Sonocatalytic degradation of the insecticide parathion in water

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Abstract: This work discusses the effects of ultrasound (US) irradiation on the decomposed of parathion in US/ZnO system. The influences of initial concentration of catalyst, initial parathion concentration, irradiation time, and temperature was studied, Gas chromatography mass spectroscopy (GC – MS) was used for analyses of pesticide. The decomposed ratio of parathion increased with the ZnO dosage in 200–800 mg/l in the UV/ZnO system. It was found out that the optimal concentration of catalyst was 600 mg/l .Results showed that the degradation of pesticide increased with increasing temperature and decreased with increasing pesticide concentration. At 100 min, the decompose ratio of ZnO, US and US/ZnO were 30.2%, 47.6%, 70.2%, respectively. The experimental results showed that the US/ZnO system cannot only completely decomposed but can effectively degradation parathion.

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Key words: sonocatalytic degradation; parathion; zinc oxide.

1. Introduction

Parathion is an organophosphorous insecticide. It was used worldwide for controlling insect pests in soil, ornamental plants, fruits and vegetables, and has been frequently detected in groundwater and surface water(Zulin et al. 2002). Parathion has been classified as an acutely toxic pesticide by US EPA, this pesticide is potent inhibitors of acethylcholinesterase (Wu and Linden 2008). Parathion is relatively water soluble (24 mg/L at 25°C)(Sakellarides et al. 2003) and has a log K_{ow} (octanol–water partition coefficient) of 3.83 and vapor pressure of 5.32 mPa(Wu and Linden 2008). Advanced oxidation processes (AOPs) are very efficient methods for decomposition and mineralization of hazardous organic compounds in water. Recently, Ultrasonic irradiation mediated by suitable catalysts (sonocatalysis) has been receiving attention as a promising method for the treatment of organic pollutants in water (Meng and Oh 2011; Merouani et al. 2010; Song et al. 2011). The chemical effects of US in liquid include cavitation which consists of nucleation, growth and collapse of bubbles. The collapse of the bubbles results in localized supercritical condition such as high temperature, pressure, electrical discharges and plasma effects(He et al. 2011).

The gaseous contents of a collapsing cavity reach temperatures of approximately 5500°C and the liquid immediately surrounding the cavity reaches up to 2100°C. The localized pressure is estimated to be around 500 atmospheres resulting in the formation of transient supercritical water(Pang et al. 2011a; Pang et al. 2011b). In the sonophotochemical process or sonophotocatalysis, a photocatalysts (usually a semiconductor powder such as TiO_2 or ZnO) is irradiated with ultraviolet radiation in the presence of ultrasonic sound waves. This combination provides a synergistic effect which can enhance the degradation of pollutants due to the highly reactive free radicals. These supplementary radicals are generated by the electron-hole couples created by excitation of TiO_2 particles with ultraviolet radiation Many researchers reported that Sonocatalytic process was capable of degrading various persistent organic compounds such as perchloroethylene(Sáez et al. 2011), Aldehydes(Sekiguchi et al. 2011) bisphenol A and 17α-ethinyl estradiol(Park et al. 2011), herbicides (Bahena et al. 2008), organic dyes(Wang et al. 2011; Wang et al. 2010), and pesticides: methyl parathion and dichlorvos(Senthilnathan and Philip 2011), monocrotophos (Madhavan et al. 2010), methyl parathion(Wang et al. 2007). The aim of this work was to study the degradation of parathion by means of sonolysis, sonocatalytic .The effect of parameters such as initial concentration of catalyst, initial parathion concentration, irradiation time, and temperature was studied.

2.Materials and methods

2.1. Reagents

The ZnO catalyst was sourced from FLUKA. The diameter specific surface area and band gap energy of ZnO were 14 nm, 10 $m^2.g^{-1}$ and 2.92 ev respectively. The tested compounds in this study parathion (from supellco), NaOH, HNO3 were obtained Merck co. (Germany).

2.2. Procedures

The concentration of parathion in samples was 25, 50, 75 $mg.L^{-1}$ and used the 30% insecticide. The dosage of zinc oxide in samples was 200,400,600,800 $mg.L^{-1}$. The samples were adjusted in reactor in 5 time of remaining (20, 40, 60, 80, 100 min). The pH of the samples solution parathion were 4, 7, 9 and reaction temperature in 20-60^{o}C. Samples of this study are synthetic from deionized water in the all systems. For the development of the processes performed by US irradiation and ZnO separately and later combinations of US/ZnO .For the sonocatalytic of parathion, a solution containing known concentration of the pesticide and ZnO nanopowder was prepared and it was allowed to equilibrate for 30 min in the darkness, then 50 ml of the prepared suspension was transferred to a 800 ml Pyrex reactor .Irradiation was carried out with a 500 w .During irradiation, agitation was maintained by magnetic stirrer (IKA, werke , Germany) to keep the suspension homogeneous, and the suspension was sampled after an appropriate illumination time. Ultrasonic in this study was model (T1-H-5, Germany) capacity 3.7 L, dimensions= 30 cm, W = 25 cm, H= 32 cm, flow type batch, altered number 2, ultrasonic irradiation of 800 ml parathion solution operating at 130 kHz working frequency and 500 w power . For the extraction of parathion was used techniques (DLLME) dispersive liquid – liquid microextration(Farajzadeh et al. 2009).

A 5 ml of sample (water + analyte) mixed with 500 ml extraction solution (2 ml internal standard: chlorpyrifos 1000 mgL^{-1}, 10 ml chloroform with 100 ml acetone). The mixture was then centrifuged for 5 min at 3500 rpm. After this process, the upper of aqueous phase was collected by pipette, the droplets were sedimented at the bottom of the conical test tube and 1 ml injected in to GC/MS.Analyses were performed by gas chromatography mass spectroscopy (GC-MS). For identification, 1ml samples were injected into the GC-MS (Varian CP-3800 GC with MS trap detector Varian Saturn 2200, run in EI mode). Injector temperature was 270^{o}C and analysis was done using a capillary column (Varian DB-5 column; 30m 250µm I.D., film thickness 0.25 µm). The method started at 150^{o}C , which was held for 2 min, then ramped to 120^{o}C at a rate of 25^{o}C/ min, followed by an increase to 270^{o}C (held for 2 min) the method used a split, split ratio 1:10 Helium (99.999%) was used as carrier gas at 1 ml/min . Data were analyzed using T – test, ANOVA one way test using SPSS software.

3. Results

3.1. Influence of irradiation time on the sonocatalytic

The comparisons of degradation ratios of parathion were carried out in the three systems ZnO, US and US/ZnO. It can be observed from Figure 1, that all degradation ratios of parathion in these three systems increased with the increase of irradiation time, but their difference is tremendous. Within 100 min, in the absence and presence of ZnO powder without any oxidant, the degradation ratio of parathion is 47.6% and 70.2%, respectively.

3.2. Effect of parathion initial concentration

It was found from Figure 2. That the decomposed efficiency of the parathion decreases as the parathion concentration increases. The increase of the concentration of pesticide from 25 mg/L to 75 mg/L decrease the decomposed ratio percent from 70.2% to 49.1%.

3.3. Effect of temperature on decomposed ratio

The effect of systemic temperature on the sonocatalytic decomposed of parathion was discussed in the range between 20 and 60°C. It can be seen in Figure 3 that both cases of sonocatalytic decomposed in the presence of ZnO powder and ultrasonic decomposed in the absence of any ZnO catalyst decrease gradually along with the temperature heightening.

3.4. Effect of ZnO amount

In heterogeneous sonocatalytic processes, the adding amount of sonocatalyst is an important parameter that can affect the decomposed rate and decomposed ratio of organic pollutants. The effects of adding amount of ZnO catalyst on decomposed ratio were studied in the range from 200 to 800 mg L^{-1}. However, the optimal adding amount generally depends on the nature of the organic pollutants and other many factors. Figure 4 shows that the decomposed ratios of parathion under 100 min ultrasonic irradiation in the presence of ZnO catalyst increase with enhancing adding amount of ZnO before 600 mg L^{-1}, while begin to decrease after 600 mg L^{-1}. Hence, the optimal adding amount of ZnO catalysts should be 600 mg L^{-1}.

3.5. US/Znic oxide

The effect of ZnO particles on the sonolytic degradations of parathion was studied and the results are shown in Fig. 5.The removal of efficiency parathion by zinc oxide (ZnO),ultrasounic (US) ,ultrasounic and zinc oxide(US+ZnO) systems was 28.6%,47.5% and 70.2%,respectively.

4. Discussion

The increase in the pesticide concentration increase the number of parathion molecules for the same number of hydroxyl radical so the degradation rate constant decreases(Lucas and Peres 2006; Modirshahla et al. 2007).The presumed reason is that the generation of ˙OH radicals on the surface of nanometer ZnO particles is reduced at high parathion since the active sites are covered by parathion ions.

In general, for the most of chemical reactions, the higher the temperature in reaction system is, the quicker the reaction rate becomes, while it has been known that the radical reactions hardly depend on the systemic temperature. However, the acoustic cavitation which produces the holes on the surface of ZnO particles or ˙OH radicals in aqueous solution lies on the change of systemic temperature. It is well known that both sonocatalytic and ultrasonic decomposed of organic pollutants relate to the acoustic cavitation. The acoustic cavitation can bring the holes with strong oxidbillity on the surface of ZnO particles which either can directly decompose the organic pollutants adsorbed on the surface of ZnO particles or indirectly degrade the organic pollutants in aqueous solution through the ˙OH radicals resulting from hole oxidation of H_2O molecules. When the temperature in aqueous solution becomes exorbitantly high, the vapor or gas bubbles fleetly escape from reaction system so that they do not grow up or collapse be times, which badly weaken the acoustic cavitation. For the ultrasonic decomposed, the ˙OH radicals mainly result from the acoustic cavitation.Hence, the high temperature makes against the ultrasonic decomposed. Similarly, the high temperature also makes against the sonocatalytic decomposed because the holes on the surface or in the inner of nanometer ZnO particles result from the acoustic cavitation. In addition, the sonocatalytic decomposed relates to the adsorbability of ZnO particles. In general, the appropriate adsorbability is propitious to the sonocatalytic decomposed. The proper quantities of organic pollutants adsorbed on the surface of nanometer ZnO particles can directly decomposed by the holes. However, the high temperature generally weakens the adsorbability of nanometer ZnO particles, which makes large numbers of organic pollutants freely and fleetly to move in solution and then miss the chance of decomposed. Recently, it has been reported that the presence of solid particles during sonolysis (sonocatalysis) can improve sonolytic degradation(Wang et al. 2009). Suggested to be due to the formation of more cavitation bubbles on the surface of the catalyst. However, others have found no enhancement in sonolysis degradation rates in the presence of solids, therefore the reason for enhancement effects remains unknown. Hence, the presence of catalyst can enhance the dissociation reaction of H_2O molecules to increase the number of free radicals generated, thereby increasing the rate of decomposed of pesticide (Fadaei et al.,2012). However, excessive amount of catalyst present in the solution could result in the scattering of ultrasound waves that may decrease the rates of sonochemical decomposed reactions(Wang et al. 2007; Gogate et al. 2004).

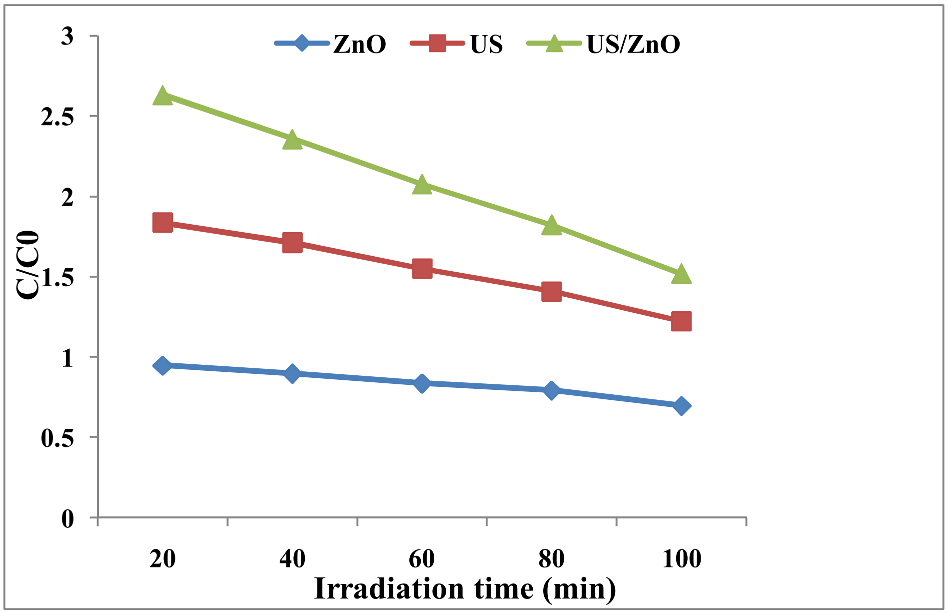

Figure1. Effect of irradiation time on decomposed ratio

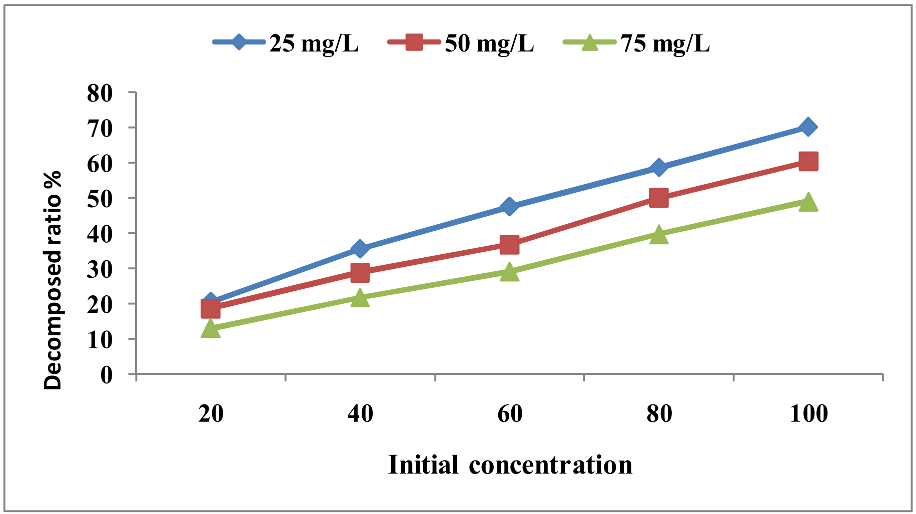

Figure 2. Effect of initial concentration on decomposed ratio of parathion

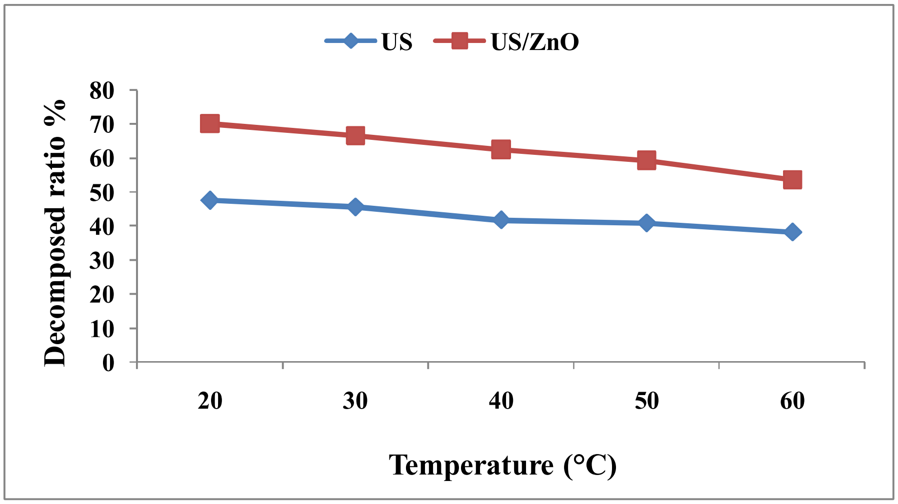

Figure 3. Effect of temperature on decomposed ratio of parathion

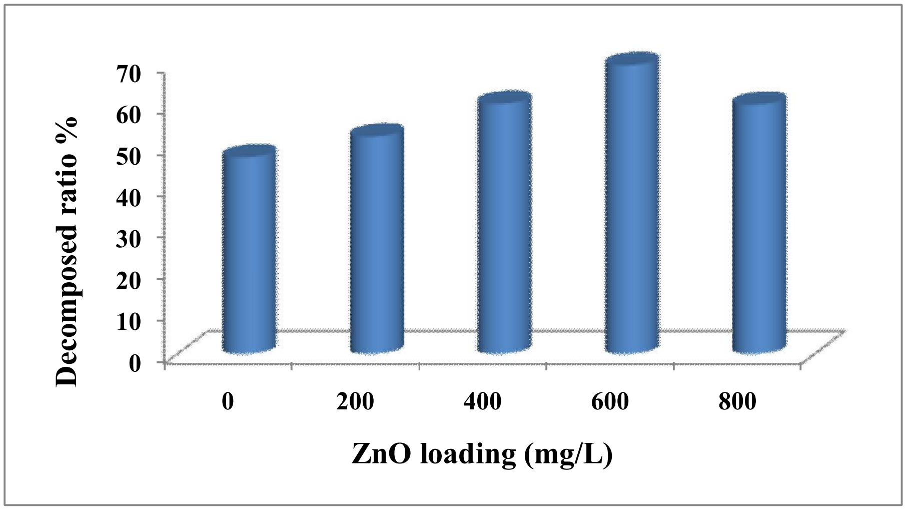

Figure 4. Effect of ZnO adding amount on decomposed ratio of parathion

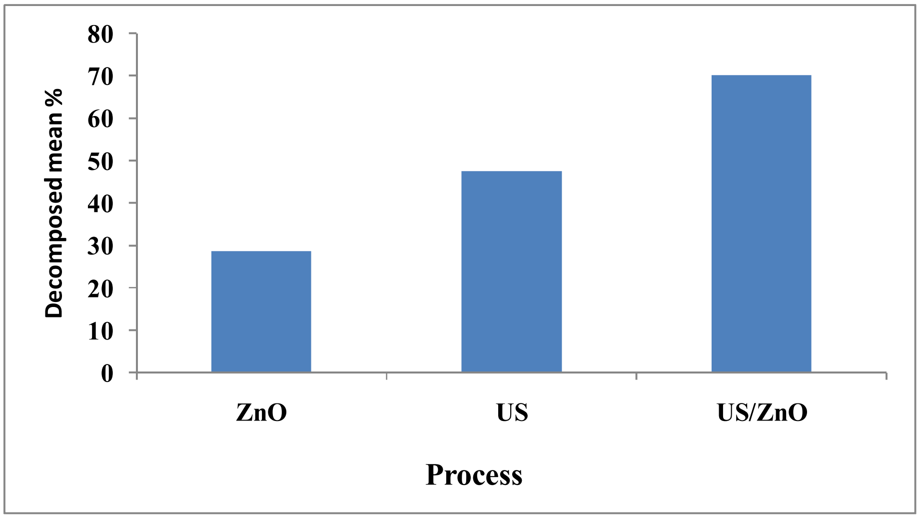

Figure 5. Comparison of removal mean percentage parathion at different processes

Sonolysis of water is known to produce active radicals $H^{\bullet}$ and $OH^{\bullet}$ via cavitation which attack organic compounds in solution. The presence of ZnO particles enhances this phenomenon as the microbubbles tend to break up into smaller ones thus increasing the total number of regions of high temperature and pressure (Dehghani and Fadaei,2012). Dissolved oxygen serves as a source for nucleus cavitation. The OH radicals attack and degrade parathion. Sonolysis can also result in the pyrolysis of vaporized molecules and eventual mineralization(Chen and Smirniotis 2002). Thus it is evident that the degradation of parathion under (US + ZnO) irradiation is more than the sum of degradation under individual ZnO and US irradiation, thereby showing a synergistic effect.

The sonocatalytic degradation of the insecticide parathion in water was studied using ZnO. The obtained results indicate that the sonodegradation of parathion was affected by the concentration of ZnO, irradiation time, temperature and the initial parathion concentration. It was found out that the optimal concentration of catalyst was 600 mg/l.Concerning the initial parathion concentration, it can be concluded that there was a decrease in the sonodegradation of parathion with increasing initial parathion concentration. In addition to, there was an increase in the sonocatalytic degradation of parathion with increasing reaction temperature. Sonochemical processes could be an effective alternative way for oxidation and completely mineralizing recalcitrant organic compounds. Also, by converting the pollutants into less harmful or lower chain compounds.

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