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Photocatalytic degradation of Lidocaine HCl using CuO/ZnO nanoparticles

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ABSTRACT

In this paper, the photocatalytic degradation of Lidocaine HCl, an anesthetic was investigated in aqueous solution using CuO/ZnO as a photocatalyst. The degradation was studied under different conditions including the amount of the photocatalyst, irradiation time, initial concentration of drug, pH of the system, initial concentration, addition of oxidant on the reaction rate and anion presence. The results showed that the photocatalytic degradation of Lidocaine HCl was strongly influenced by these parameters. The best conditions for the photocatalytic degradation of Lidocaine HCl were obtained. The optimum amount of the photocatalyst used is 0.48 g/L. The photodegradation efficiency of Lidocaine HCl increases with the increase of the illumination time. It was found that the photodegradation efficiency decreased with increasing the initial concentration of Lidocaine HCl. The photodegradation efficiency of Lidocaine HCl was accelerated by adding a small amount of H_2O_2. The possible roles of the additives on the reactions and the possible mechanisms of effect were also discussed.

Keywords: Photocatalytic degradation; Lidocaine HCl; CuO/ZnO; Photocatalyst

INTRODUCTION

Waste pharmaceutical disposal practices involve a number of conventional techniques, such as sewer and incineration. Despite the widespread utilization of these techniques, they do not help remove drugs from contaminated waters. Waste drugs are disposed into water through sewer or direct disposal. Such practices could be hazardous and cause serious water contamination. Therefore, two strategies need to be adopted: prevention of disposing waste drugs into sewage system before suitable treatment, and purification of contaminated waters from contaminant drugs. Large band gap semiconducting particles are being investigated as catalysts for photo-degradation of drugs and organic contaminants in water [1-6].

Zinc oxide is one of the most important semiconductor materials today, having a wide range of applications such as varistors, thyristors, catalysis, optical coating, photoelectricity, etc. because of its remarkable optical and electronic properties. ZnO has been extensively investigated as a semiconductor photocatalyst due to its wide direct band gap (3.37 eV), which is the same as TiO_2. Moreover, ZnO is abundant, not hazardous and not costly. For these reasons, ZnO particles have been used to degrade

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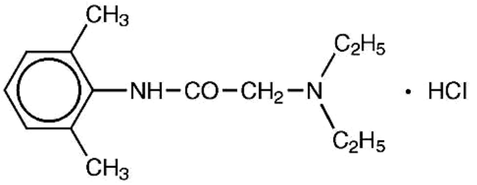
different organic contaminants in water. In order to make ZnO suitable for degradations with good efficiency, modification of ZnO by addition of another semiconductor has been used. In principle the coupling of different semiconductor oxides can reduce its band gap, extend its absorption range to visible light region, promote electron–hole pair separation under irradiation and, consequently, achieve a higher photocatalytic activity. In the past several years, coupled semiconductors formed by ZnO and other metal oxides or sulfides such as TiO_2, SnO_2, Fe_2O_3, CdS, ZnS,CuO and so on, have been reported. There are also a large colume of reports about CuO/ZnO nanocomposites [7-10].

Lidocaine is one of the most widely used anesthetic drugs today, especially during surgery and dental procedures. There are two forms of lidocaine (2-diethylamino-N-(2,6-dimethylphenyl) acetamide): lidocaine hydrochloride (lidosalt) and lidocaine base (lidobase). Lidocaine hydrochloride is the anesthetically active form and is soluble in water, whereas lidobase is not soluble in water and anesthetically much less active [11].

EXPERIMENTAL

Materials

The Lidocaine HCl powder (formula: $C_{14}H_{22}N_2O$, Molar mass: 270.8 g/mol) was obtained from behdasht kar pharmaceutical producer. The structure of Lidocaine HCl is shown in scheme 1. The synthesis of CuO-doped ZnO nanopowder was used.



Scheme. 1. Lidocaine Hydrochloride.

Fig. 1. shows X-Ray Diffraction (XRD) patterns of the CuO/ZnO nanoparticles fabricated. Average particle size was determined by using Debye-Scherrer formula with Full-width at Half Maximum (FWHM). The sizes are found to be 19 nm. Morphology of CuO/ZnO nano particles is evaluated by Scanning Electron Microscopy (SEM). The SEM images of nano CuO/ZnO prepared shown in Fig .2. The data indicate that the particles sizes obtained from SEM analysis are in good agreement with XRD analysis for powders synthesized. $K_2S_2O_8$, H_2O_2, Na_2SO_4, $NaNO_2$, Na_2CO_3, NaCl were from Merck. The pH of the solution was adjusted with 1M HCl or 1M NaOH.

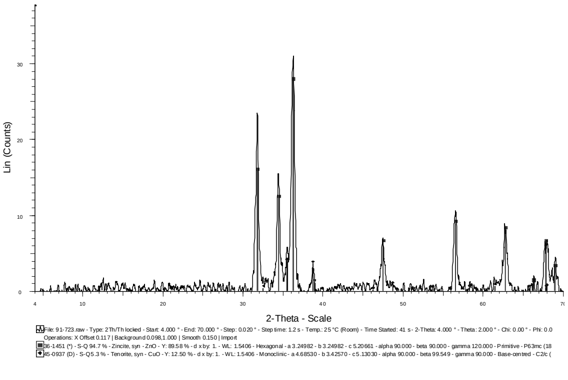


Fig. 1. XRD pattern of CuO/ZnO nanoparticles.

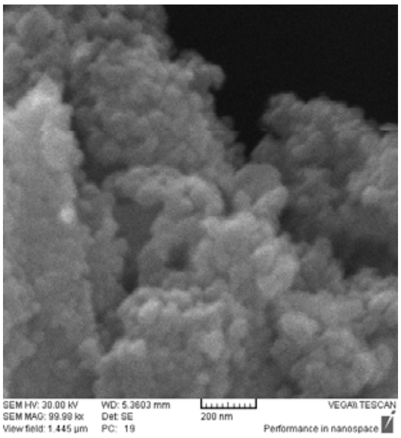


Fig. 2. SEM image of CuO/ZnO nanoparticles.

Photocatalytic Reaction

The photodegradation studies were carried out in a batch reactor system. The setup consisted of a UV chamber made up of MDF having dimensions of (90 cm×60 cm×75 cm). A high-pressure mercury vapor lamp (400 W) was fitted on the top of the chamber. An exhaust fan was fitted on the side wall of the chamber to maintain a constant temperature. The reactor used was cylindrical in shape and made a Pyrex flask, with a diameter of 3cm and a capacity of approximately 50 mL.

Procedure

In a 50 mL flask, 25 mL of the drug solution with an initial concentration range of 30 mg/L was placed. A known amount of CuO/ZnO nanopowder was added to the drug and oxidant. The pH was chemically controlled at 6. The mixture was irradiated with the UV lamp for 6 h. The aqueous suspension was magnetically stirred (speed of 80 rpm) throughout the experiment. 5 ml samples were withdrawn on regular intervals of time 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 λ_{max}= 263 nm. The degree of photo degradation (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 UV irradiation and CuO/ZnO particles

Fig. 3. shows a typical time-dependent UV-Vis spectrum of Lidocaine HCl solution during photoirradiation. These experiments demonstrated that both UV light and a photocatalyst, were needed for the effective destruction of Lidocaine HCl. Because it has been established that the photocatalysed degradation of organic matter in solution is initiated by photoexcitation of the semiconductor, followed by the formation of an electron–hole pair on the surface of catalyst (Eq. (1)). The high oxidative potential of the hole (h^{+VB}) in the catalyst permits the direct oxidation of organic matter (drug) to reactive intermediates (Eq. (2)). Very reactive hydroxyl radicals can also be formed either by the decomposition of water (Eq. (3)) or by the reaction of the hole with OH^- (Eq. (4)).

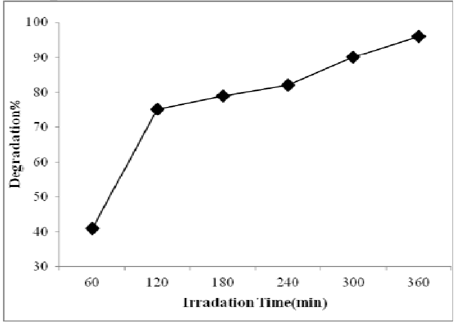


Fig. 3. UV–Vis spectra changes of Lidocaine HCl in aqueous CuO/ZnO dispersion.
Conditions: Lidocaine HCl=30 mg/L, CuO/ZnO=0.48 g/L, H_2O_2=7 mM, irradiated with a mercury lamp light at pH 6, at various irradiation times.

The hydroxyl radical is an extremely strong, non-selective oxidant which leads to the partial or complete mineralization of several organic chemicals [12- 14].

$$CuO - ZnO + h\nu \rightarrow e^-_{CB} + h^+_{VB} \qquad (1)$$

$$h^{+\,VB} + \text{drug} \rightarrow \text{drug}^{\bullet}+ \rightarrow \text{oxidation of the drug} \qquad (2)$$

$$h^{+\,VB} + H_2O \rightarrow H^+ + OH^{\cdot} \qquad (3)$$

$$h^{+\,VB} + OH^- \rightarrow OH^{\bullet} \qquad (4)$$

Electron in the conduction bond (e^-_{CB}) on the catalyst surface can reduce molecular oxygen to superoxide anion (Eq. (5)). This radical, in the presence of organic scavengers, may form organic peroxides (Eq. (6)) or hydrogen peroxide (Eq. (7)).

$$e^-_{CB} + O_2 \rightarrow O_2^{\bullet -} \qquad (5)$$

$$O_2^{\bullet -} + \text{drug} \rightarrow \text{drug}^- OO^{\bullet} \qquad (6)$$

$$O_2^{\bullet -} + H_2O^{\bullet} + H^+ \rightarrow H_2O_2 + O_2 \qquad (7)$$

Electrons in the conduction bond are also responsible for the production of hydroxyl radicals, species which have been indicated as the primary cause of organic matter mineralization (Eq. (8)).

$$^{\bullet}OH + \text{drug} \rightarrow \text{degradation of the drug} \qquad (8)$$

Effect of the amount of CuO/ZnO

Experiments performed with different concentrations of CuO/ZnO are shown in Fig. 4. It can be seen that the photodegradation efficiency increases with an increase in CuO/ZnO concentration up to 0.48 g/L, and is then decreased. This observation 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 dosage. At the same time, due to an increase in the turbidity of the suspension, there is a decrease in UV light penetration as a result of increased scattering effect and hence the photoactivated volume of suspension decreases. Since the most effective decomposition of Lidocaine HCl was observed with 0.48 g/L of CuO/ZnO, the other experiments were performed in this concentration of CuO/ZnO [15].

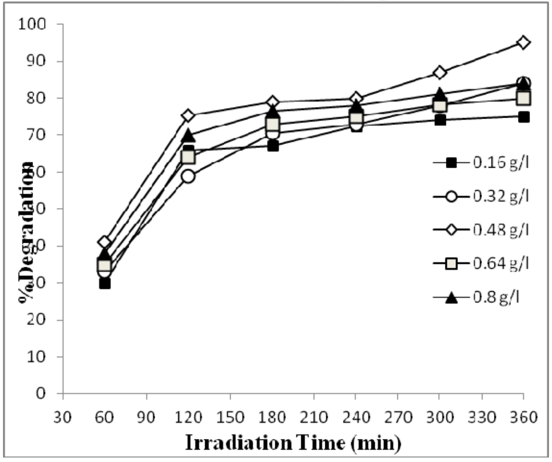


Fig. 4. Effect of the amount of ZnO/CuO on the photodegradation efficiency
Conditions: Irradiation time =360 min, drug concentration=30 mg/L, CuO/ZnO=0.48 g/L, H_2O_2=7 mM, pH= 6, V=25 mL.

Effect of initial drug concentration

The influence of initial drug concentration on degradation was examined in the range of 10– 50 mg/L at 0.48 g/L catalyst loading and H_2O_2 (7 mM) under UV irradiation. The representative concentration-time profiles are shown in Fig. 5. The rate of photodegradation of the drug decreased at higher concentrations. With increasing the amounts of Lidocaine HCl, the more of 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. The more light is absorbed by molecules of drug and the excition of photocatalyst particles by photons will be reduced. Thus, photodegradation efficiency diminished [16].

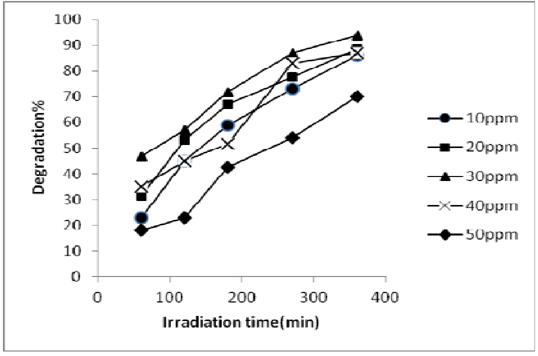


Fig. 5. Effect of initial concentration
Conditions: Irradiation time =360 min, drug concentration=30 mg/L, CuO/ZnO=0.48 g/L, H_2O_2=7 mM, pH= 6, V=25 mL.

Effect of electron acceptors on the photodecomposition of Lidocaine HCl

The addition of other powerful oxidizing species, such as hydrogen peroxide and potassium peroxydisulfate, to CuO/ZnO suspensions is a well-known and extensively studied procedure and in many cases leads to an acceleration of the rate of the photocatalytic degradation. The degradation rate for the decomposition of Lidocaine HCl in the presence of H_2O_2 and $K_2S_2O_8$ is shown in Fig. 6. According this Fig., presence of H_2O_2 increase rate of degradation compared to other kinds. H_2O_2 is considered to have two functions in the process of photocatalytic degradation. It accepts a photogenerated electron from the conduction band and thus promotes the charge separation:

$$H_2O_2 + e^- \rightarrow OH^- + OH^\bullet \qquad (9)$$

And it also forms $OH^\bullet$ radicals according to equation 10:

$$H_2O_2 + O_2^- \rightarrow OH^- + OH^\bullet + O_2 \qquad (10)$$

However, a possible reaction between the H_2O_2 with the photogenerated intermediates cannot be excluded. In the presence of excess H_2O_2, it may act as a hole or OH scavenger or react with CuO/ZnO to form peroxy compounds, which are detrimental to the photocatalytic action. In addition, it can also compete with the organic compound for the adsorption sites on the semiconductor's surface [17-20].

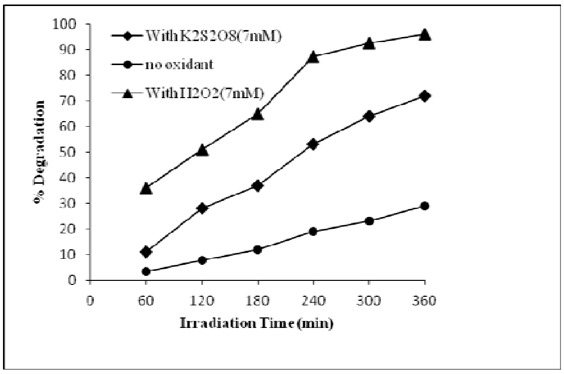


Fig. 6. Effect of electron acceptors on the photodegradation efficiency.
Conditions: Irradiation time=360 min, drug concentration=30 mg/L, H_2O_2=7 mM, $K_2S_2O_8$=7 mM, CuO/ZnO=0.48 g/L, V=25 mL, pH=6.

Effect of pH

Photodegradation of drug was studied in amplitude pH of 3.0–11 in the presence of ZnO catalyst (0.48 g/L) and H_2O_2 (7 mM).The results for irradiation time of 360 min are shown in Fig. 7. In all cases, the maximum degradation efficiency was obtained in acidic pH 6 For Lidocaine HCl. In the presence of CuO/ZnO and in pH 6, degradation efficiency 93% is obtained. The interpretation of pH effects on the photocatalytic processes is 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 [21, 22].

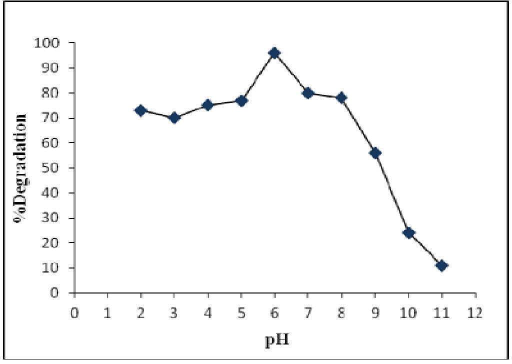


Fig. 7. Effect of pH on the photodegradation efficiency.
Conditions: Irradiation time=360 min, drug Concentration=30 mg/L, H_2O_2=7 mM, CuO/ZnO=0.48 g/L, V=25 ml.

The pH influences the characteristics of the photocatalyst surface charge. Therefore, pH of the solution is a significant parameter in performing the reaction on the surface of semiconductor particles. In acidic solutions photodegradation efficiency was more than that in alkaline solutions. This is because photodecomposition of CuO/ZnO takes place in acidic and neutral solutions.

CONCLUSIONS

In this study, lidocaine HCl was appropriately mineralized by a photocatalytic reaction in the presence of CuO-doped ZnO (CuO-ZnO) nanoparticles in the form of slurry. The optimal degradation conditions of lidocaine HCl are: 0.48 g/L catalyst, pH 6.0 and 7 Mm H_2O_2. Under optimal degradation conditions of drug, the photodegradation percent of lidocaine HCl was 93% when the solution was irradiated by the 400w high pressure mercury vapor lamp for 6h.

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