Environmental Health Engineering and Management Journal

Original Article

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Removal of blue cat 41 dye from aqueous solutions with ZnO nanoparticles in combination with US and US-H$_2$O$_2$ advanced oxidation processes

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Abstract

Background: The purpose of the present study was to assess the efficiency of ultrasound/hydrogen peroxide processes and ultrasound/hydrogen peroxide/ZnO nanoparticles in the removal of blue cat 41 dye from aqueous solutions.

Methods: ZnO nanoparticles were prepared using the hydrothermal method. Variables including pH, concentration of ZnO nanoparticles, initial dye concentration, concentration of hydrogen peroxide, and contact time were investigated.

Results: H$_2$O$_2$ alone is not effective in dye removal. In conditions of H$_2$O$_2$ = 20 mg/L and US = 30 kHz, removal efficiency rates of 6.5%, 23.5%, 30%, 51.8%, and 55%, respectively, were obtained. The maximum removal efficiency rate was obtained at the nanoparticle concentration of 3 g/l. Also, removal efficiency was reduced when the initial dye concentration was increased.

Conclusion: The combination of nanoparticles and US and H$_2$O$_2$ is very effective in removing blue cat 41 dye. As a result, photo catalytic processes can be considered to effectively remove environmental pollutants.

Keywords: Advanced oxidation process, Ultrasonic waves, ZnO nanoparticles, Hydrothermal, Hydrogen peroxide, Dye

Citation: Golmohammadi S, Ahmadpour M, Mohammadi A, Alinejad A, Mirzaei N, Ghaderpoori M, Ghaderpoori A. Removal of blue cat 41 dye from aqueous solutions with ZnO nanoparticles in combination with US and US-H$_2$O$_2$ advanced oxidation processes. Environmental Health Engineering and Management Journal 2016; 3(2): 107–113. doi: 10.15171/EHEM.2016.08.

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Introduction

Dye is an environmental pollutant that enters the environment through different sources such as textile, paper and pulp, printing, leather, cosmetics, and food industries (1,2). Problems in the environment such as toxicity reduce light penetration in water and the photosynthetic activity of aquatic organisms (3). Coloring processes like conventional treatments, coagulation, and adsorption are not very effective (4). According to a previous study, advanced oxidation processes (AOPs) like UV, UV-H$_2$O$_2$, Fenton, TiO$_2$, ZnO-UV, and ZnO-H$_2$O$_2$-UV are very effective in removing environmental pollutants (4,5). In this research, the strong oxidizing agent hydrogen peroxide and the catalyst ZnO were used in the presence of ultrasonic waves as the radiation source (H$_2$O$_2$-US and US). Results indicate this could be a promising process for the removal of toxic and harmful organic compounds from water and wastewater. Also, considering the application of ZnO nanoparticles as

a catalyst in the presence of US and H_2O_2/US for dye removal and the high corresponding threshold of ZnO (425 nm), the process of (ZnO/H_2O_2/US) for dye removal is an environmentally-friendly method (6). The main advantage of this process is its inherent destructive importance. Moreover, the ZnO nano-photo-catalyst is non-toxic and has a high relative chemical stability. Among the other advantages of using this reactor in the treatment of waters contaminated with dye compounds is its high capacity for absorption of the solar spectrum, low cost, and high efficiency in removing organic molecules from both acidic and basic environments (7). Thus far, this process has been used to remove different contaminants from such environments. In 2008, Wang et al and in 2004, Yu et al used this process to remove acid red B, rhodamine B, and rhodamine dyes (8,9). Many different physical and chemical methods such as activated carbon adsorption processes (10,11), absorbing resins (12), and the hydrogen peroxide oxidation process have been used to remove dyes; these processes, however, have some inherent limitations such as high costs, inefficacy, complexity, the formation of dangerous residual products, and high energy requirements. Therefore, it is necessary to find an effective method for the treatment of dye. Among the new oxidation methods known as AOPs, chemical oxidation using ultrasound in the presence of hydrogen peroxide is considered a promising technique. Ultrasound is described as the generator of very active OH°, HOO°, and H° radicals (13). These radicals perform oxidation and revival quickly. In the last decade, researchers have reported the successful applications of ultrasonic process/hydrogen peroxide for dye removal from wastewater (14,15). The effect of ultrasonic radiation on removing organic contaminants from organic solutions can be explained physically and chemically. In physical terms, the ultrasonic waves clean solid particles, reduce particle size, and transfer mass (16). In chemical terms, cavitation occurs when ultrasonic waves are radiated on the solution. A severe collision of cavitation bubbles leads to the emergence of hot spots that have extremely high temperatures, and these hot spots can generate hydroxyl radicals (17). The present study purposed to assess the efficiency of ultrasound/hydrogen peroxide processes and ultrasound/hydrogen peroxide/ZnO nanoparticles in the removal of blue cat 41 dye from aqueous solutions.

Methods

Advanced oxidation was performed using Elema (made in Germany) with a frequency of 37 kHz and in the presence of ZnO nanoparticles and hydrogen peroxide to remove the dye from liquid environments. Experiments were basic-practical work conducted on a laboratory scale. ZnO nanoparticles were prepared by the hydrothermal method. For testing, the stock solution for removing blue cat 41 (1000 mg/L) was first prepared by dissolving 1 g dye in deionized water and refrigerating it to avoid variations in concentration. Different concentrations of the stock solution were prepared and the standard method was used to determine the most appropriate wavelength for meas-

uring the concentrations of the studied dye. Finally, the wavelength which achieved maximum absorption for the desired dye was determined using the main solution to be most appropriate. Different concentrations of the desired dye solution were prepared, and their absorption rates were at the optimum wavelength were determined. Then, by drawing the standard curve, an unknown dye concentration was obtained in the testing steps. The variables pH, concentration of ZnO nanoparticles, initial dye concentration, hydrogen peroxide concentration, and contact time were also assessed. In the first step of the US process, the optimum pH was obtained such that under constant conditions, the dye concentration of 50 mg/L, contact time of 60 minutes, nanoparticle concentration of 1 g/L, and removal efficiency rates at pH 4, 9, and 7 were assessed, and optimum pH was achieved. In the next step, the optimum nanoparticle concentration was obtained; under constant conditions, the obtained pH, dye concentration of 50 mg/L, contact time of 60 min, and nanoparticle concentrations of 0.5, 1, 2.5, and 3 g/L were used, and the percentage of removal was calculated. Afterwards, the effect of contact time was investigated; samples with the optimum pH, optimum nanoparticle concentration, contact times (10, 30, 60, 90, and 120 minutes), and a dye concentration of 50 mg/L were prepared and the removal percentage of each was calculated. To investigate the effect of initial blue cat 41 dye concentration, samples with an optimum pH, optimum nanoparticle concentration, optimum contact time, and different dye concentrations (20, 50, 100, 150, and 200 mg/L) were then prepared, and the removal percentage of each was determined. In the final step, all the above variables were re-assessed in the presence of hydrogen peroxide, and its optimum concentration was determined. A total of 250 samples were tested. All experiments were carried out according to standard methods (13). To evaluate and analyze the results, MS Excel 2013 software and statistical tests of analysis of variance (ANOVA) and t-test were used in SPSS 20 software.

Synthesis method of ZnO nanoparticles

In a Teflon liner, a 2M concentration of ZnO was prepared in 10 cc of normal NaOH and 1 cc of surfactant (N-butyl amine) was added to it. Then, the liner was placed in the steel autoclave (Memmert model, UNE 400 type, Germany) and placed in an oven set at 120°C for 12 hours. The contents of the liner were moved to a beaker, washed five times using deionized water, and dried at laboratory temperature(18,19). ZnO nanoparticles were prepared and could be used for analysis. To approve the formed ZnO nanoparticles, x-ray diffraction (XRD) spectrometer was used. A scanning electron microscope (SEM) was also applied to determine the pore diameter and shape of the ZnO nanoparticles.

Results

Figures 1 and 2 show the structural characteristics and the XRD pattern of as-synthesis ZnO particles, respectively. The results of placing H_2O_2 solutions in contact with con-
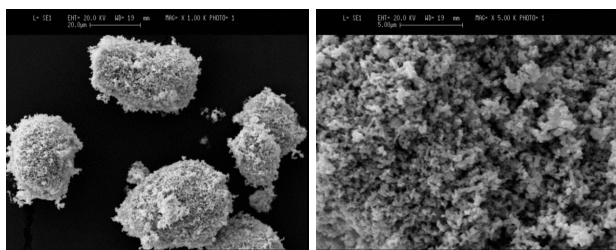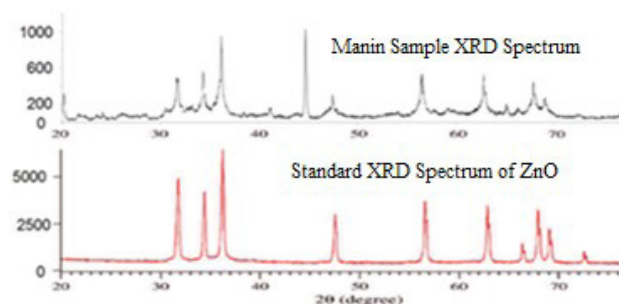
Figure 1. SEM image for ZnO nanoparticles.

Figure 2. XRD spectrum of the synthesized ZnO nanoparticles and standard spectrum of ZnO nanoparticles

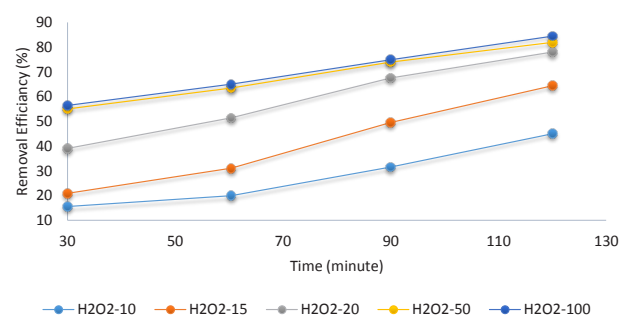H2O2-10   H2O2-15   H2O2-20   H2O2-50   H2O2-100

Figure 3. Efficiency variations of ultrasonic process in the removal of blue cat 41 dye with hydrogen peroxide concentration changes (initial dye concentration: 50 mg/L; ultrasonic intensity: 30 kHz and pH = 4)

0.5   1   1.5   2   3

Figure 4. Efficiency variations of ultrasonic process in removal of blue cat 41 dye with changes in ZnO nanoparticle concentrations (initial dye concentration: 50 mg/L, ultrasonic intensity: 30 kHz and pH = 4)

20 mg/L   50 mg/L   150 mg/L   200 mg/L   100 mg/L

Figure 5. Effect of variations in initial concentration of bleaching on the efficiency of US-H_2O_2-ZnO nanoparticle process in removal of blue cat 41.

centrations of 50 mg/L blue cat 41 for 60 minutes and through an ultrasonic process are presented in Figure 3. Figure 4 shows the variations in efficiency of the ultrasonic process in removing blue cat 41 dye with changes in the ZnO nanoparticle concentration. Figure 5 shows the effects of variations in the initial concentration of bleaching on the efficiency of the US- H_2O_2-ZnO nanoparticle process in removing blue cat 41 dye. Figure 6 presents the variations in efficiency of the ultrasonic and hydrogen peroxide process with pH changes. The results of kinetic studies of blue cat 41 degradation with ZnO-US and ZnO-US-H_2O_2 processes are shown in Figure 7.

Discussion
Characteristics of nanoparticles synthesized by the hydrothermal method
The average particle size of synthesized nanoparticles was 88 nm. An electron microscope was used to identify the shape and size of ZnO particles. Figure 1 shows that particle size was 80 nm; hence, the particle size distribu-
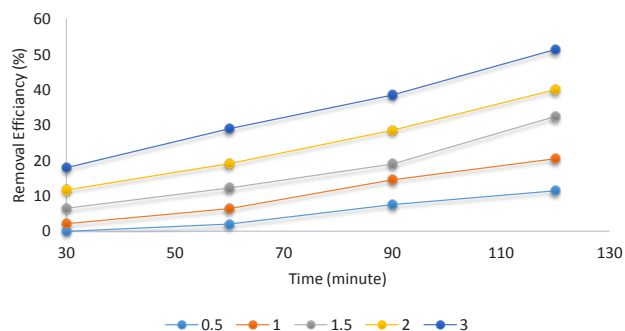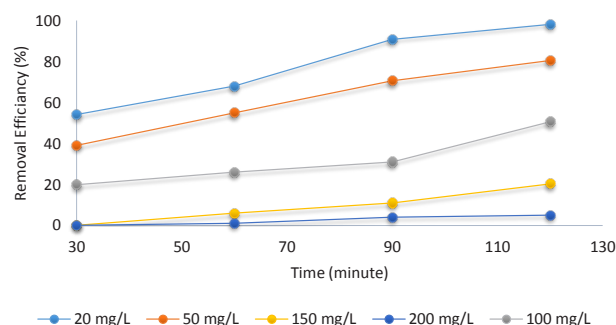
tion was appropriate (20,21). XRD analysis was used to approve the crystal structure and purity of ZnO nanoparticles. The results showed that copper had 99.6% purity and 0.4% impurity. The comparison of the XRD spectrum and ZnO standard spectrum, presented in Figure 2, demonstrated their good correspondence.

Investigating the effect of hydrogen peroxide alone and in combination with ultrasonic process for removing blue cat 41
The effects of hydrogen peroxide on the removal of blue cat 41 dye were determined by preparing a concentration of 50 mg/L of dye, exposing it to hydrogen peroxide at a concentration of 50 mmol/l, and sampling it at test times (10, 30, 60, 90, and 120 minutes). Results showed that, during these times, the initial dye concentration was unchanged, and hydrogen peroxide alone did not affect dye removal; these results are in agreement with those of other studies (22). In order to obtain the best concentration of hydrogen peroxide (optimum concentration), solution concentrations of 10, 15, 20, 50, and 100 mmol/l were prepared and placed in contact with 50 mg/L concentrations of blue cat 41 for 60 minutes. Then the ultrasonic process was performed, and the results are presented in Figure 3. For the prepared hydrogen peroxide concentrations, removal efficiency rates were 20%, 31%, 51.5%, 63.5%, and 65%, respectively. The maximum removal efficiency was obtained at a concentration of 100 mmol/l. The increased

dye removal efficiency obtained by adding hydrogen peroxide could be described as follows: By increasing the hydrogen peroxide concentration in the solution, the hydroxyl radicals (OH^o) that play the main role in decomposition of dye and other contaminants are always increased; the collision probability of these very active radicals with the target contaminants is also increased, and decomposition and removal are conducted (23-25). In fact, some of the mentioned studies have reported that when the concentration of hydroxyl radicals exceeds a particular concentration, it has no noticeable effect on removal, which is attributed to the re-combination of hydroxyl radicals. In other words, when the concentration increases beyond a certain level, the hydrogen peroxide itself removes the hydroxyl radicals (through their re-combination) (22,26,27). Ghaderpoori et al determined that the maximum detergent removal efficiency was obtained at a concentration of 40 mg/L, and increased concentrations had no great effect on the increase in removal rate (5). However, this phenomenon was not observed in the present study.

Effects of ZnO nanoparticles on removal of blue cat 41 in ultrasound (US) and hydrogen peroxide (US- H_2O_2) processes

To determine the best dose of ZnO nanoparticles in the ultrasonic-hydrogen peroxide process, the concentrations of 0.5, 1, 2.5, and 3 g/L nanoparticles were investigated. A solution of 50 mg/L blue cat 41 and hydrogen peroxide with a concentration of 20 mmol/l was prepared and nanoparticles were exposed to contact, as demonstrated in Figure 4. As can be seen, in the ultrasonic process for the above-mentioned nanoparticle concentrations, the removal efficiency rates were 2%, 6.4%, 12.3%, 19.2%, and 29% for 60 minutes; these rates increased with increased doses of ZnO nanoparticles (direct relationship). The effect of using ZnO nanoparticles in the combination process of ultrasound and hydrogen peroxide was investigated by preparing a solution of 50 mg/L blue cat 41 and hydrogen peroxide with a concentration of 20 mmol/l at pH 4; various concentrations of nanoparticles were then added and assessed. The results are presented in Figure 4. As can be seen, for the concentrations of 0.5, 1, 2.5, and 3 g/L of ZnO nanoparticles in the mentioned conditions (hydrogen peroxide concentration of 20 mg/L and ultrasonic intensity of 30 kHz), removal efficiency rates were 6.5%, 23.5%, 30%, 51.8%, and 55%, respectively, and maximum removal efficiency in ZnO nanoparticles was obtained at the concentration of 3 g/L. Ghaderpoori et al reported that increased concentrations of ZnO nanoparticles from 2 g caused the penetration of ultraviolet radiation into the solution to decrease because of increased opacity; as a result, the concentration of hydroxyl radicals was also decreased and, eventually, the efficiency of the process was reduced (5). However, in some studies, the positive effect of nanoparticle concentration (as a catalyst) has been mentioned. Masombaigi et al reported that improved catalyst performance at higher concentrations was related to more active places on the catalyst surface

and possibly the stronger ultraviolet radiation effect on it. In this study, as mentioned earlier, removal efficiency was increased with increased concentrations of nanoparticles (28). By comparing the results in two US-ZnO and US-H_2O_2-ZnO processes (Figures 4 and 5), it can be found that the second process (US- H_2O_2-ZnO) was much more effective than the ultrasonic/ZnO nanoparticle process in the removal of blue cat 41; removal was increased by 69%, 73%, 54%, 63%, and 47% for the used ZnO nanoparticle concentrations, respectively, at 60 minutes. Also, it was observed by performing t tests that the difference between the two processes was significant (P value < 0.014), i.e. the combination process of ultrasonic-peroxide hydrogen-ZnO nanoparticles was more efficient in removing blue cat 41 than the US-ZnO process.

Effect of initial blue cat 41 concentration on the combination process of ultrasound and hydrogen peroxide

The effect of increasing bleaching concentration on the efficiency of the ultrasonic process in combination with ZnO nanoparticles and hydrogen peroxide was investigated. Concentrations of 20, 50, 100, 150, and 200 mg/L were prepared and tested in the above process. Results are shown in Figure 5. As can be seen, the mentioned efficiency rates for the dyes at the mentioned concentrations at 60 minutes was 68%, 55%, 26%, 5%, and 1%, respectively; by increasing initial dye concentration, removal efficiency was decreased (increasing dye concentration had an inverse relationship with dye removal). Thus, at the concentration of 200 mg/L, 99% of the initial dye exited the system without being removed, because by increasing the dye concentration, competition between the constituting interfaces became possible by decomposition and dye molecules, and this disturbance was increased in the large amounts of the generated interfaces at high initial dye concentrations (29,30). Also at high dye concentrations, the catalyst's active places were covered with negatively-charged dye molecules. The absorption of ultraviolet radiation by dye molecules also played an important role in reducing the bleaching rate. These factors decrease the generation of hydroxyl radicals in the catalyst surface (31,32). Therefore, dye removal efficiency in this process is higher for diluted solutions.

pH variations in removal of blue cat 41 in the combination process of ultrasound and hydrogen peroxide

Because of the amphoteric behavior of most semiconductor oxides, pH is an important parameter in these reactions. Solution pH affects the speed of the reactions that occur on the surface of semiconductor particles by influencing the properties of the surface charge (33). Dye removal relative to pH variations in acidic, neutral, and basic conditions (pH of 4, 7, and 9) was investigated. A solution of blue cat 41 with a 50 mg/L concentration and hydrogen peroxide with a concentration of 20 mmol/l was prepared, and pH variations on the process efficiency were assessed. The results are shown in Figure 6. As can be observed, the process efficiency rates relative to pH variations at point 4

for the periods of 30, 60, 90, and 120 minutes were equal to 39%, 51.8%, 67.5%, and 78%, respectively. Among the studied pH values, the best removal efficiency was obtained under acidic conditions; removal efficiency rates at 60 minutes at this pH were 17.95% and 36.29% greater than those of pH 7 and 9, respectively. Li et al used pH values of 1 to 10 to decompose red, and the results showed that the ultrasonic-hydrogen peroxide process had maximum decomposition power in acidic conditions. The removal efficiency rates of red 24 at pH=1 and pH=10 were 98.09% and 33.9%, respectively (17). ANOVA test results revealed that these differences were significant, and process efficiency was significantly higher at pH = 4 than at other pH values (P value < 0.001). The variations in process efficiency with pH changes in the ultrasonic process were also evaluated. The results showed that removal rates at pH 4, 7, and 8 were 18.2%, 16.1%, and 6.8%, respectively. In this process, the maximum removal amount was also obtained at pH = 4, and ANOVA test results demonstrated that removal efficiencies at these pH values were different and statistically significant (P value < 0.001). pH = 4 was effective for the removal of blue cat 41.

Kinetic studies of blue cat 41 degradation

Figure 7 shows the results of kinetic studies of blue cat 41 degradation with ZnO-US and ZnO-US- H_2O_2 processes. The kinetic model of the pseudo first order reaction was used (34).The kinetics constants of blue cat 41 are shown in Table 1. Study results showed that US, US- H_2O_2, and ZnO-H_2O_2-US follow pseudo first order kinetics. The pseudo first order reaction had the highest coefficient of determination among the studied processes (35). As illustrated in Table 1, the K1 constant increased in US, US-
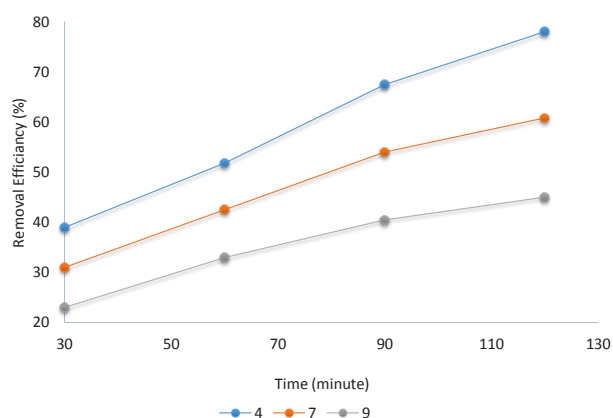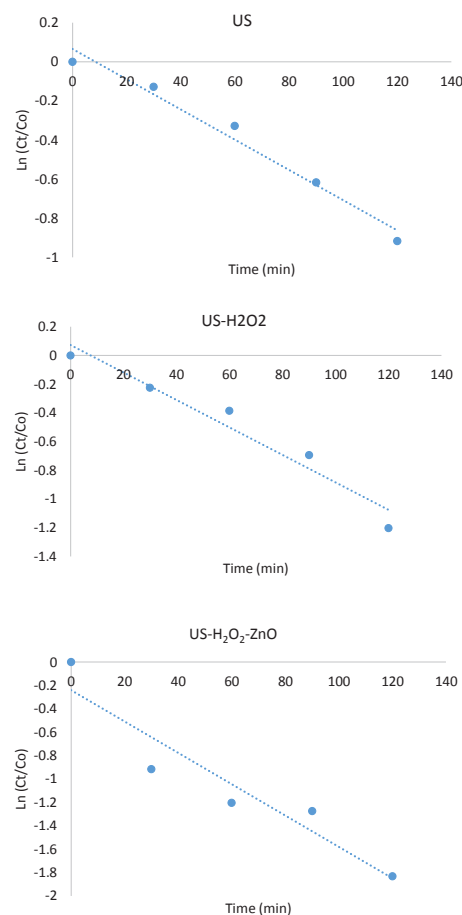

Figure 7. Degradation kinetics for removal of blue cat 41 from aqueous solutions.

H_2O_2, and US-H_2O_2-ZnO processes, respectively. With an increase in the K1 constant, the degradation rate of blue cat 41 also increased (36). Due to the synergistic effect of combination processes like AOPs, the rate of degradation of a pollutant can be increased. The synergistic effect of AOPs has been assessed in various studies (37-39).

Conclusion

In studying the combination process of ultrasound/hydrogen peroxide/ZnO nanoparticles, the following results were obtained:

- Hydrogen peroxide alone has no effect on dye removal.
- Process efficiency in dye removal is decreased by increasing initial dye concentration.
- The efficiency of the above-mentioned process in dye removal is higher at acid pH ($\cong 4$).
- Removal efficiency is increased by increasing retention time.

Competing interests

The authors of this article declare that they have no competing interests.

Ethical issues

The authors of this article confirm that this article is their

Figure 6. Efficiency variations of ultrasound and hydrogen peroxide process with pH changes.

Table 1. Kinetics constants of the photo-catalytic degradation of blue cat 41 from aqueous solutions. (Initial con. = 20 mg/L, pH = 4)

Kinetics models	R^2	K (min^{-1})
US	0.9751	0.0077
US-H_2O_2	0.9492	0.0096
US-H_2O_2-ZnO	0.9875	0.0134

original work. It has not been published, nor is it under review in another journal, and it is not being submitted for publication elsewhere.

Authors' contributions

Acknowledgments

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