Preparing and Investigation a New Nanofluid for Employing in Machining Process: Synthesis and Characterization of Graphene Oxide Nanoparticles

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ARTICLE INFO

Article history:

Received 22 September 2017
Accepted 14 June 2018
Available online 15 September 2018

Keywords:

ZnO nanoparticles
Decolorization efficiency
Acid blue 193
Advanced oxidation process

ABSTRACT

In this research, ZnO nanoparticles (NPs) were synthesized using a binary Zn(II) Schiff-base complex. The complex was heat-treated to prepare ZnO nanoparticles via thermal decomposition route at 500 °C. The formation of single-phase ZnO nanoparticles and their microstructures were studied by XRD pattern, SEM and TEM observations. The photo-degradation characteristic of the as-prepared ZnO NPs was evaluated and acid blue 193 was investigated as the organic colorant in a photocatalytic reactor by advanced oxidation process (AOP). The effects of operating parameters such as initial concentration of the dye, the amount of catalyst and the pH value of the solutions were studied to determine the optimum condition of the process to improve the photo-degradation performance. According to the results, impressive photo-degradation of acid blue is conceivable by the as-synthesized ZnO NPs. The optimum operating conditions to achieve photo-degradation were found to be a solution with the pH value of 6, the catalyst concentration of 0.04 g/L, and the dye concentration of 10 g/L. The highest efficiency would be achieved at the natural pH of the solution (pH=~6). The optimum concentration of ZnO NPs is about 0.04 g/L. More or less amount of the photocatalyst could not enhance the photodegradation efficiency. At the constant photocatalyst concentration, any increase in the dye amount leads to the decrease in degradation efficiency.

1-Introduction

Organic colorants have become an inevitable part of our life. Synthetic dyes have replaced natural types in paper, clothes, drugs, and even food industries. However, the waste of these materials is considered as pollutant and dye treatment has become a scientific challenge. The membranes, adsorbent, floated foams, and coagulation agent are usually applied to remove the pollutants. These methods are not efficient and exert side effects. Oxidation of pollutants is a modern method with high efficiency and without any destructive effect. A method entitled "*advanced oxidation process (AOP)*" has been developed. The photocatalytic reactions provide the required conditions of AOP; therefore, the semiconductor materials are identified as suitable agents for AOP [1].

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Zinc oxide is a momentous semiconductor ceramic material with a hexagonal wurtzite crystal structure, possesses a direct band gap of 3.37 eV, and an excitonic binding energy of 60 meV [2]. These characteristics make it an ideal candidate for several applications, such as gas sensors [3], biosensors [4], solar cells [5], electrochemical cells [6], ultraviolet (UV) photodiodes [7], and electrical/optical devices [8].

As one of the major properties of ZnO is photodegradation of organic materials, its photocatalytic behavior in various systems has been frequently investigated.

Akyol et al. studied the photocatalytic decolorization of aqueous solutions of Remazol Red, a commercial azo-reactive textile dye, in the presence of various semiconductor powder suspensions with the use of artificial UV-C light sources. They showed that the decolorization efficiency increases with an increase in pH, attaining maximum value at pH 10 for ZnO. The zero-point charge for ZnO is 9.0 above which ZnO surface is negatively charged by adsorbed OH^- ions, favoring the formation of strong oxidant $OH^\bullet$ radical. The efficiency is inversely related to the dye concentration, increasing dye concentration enhances dye adsorption on the active sites of the catalyst surface, and consequently hinders OH^- adsorption on the same sites with a decreasing $OH^\bullet$ radical formation rate [9].

Habib et al. investigated the decolorization/degradation of crystal violet (CV), a cationic dye which is extensively used in dyeing/textile industries, under visible light through adsorption studies of the dye solution with ZnO in the dark. The results show that the adsorption of CV on ZnO takes about 200 min to reach equilibrium, and the equilibrium time at a certain concentration of the dye seems to be independent of temperatures that are used for the preparation of ZnO samples. The adsorption data follow the pseudo-first-order kinetic model, and the adsorption pattern follows the Langmuir model [10].

Chang et al. studied a photocatalytic system by utilizing both cold cathode fluorescent light (CCFL) UV irradiation and steel mesh supported ZnO NPs in a closed reactor for the degradation of azo dye C.I. Orange G (OG). Various operating parameters such as reaction time, preparation temperature, mixing speed, ZnO dosage, UV intensity, pH, initial dye concentration, and service duration were investigated. Results presented efficient color and total organic carbon (TOC) removal of the OG azo dye by the designed photocatalytic system. The optimal ZnO dosage for color removal was 60 g/m^2. An alkaline pH of 11.0 was sufficient for photocatalytic decolorization and mineralization. The rate of color removal decreased with the increase in the initial dye concentration. However, the rate of color removal increased with the increase in the UV intensity [11].

Umukoro et al. believed that ZnO is a suitable semiconductor for the decomposition of organic dyes, whereas some limitations are associated with it. High recombination rate and narrow light absorption region diminish its applications. They designed a new composite of ZnO/Ag/Ag_2O/ graphene to overcome these restrictions and evaluated it by using acid blue as an organic dye [12].

Chamjangali et al. synthesized Ag-ZnO with multipods morphology to enhance the photocatalytic degradation of a mixture of dyes. They showed that the efficiency of the decolorization process is influenced by the solution pH, the amount of the catalyst, initial dye concentrations, and Ag doping [13].

Li et al. prepared ZnO/rectorite as an adsorbent and photocatalyst for dye treatment process. This nanocomposite exhibited high activity under solar irradiation and removed more than 99% of dye solution after 2 h [14].

Most of the early research focused on the impact of dopants on the ZnO photoactivity. In the present study, the photodegradation of the as-prepared ZnO NPs by a novel green chemistry method would be evaluated. For this reason, the acid blue 193 was investigated as organic colorants in a photocatalytic reactor by AOP. The effect of operating parameters such as the initial concentration of the dye, the amount of catalyst and the pH of the solutions was studied to determine the optimum condition of the process. The results may be useful for designing and controlling the conditions in which the AOP efficiency can be studied well.

2- Experimental procedure

ZnO NPs were prepared using a green chemical method [15]. L-alanine ($CH_3CH(NH)_2COOH$) (d = 1.40 g/cm^3, molar mass = 89.09 g/mol, and purity ≥ 99.0 %) and zinc(II) acetate dehydrate (d = 1.74 g/cm^3, molar mass = 219.49 g/mol, and purity = 99.0 %) were purchased from Merck. Sodium salicylaldehyde-5-sulfonate ($C_7H_5O_5SNa$) was synthesized in another work [16]. 5 mmol of alanine was dissolved in 10 mL of deionized water. 5 mmol of salicylaldehyde-5-sulfonatewas was dissolved in 10 mL of water. After that, the alanine solution was added to the aldehyde solution. A yellow mixture was formed. This mixture was stirred at 70 °C for 30 min. Zinc (II) acetate dihydrate was dissolved in water and added to the yellow mixture, while the pH was kept at 7 through adding NaOH. The obtained mixture was stirred for 1 h at 70 °C. It was then concentrated and left at room temperature overnight. A white precipitate was formed, washed with deionized water and ethanol (1:1) followed by air drying. To preparation of ZnO NPs, the Schiff-base complex was heat treated at 500 °C for 2 h where the temperature was ramped at 5 °C/min. In order to prevention of agglomeration, ZnO NPs were milled in a planetary mill with a zirconia milling assembly operating at 200 RPM for 5 min.

Phase structure of the NPs was studied by the X-ray diffraction (XRD) technique where a Philips PAN-analytical diffractometer equipped with a Cu-Kα radiation (λ_{ave}=0.154 nm) source was used. Transmission electron microscope (TEM) micrographs were acquired using a Philips CM 200 FEG microscope.

In the present study, the nano photocatalytic decolorization of acid blue 193 as an anionic dye was investigated in a photo catalytic reactor by AOP. One of the advantages of these dyes is that their adsorption on the surface of the as-synthesized ZnO NPs is negligible. The effect of operating parameters such as the initial concentration of the dye, the amount of catalyst and the pH of the solutions were studied to determine the optimum condition of the process. The batch experiments were carried out with 500 mL in a batch photo reactor equipped by a low-pressure UV lamp (Osram, 15 W) under the same conditions where the photocatalyst was used in a heterogenic phase. The progress of photocatalytic decolorization was monitored through measuring the absorbance of the solution samples by UV-visible spectrophotometer (Lambda EQ–OC1, Perkin Elmer, USA) at λ_{max} = 609 nm. The percentage of degradation was calculated by using the Equation 1, in which C_0 is the initial dye concentration and C is the dye concentration after treatment.

$$\text{Degradation \%} = [(C_0\text{-}C) / C_0] * 100 \quad (1)$$

Effect of pH was investigated by the addition of NaOH (0.01 M) or H_2SO_4 (0.01 M) to adjust the solution's pH to 2, 4, 6 and 8. The concentration of the NPs and dye was chosen as the minimum amounts, i.e. 0.01 g/L and 10 ppm, respectively. After determination of the optimum pH value, it would be applied in the next steps.

To investigate the effect of ZnO NPs concentration on the degradation percentage, four solutions with the constant pH of 6 and different photocatalyst amounts (0.01, 0.02, 0.04, and 0.06 g/L) were prepared. The dye concentration was 10 ppm. After determination of the optimum ZnO NPs concentration, it would be applied in the next step.

To determine the influence of the dye concentration on the decolorization process, five experiments were designed. The pH and photocatalyst concentration values would be specified based on the previous tests. The dye concentrations were chosen as 10, 20, 30, 40, and 50 ppm.

It should be noted that all the tests were performed three times, and the actual results are calculated as the average values and the error bars are presented on the graphs.

3- Results and discussion

3-1- The characteristics of the as-prepared ZnO NPs

Fig. 1 shows the XRD pattern of the NPs. All peaks can be indexed to the hexagonal wurtzite structure of ZnO [JCPDS No. 1-76-704]. It can be seen that there are no diffraction peaks from other phases of ZnO or impurities, showing that the obtained ZnO is of high purity. Furthermore, all the peaks are sharp and intense, which indicates that the samples are highly crystalline. According to the Williamson-Hall method [17], the crystallite size of the as-synthesized NPs was

calculated about 77 nm. The mechanism of the NPs preparation has been discussed previously [18].

The morphology and particle size of the prepared NPs were examined by TEM (Fig. 2). The formation of NPs with semi-spherical morphology with the average particle size of 70nm is confirmed. As can be seen in the TEM image, the degree of crystallinity of the as-prepared particles is high and the resolution of the image is acceptable. The corners of the particles are sharp and the boundaries are clear. The photocatalytic properties of a semiconductor refer to its size, crystallinity, and purity. The mentioned characteristics could be useful to evaluate the photoactivity of the as-synthesized ZnO NPs.

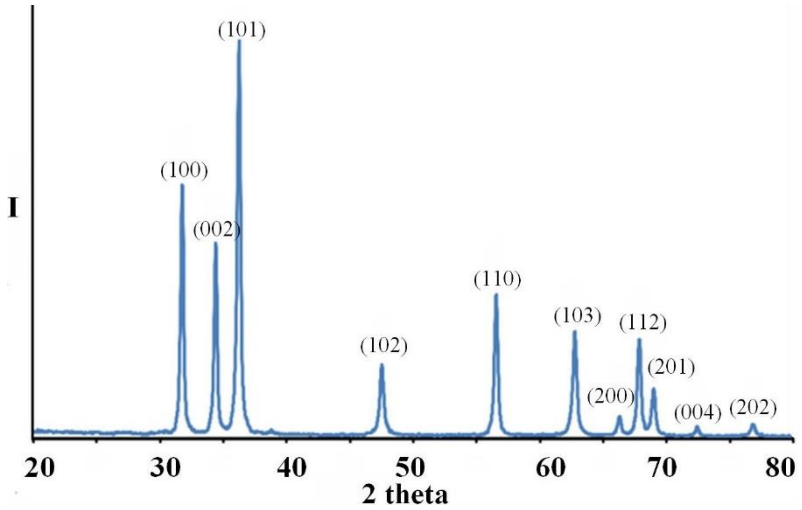

Fig. 1. X-Ray diffraction pattern of ZnO NPs, consisting of ZnO [JCPDS No. 1-76-704] as a unique phase.

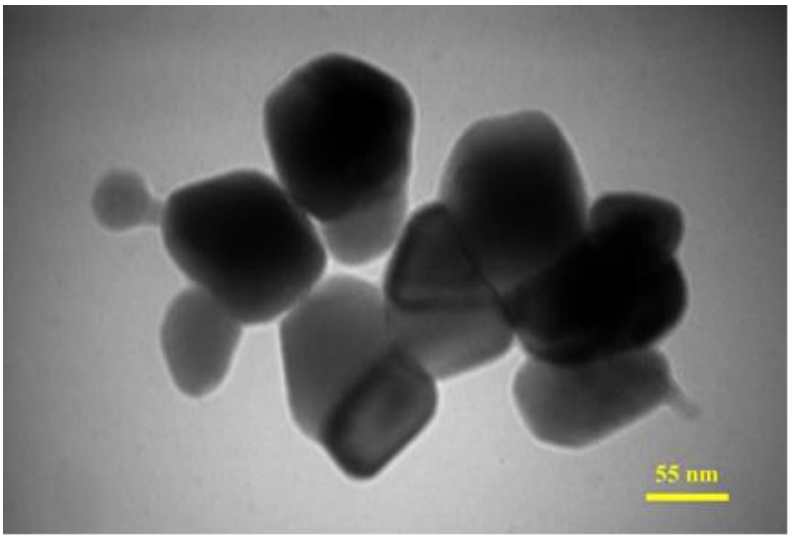

Fig. 2. TEM micrograph acquired from ZnO NPs.

3-2- Decolorization process

3-2-1- pH optimization

As the pH values of the wastewater from different sources are not similar, its effect on the AOP should be determined. The effect of pH on the photocatalytic performance is explained by electrostatic forces between catalyst and dye [19, 20]. The variation in the decolorization versus the pH of solution is shown in Fig. 3. The natural pH of the dye solution was 6.1. NaOH and H_2SO_4 were used to adjust the pH value. It has been observed that the decolorization efficiency reaches the highest amount in natural pH. Any changes in pH leads to decrease the

decolorization percentage under UV illumination.

The analysis of pH influences on the AOP is a very complicated task due to its multi-faceted behavior. (i) The ionization of the particles surfaces, (ii) the formation of hydroxyl radicals, and (iii) the influence of the surface chemistry on agglomeration tendency. The first one influences the adsorption of dye onto the particles surfaces. The second one is related to the reaction of hydroxide ions and holes. At lower pH, the holes with the positive charges act as the oxidation agents. On the other hand, hydroxyl radicals are considered as the dominant agents at natural and alkaline pH. The third parameter is related to the effects of pH on agglomeration and sedimentation of NPs [21, 22].

The adsorption of the NPs at the natural pH is higher than the adsorption at the other pH (see Fig. 3). At the natural pH, the colorants and NPs tend to adhere; therefore the electronic exchanges between NPs and dyes molecules occur effectively. Entrance of OH^- or H^+ ions thorough the addition of NaOH or H_2SO_4 leads to change in the surface charge of ZnO NPs, diminishing adsorption of dyes molecules to the surface of NPs [13]. Abbasi et al. and Shahmoradi et al. showed that the removal efficiency of the dyes via MWCNTs-ZnO and Cr-TiO_2 NPs at acidic condition (pH = 4) is higher than that of neutral (pH = 7) and basic (pH = 10) condition [23, 24]. Based on these observations, the influence of the pH value on the decolorization performance depends on the catalyst type.

3-2-2- Catalyst concentration optimization

Fig. 4 shows the influences of the catalyst concentration on the decolorization efficiency. As can be seen, an increase in catalyst concentration from 0.01 to 0.04 g/L leads to an increase in the decolorization efficiency. Meanwhile, further increase in this parameter from 0.04 to 0.06 g/L decreased efficiency. The highest efficiency was obtained at the catalyst concentration of 0.04 g/L. This phenomenon can be attributed to the fact that the number of available active sites on the catalyst surface enhanced, which in turn leads to increase in the number of hydroxyl and superoxide radicals. It is clear that there is a limit in increasing the catalyst concentration. This fact has been reported by several researchers. At the low concentration, the increase in photocatalyst concentration leads to the increase in the amount of hydroxyl and superoxide radicals. UV illumination is required to activate the photocatalysis site. Any more increase in photocatalyst would require the addition of UV light, which is not possible for an aqueous system due to turbidity of the solution [25]. Buyukada et al. observed a similar behavior in a system containing basic blue 3 dye and TiO_2 NPs [26].

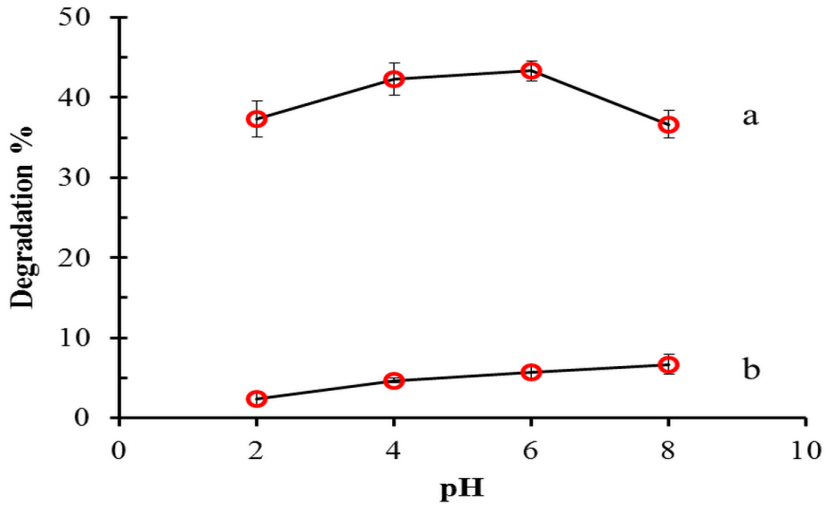

Fig. **3.** The influences of pH values on the decolorization efficiency. (a) The ZnO NPs and dye concentration values are equal to 0.01 g/L and 10 ppm, respectively. (b) The 10 ppm dye solution without ZnO NPs catalyst.

3-2-3- Dye concentration optimization

Fig. 5 shows the influences of the dye concentration on the decolorization efficiency. As can be seen, an increase in dye concentration from 10 to 50 g/L leads to a decrease in the decolorization efficiency. The highest efficiency was obtained at the dye concentration of 10 g/L. However, at the constant photocatalyst concentration, any increase in the dye amount leads to a decrease in the degradation efficiency [27]. This phenomenon refers to the surface coverage of NPs by the dye molecules, hindering penetration of UV-light to the surface of ZnO NPs and limiting the photoexcitation quantum efficiency in high dye concentrations [28]. Nezamzadeh et al. could find similar results in a system containing an azo dye and Ni/P zeolite. They believed that the lifetime of hydroxyl radicals is only a few nanoseconds. Increasing the dye concentration logically enhances the probability of collision between organic matter and oxidizing species leading to an increase in the photodecolorization [29].

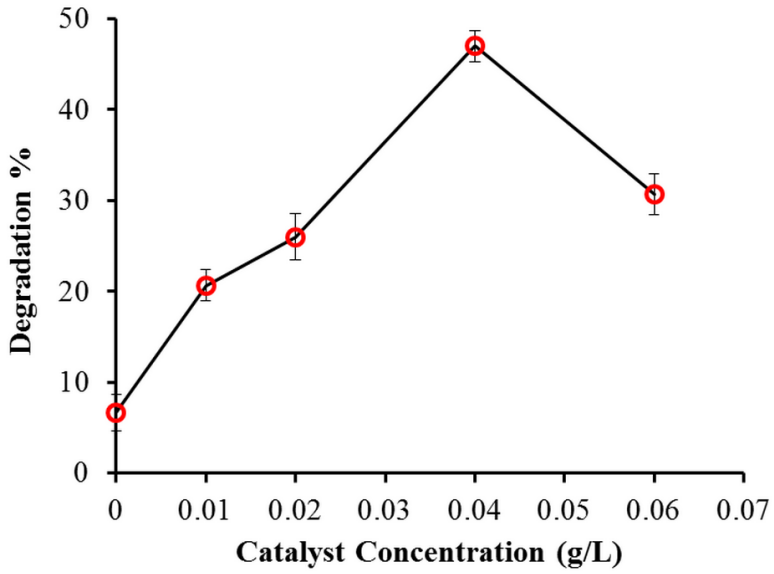

Fig. **4.** The influences of the catalyst concentration on the decolorization efficiency. The pH and dye concentration values are equal to 6 and 10 ppm, respectively.

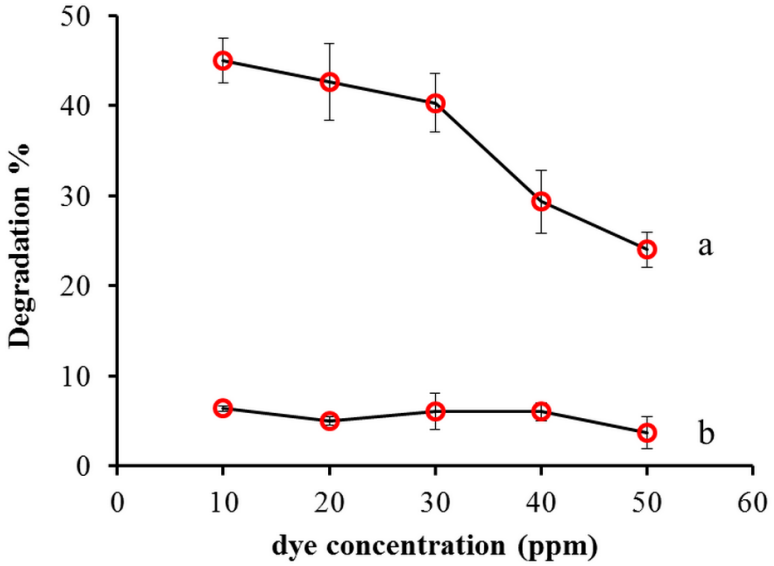

Fig. **5.** The influences of the dye concentration on the decolorization efficiency. (a) The pH and ZnO NPs concentration values are equal to 6 and 0.04 g/L, respectively. (b) The dye solutions without ZnO NPs catalyst.

4- Conclusions

e reported an environmentally friendly and clean chemical method to synthesize ZnO NPs through thermal decomposition of a Zn(II) Schiff-base complex. In our paper, all the starting materials were biologically compatible and nontoxic. Moreover, no high temperature treatment was required. Impressive photo-degradation of the acid blue is conceivable by the as-synthesized ZnO NPs. Several operational variables (i.e. pH of the solution, ZnO NPs concentration, and dye concentration) which are important in water treatment process have been investigated. The highest photodegradation efficiency would be achieved at the natural pH of the solution (pH=~6). The optimum concentration of ZnO NPs in the solution was about 0.04 g/L. The more or less amount of the photocatalyst could not lead to enhance the photodegradation efficiency. At the constant photocatalyst concentration, any increase in the dye amounts leads to decrease in the degradation efficiency. It should be mentioned that having knowledge about the photodegradation process, the affected parameters, and the operative conditions would provide remarkable opportunities for dye treatment process.

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