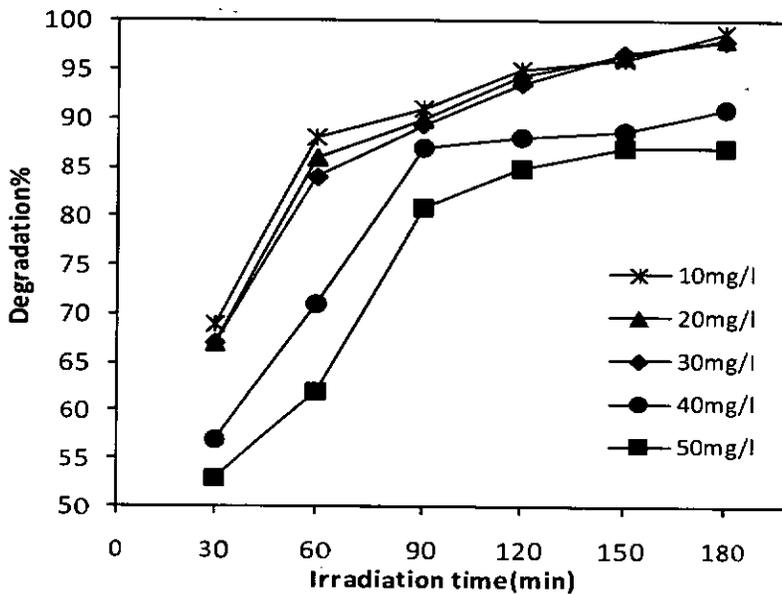


Fig. 3. Effect of initial concentration on the photodegradation efficiency. Irradiation time 180 min, ZnO 0.44g/l, $K_2S_2O_8$ 1mM, pH 9.0 and V=25ml.

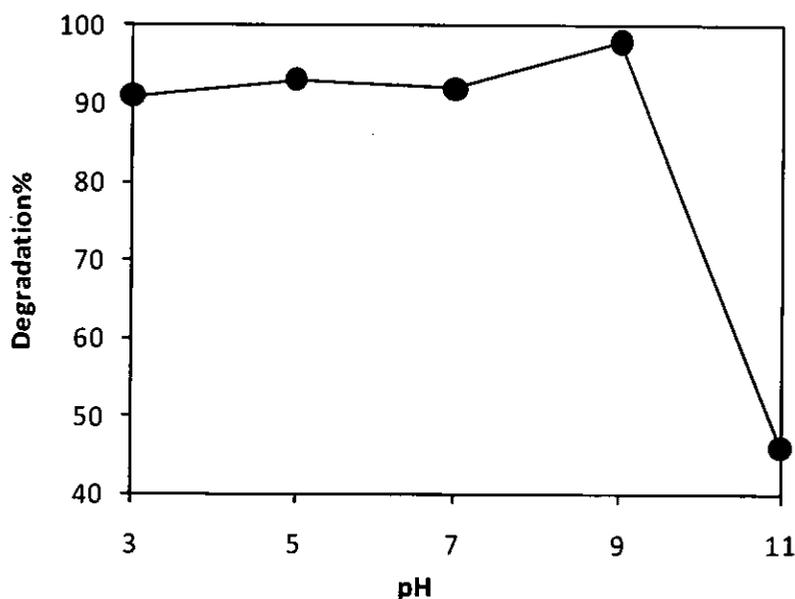
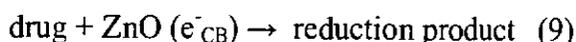
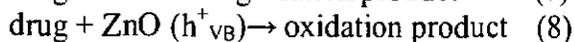
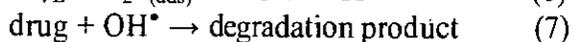
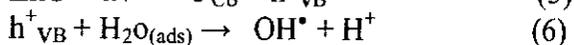
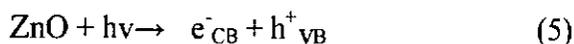


Fig. 4. Effect of pH on the photodegradation efficiency. Irradiation time 180 min, drug concentration 30mg/l, $K_2S_2O_8$ 1mM, ZnO 0.44g/l and V=25ml.

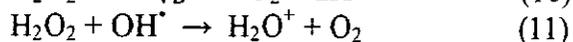
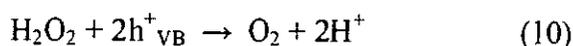
Effect of electron acceptors

One practical problem in using ZnO as a photo catalyst is the under sired electron hole recombination, which in the absence of proper electron acceptor or donor, is extremely efficient and represents the major energy wasting step in this limiting the achievable quantum yield. One strategy to inhibit electron hole pair recombination is to add other (irreversible) electron acceptors to the reaction. They could have several different effect, such as (1) to increase the number of trapped electrons and consequently, avoid recombination (2) to generate more radicals and other oxidizing species (3) to increase the oxidation rate of intermediate compounds and (4) to avoid problems caused by low oxygen concentration.



In highly toxic wastewater where the degradation rate many often be justified with this view, we have studied the effect of electron acceptor, such as hydrogen peroxide and potassium peroxide disulfate. In the presence of ZnO on drug under investigation, the highly oxidative h^+_{VB} can react easily with surface bound H_2O to produce hydroxyl radicals or can directly react with the surface sorbet organic molecules (R) to form R^+ [21-24].

According to Fig 5 presence of H_2O_2 decrease rate of degradation compares to other kind. This presence of H_2O_2 case reaction between valance band and oxidant and hindered action H_2O_2 . This hindered is due to hydroxyl radical need here. Equation (10) and (11) shows these reactions.



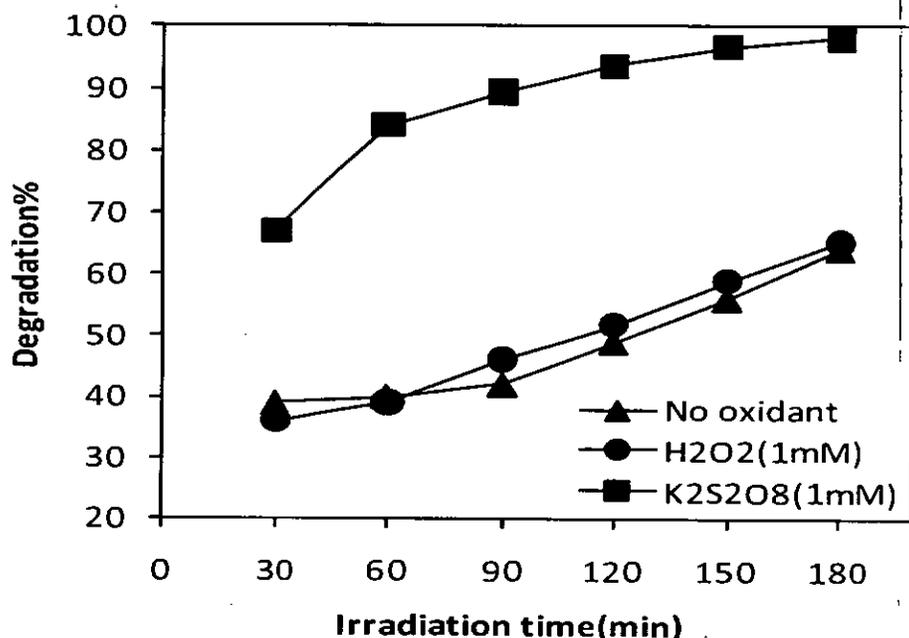
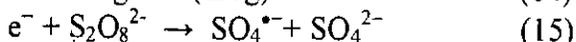
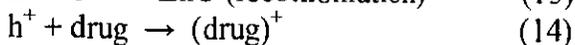
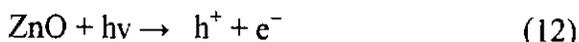


Fig. 5. Effect of electron acceptors on the photodegradation efficiency. Irradiation time 180 min, drug concentration 30mg/l, K₂S₂O₈ 1mM, H₂O₂ 1mM, ZnO 0.44g/l, pH 9.0 and V=25ml.

Effect of K₂S₂O₈

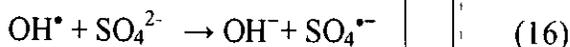
Acceleration of the degradation rate photo catalytic oxidation on ZnO occurs by photo generated holes. It is well known that oxidation rate increase when recombination process is suppressed. Proxy disulfate has been known to be a more reliable and a cheaper electron acceptor [25]. The effect of proxy disulfate as the electron acceptor was examined and is presented in Fig 6.

The degradation of Betamethasone sodium phosphate was remarkably accelerated by addition of proxy disulfate: 30mg/l betamethasone sodium phosphate and in the presence of 0.44 g/l ZnO was completely degradation under the irradiation of 6 to 3h, in the absence and in the presence of 1mM K₂S₂O₈ respectively.



The decrease in the mineralization efficiency of drug with increasing SO₄²⁻

concentration is mainly due to scavenging the valuable hydroxyl radicals with SO₄²⁻ ion as shown in Eq. (16).



Irradiation time, 180 min, drug concentration 30mg/l, ZnO 0.44g/l, pH 9.0 and V=25ml.

Kinetic studies

Fig. 7 shows the kinetics of disappearance of betamethasone sodium phosphate for an initial concentration of 30 mg/L under optimized conditions. The results showed that the photocatalytic degradation of the drug in aqueous ZnO can be described by the first order kinetic model as $\ln(C_0/C) = kt$, where C₀ is the initial concentration and C is the concentration at any time [26]. The semi logarithmic plots of the concentration data gave rise to a straight line. The correlation constant for the fitted line and rate constant were calculated as R²=0.9942 and 0.0216 min⁻¹ respectively.

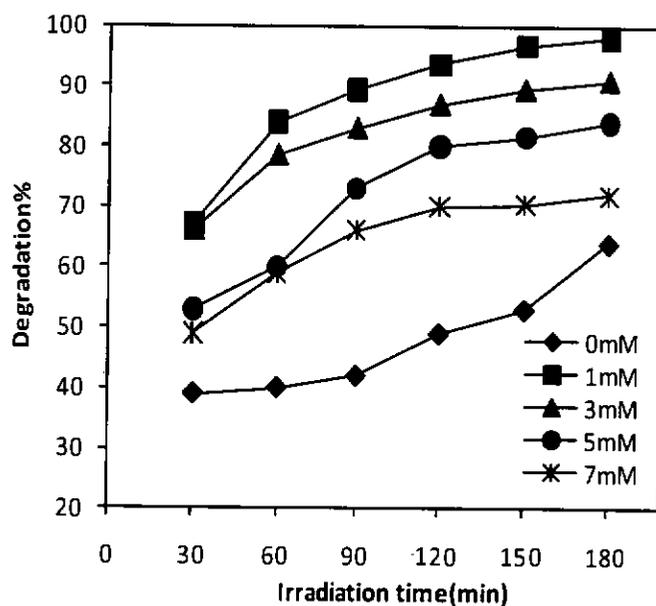


Fig. 6. Effect of $S_2O_8^{2-}$ concentration on the degradation of betamethasone sodium phosphate.

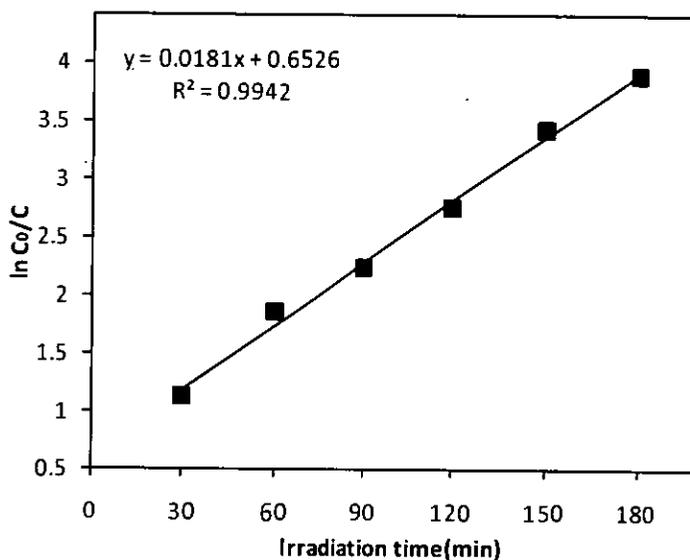


Fig. 7. Kinetic analysis of betamethasone sodium phosphate under optimized conditions

CONCLUSIONS

In this study, betamethasone sodium phosphate was appropriately mineralized by a photo catalytic reaction in the presence of Zinc oxide nanoparticles in the form of slurry. Under optimal degradation conditions of drug, the photo degradation percent of betamethasone sodium phosphate was 98% when the solution was irradiated by the 400w high pressure mercury vapor lamp for 3h. Degradation of betamethasone sodium

phosphate was markedly accelerated by addition of proxy disulfate. Therefore, when proxy disulfate was added to the UV/ZnO system, surfactant degradation increased from 64% to 98% after 120 min and photocatalytic degradation followed a pseudo-first order type of kinetics.

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