Decolorization of Reactive black-5 Dye by UV based photocatalytic with immobilized ZnO nanoparticles onto ceramic plate surface

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Abstract. The textile wastewater contains components of dye and inorganic salts which are very dangerous when they are directly discharged into the water body without any prior treatment. In this study, the ability of immobilized ceramic/ZnO nanoparticles (NPs) for decolorization of Reactive black 5 dyes was investigated. A laboratory scale of rotating disc type reactor with UV-C lamp and dip coating method to immobilize nanoparticles were used in this study. Ceramic/ZnO NPs were then characterized by SEM-EDS. EDS result has shown that 82% of ZnO NPs were dispersed on the ceramic surface with maximum catalyst dosage of 5.5 mg/cm². It was achieved after 3 cycles of impregnation process at 500°C. Photocatalytic activity of ceramic/ZnO NPs was strongly depended on pH and RB5 initial concentration. It possesses the highest photocatalytic activity (100% of decolorization efficiency) at the extreme alkaline condition and low RB5 concentration (3 mg/L) after 90 min of treatment time.

1. Introduction
Textile industries have been considered as the major source of environmental pollution in terms of quality as well as quantity. These industries consume large quantities of water out of which around 90% appears as wastewater [1]. Moreover, among various industries, the textile industry is the second world’s biggest in term of water consumption (approx. 200 L of water per kg of fabric produced per day) and disposal. Textile wastewater contains the high concentration of dye, suspended solids, surfactants, minerals and other toxic compounds [2,3]. All of these components are very dangerous and possess bad aesthetics when they are directly discharge into the water body without any prior treatment.

Figure 1. Structure of Reactive Black 5 (Hydrazone type) [4] [16]
Some of this dye (ex. Reactive Black 5) not only are toxic, mutagenic and carcinogenic compounds, but also resistant to aerobic biodegradation, and their half-lives under sunlight are greater than 2000 hours [5]. Therefore, the treatment of colored water is necessary before being released to the environment. There are several methods that have been reported to treat the colored wastewater. These include adsorption as a physical method, chlorination, ozonation [6] as chemical methods and biodegradation [5,7]. Lately, advance oxidation processes (AOPs) emerged as a suitable route for mineralization of organic contaminants in wastewater [8]. AOPs include photolysis, ozonation, ultrasounds, Fenton reaction, wet air oxidation, and photocatalysis. Moreover, photocatalysis using different metal semiconductors (ex. TiO$_2$, WO$_3$, SrTiO$_3$, and ZnO) stands out as the most environmentally friendly AOP with a wide application for degradation of organic contaminants into H$_2$O and CO$_2$ [8,9].

Zinc oxide (ZnO) due to its excellent chemical and thermal stability has been attracted tremendous attention among researchers as a photocatalyst agent [10]. ZnO is the n-type semiconductor with a wide band gap around 3.37 eV at room temperature and with relatively large exciton binding energy (60 meV). ZnO is also a non-toxic metal oxide and it can be synthesized by low-cost chemical methods at low temperature [9]. Some studies have been shown that ZnO is more effective than TiO$_2$ as a photocatalyst [10]. So, in this study, ZnO has been selected as photocatalyst because of its high catalytic efficiency, low cost, and non-toxic nature.

Indeed, photocatalyst applied in suspension must be separated after their use for water treatment. This process is rarely used in actual applications and powder form of photocatalyst will be difficult to separate after the process and hinder the economic capability [11][12]. The very important challenges have therefore arisen to immobilize photocatalyst particles in the form of photocatalytically active surfaces and result in economic applications without any separation costs. The simplest method of immobilization is dip coating [13].

The ceramic support that used in this study was dipped in gelatin/ZnO solution at certain times and several repetitions of the dipping/drying procedure. The previous study [14,15] has been reported that the addition of gelatin can improve the quality of final products. Gelatin is used as a polymerization agent, and it served as a terminator for the growth of the ZnO nanoparticles because it expanded during the calcination process, which prevented the particles from coming together easily. Gelatin was also used in this study to increase adhesiveness ability between ceramic media and dip solution of gelatin/ZnO in form of highly viscous solution. Therefore, this study was focused to investigate Reactive Black 5 (RB5) dye decolorization efficiency by immobilized ceramic/ZnO nanoparticles.

2. Experimental

2.1. Materials

Ceramic disc plate (approximately 10 cm in diameter and 1 cm of thickness with a slot at the center) as attached media for ZnO nanoparticles was procured from Ceramic Research Center (Bandung, Indonesia). All materials used for ceramic disc plate production were commercially available in Indonesian market and some portions of the composition were derived from natural materials. ZnO nanoparticle Pro Analysis grade (99%) was procured from Merc, Germany. Commercially food grade of gelatin and Reactive black 5 (RB-5) dye powder were procured from local market in Bandung, Indonesia. Both were directly used without further purification. Tap water was used to make RB-5 solution in order to make it more similar to the actual condition of textile wastewater. Meanwhile, distillate water was used for immobilization process of ZnO NPs on ceramic disc plate.

2.2. Preparation of immobilized ZnO on the ceramic plate surface

2.2.1. Preparation of ceramic disc plate

Ceramics as immobilized media for ZnO NPs were synthesized at Ceramic Research Center, Bandung. Appropriate amount of Sukabumi fine clay (50% w/w), Bangka fine Kaolin clay (30% w/w), Sodium Feldspar from PT. Sibelco (10% w/w) and Chamote refractory (10% w/w) were mixed with
special liquid (35% of tap water and 65% water glass) by ratio 4:1 (dry mixture: special liquid by w/w).
High-speed mixer was used to mix all of the components for about 15 minutes at low speed and then 10 minutes at high speed. The slurry form of mixture was then poured into the mold and solidified for 5 minutes. Solidified mixture was then pulled out from the mold and dried by air for 5 days at room temperature. Solidified mixture then placed the in furnace and continuously heated with temperature setting of 100°C for 1 hour followed by 300°C for 1 hour then 900°C for 3 hours (Ceramic Research Center, Bandung-Indonesia). After the heating process for about 5 hours, ceramic was cooled by air, placed in desiccator and ready to be used as immobilized media for ZnO nanoparticle. The surface area of ceramic disc plate media was measured by manual calculation using a standardized meter. Annova test was done using R software for the approximate surface area of each 4 plates used at each variation to ensure that there is no significant difference between all plates used in this study.

2.2.2. ZnO immobilization on ceramic plate

Dip coating method was used to attach ZnO on the ceramic surface. Dip solution of gelatine/ZnO was prepared by firstly mix the gelatin (5% w/v) with distilled water at 60°C for 30 minutes. After reaching the perfect mixture of gelatin with water, ZnO nanoparticles powder was slowly added to the mixture by 5% (w/v) in concentration and formed the milky white solution. The mixture of gelatin/ZnO was continuously mixed using magnetic stirrer for 30 minutes at 60°C and next 4 hours at room temperature and resulted in highly viscous solution. Gelatin was used as dispersant agent of ZnO nanoparticles in liquid solution and also acted for increasing adhesiveness ability between dip solution and ceramic media. Ceramic disc plate then immersed into the dip solution with dipping time of 1 min and drying time between successive dips of 5 min at room temperature then repeated for 3 times. The gelatin/ZnO/ceramic plate coated samples were then treated at 500°C for 2 hours and considered as 1 cycle. The cycle was repeated 3 times. All photocatalyst plates then placed in the reactor and rotated at 200 rpm for conditioning treatment (photocatalyst pre-treatment) using tap water. This photocatalyst pre-treatment was carried out for 4hr (without UV) to remove ZnO loosely adhered on the coating media after each cycle. ZnO/ceramic plate samples were then characterized by SEM-EDS and ready to be used for photocatalytic experiments.

2.3. Photocatalytic experiments

Rotating disc reactor (1 L of volume) with an electric motor and two Sankyo-Denki G15T8 UV-C lamps (2x15 watt @ 253.7nm) were used for this study using batch scheme. Irradiation distance between UV light and artificial wastewater (RB5) was set at 20 cm and 150 rpm for motor speed on all variations in this study and considered as the optimum condition for ZnO/ceramic photocatalyst based on our lab test. The contact between plates and RB5 solution in reactor was 75 % (approximately 4 cm from the outer edge of plate) of the ceramic surface area. 4 ZnO/ceramic plates were used at each variation at different pH (3; 5; 7; 9; and 11) and initial RB5 concentrations (3; 5 and 10 mg/L). These were done to evaluate the photocatalytic ability of new ZnO/ceramic plate photocatalyst undergo extreme pH condition and wastewater concentration. RB5 dye concentration was set in the low range concentration due to its feasibility to be applied in actual wastewater treatment facility as a post-treatment process. Treatment time for each variation was done for 120 min. The decolorization efficiency was measured at some points using Spectrophotometer UV-Vis at 595 nm. Overall, the experiment was firstly done to find the optimum pH condition using 5 mg/L of RB5. The experiment was then continued with different initial RB5 concentration using optimum pH condition based on the previous experiment. In order to evaluate the adsorption effect of the immobilized ZnO photocatalyst, the treatment process was done in dark condition (without UV lamp) for 3 hr. Blank test (ceramic media without photocatalyst with UV and non-UV) with an initial concentration of 5 mg/L were done as the control for this study.
Figure 2. Photocatalytic rotating disc reactor scheme

3. Result and Discussion

3.1. Ceramic/ZnO nanoparticles (NPs) and RB5 characterization

Ceramic/ZnO nanoparticle has been successfully synthesized in this study. It also revealed that gelatin has the ability to disperse ZnO NPs on the ceramic surface although some of them tend to form agglomerates. ZnO NPs are mostly trapped at the pores and rough surface of ceramic with particle size ranging from 100-500 nm. The SEM photos of ceramic and ceramic/ZnO NPs are shown in Figure 3.

(a)  
(b)

Figure 3. (a) SEM photo of ceramic surface 8000x (b) SEM photo of ceramic/ZnO NPs surface 10000x

The Energy dispersive x-ray spectroscopy (EDS) analysis also shown that 82% of ZnO NPs was attached on the ceramic surface with 5.5 mg/cm² (3.08 g/L) of maximum catalyst dosage achieved (3 cycles) in this study. It can be assumed that 18% more of ZnO NPs have been removed while conducting the pre-treatment process or even trapped into the pores of ceramic. Actually, there is one variable that very hard to control in ceramic production. It is nearly impossible to obtain highly precise and accurate of the ceramic surface area due to its shrinkage ability in the drying process. Furthermore, to gain more accurate result in this study, ANOVA test using R software was done for every 4 plates used in all variations of this study. The result showed that all of the ceramic surface area data were normally distributed with P > 0.05 using Saphiro-wilk test and there is no significant difference between all plates surface with 95% of confidence level (P>0.05). Ceramic used in this study is shown in Figure 4.

Meanwhile, RB5 dye solution in this study was also characterized in this study by spectrophotometer UV-Vis from 400 to 800 nm using 5 mg/L of RB5 dye concentration. The characterization was conducted at different pH from extreme acid condition (pH 3), neutral (pH 7), and extreme alkaline condition (pH 11). This procedure was done to evaluate the initial characteristic of RB5 dye at certain pH condition before conducting the experiments.
Figure 4. Ceramic plate used in this study. (a) ceramic/ZnO NPs, (b) un-coated ceramic (blank)

Figure 5. UV-Vis Spectroscopy of RB5 dye at 5 mg/L

It can be observed from the graph (figure 5) that there was a little shift of wavelength at pH 11 and clearly revealed the change of initial characteristic. This phenomenon could happen due to the occurrence of the reaction between excessive hydroxyl ion and azo compound in the RB5 dye structure to form a new type of RB5 structure [16]. The extreme acid condition (pH 3) did not clearly change the initial characteristic of RB5 dye. The discussion about the change of RB5 dye initial characteristics at different pH will be reported on different publication.

3.2. Photocatalytic experiments
3.2.1. Blank and control test

Blank and control tests were done to evaluate the other processes occurred in the photocatalytic treatment. These processes include adsorption (ceramic and ceramic/ZnO NPs) and UV irradiation. Adsorption effect in dark condition for about 3 hours was done by using ceramic and ceramic/ZnO. Adsorption effect on ceramic/ZnO NPs was slightly increased when compared to ceramic blank. Ceramic/ZnO NPs and ceramic blank achieved 7.11% and 1.67% of decolorization efficiency respectively which detained from 120 to 180 min and considered as its equilibrium state. Indeed, ZnO NPs can remove both anionic and cationic dyes by spontaneous adsorption reaction. Chemical precipitation, electrostatic attraction, and hydrogen bonding are mainly responsible for the binding mechanism [18].

The UV irradiance effect was also evaluated by using ceramic blank and ceramic/ZnO for 120 min at pH 7 and 5 mg/L of RB5. It was revealed that UV irradiance possesses great impact on decolorization efficiency. Ceramic blank and ceramic/ZnO achieved 29.18% and 80.19% of decolorization efficiency respectively. Even without ZnO photocatalyst, UV light can slightly promote the formation of radical ions (OH•) in water and interfere the stability RB5 dye. Overall, the comparison between photocatalytic activity and adsorption based on decolorization efficiency in this study is pictured in figure 6(b).
3.2.2. Effect of pH and treatment time

All the experiments were done using photocatalytic reactor scheme based on figure 2 by batch process. Different initial of pH (3, 5, 7, 9, and 11) were used to evaluate its effect to RB5 dye decolorization efficiency using 5 mg/L of RB5 dye concentration.

Based on the result, the pH was clearly affected the RB5 dye decolorization efficiency. And it is shown that extreme acid and alkaline condition will enhance the photocatalytic activity. Similar results were also obtained with the increasing of treatment time. It can be seen from figure 7(b) that extreme alkaline condition possesses the best result with 100% of decolorization efficiency when it is compared to neutral and extreme acid condition. Similar results also have been reported on the previous study to treat RB5 [16] and methylene blue using TiO$_2$ [17].

In acid condition, it is easier for RB5 to obtain hydrogen atom from neighbor molecule to produce RB5 radicals, which may further produce OH$^\bullet$. The RB5 radicals also can form hydrazyl intermediates, which causes photo-reduction decolorization of RB5. It is considered that both oxidation and reduction may contribute to the decolorization of RB5 at low pH. Nevertheless, the oxidation by OH$^\bullet$ is considered to be the main decolorization pathway, because the hydrazone form of RB5 is more favored in acid condition. Meanwhile, the increase of pH of the dye solution is beneficial to the production of OH$^\bullet$. Therefore, the decolorization of RB5 is also increased with increasing pH in alkaline solution [16].

![Figure 6](image)

(a) Adsorption and control test at pH 7 using 5 mg/L of RB5. (b) Comparison of decolorization efficiency at pH 7 using 5 mg/L of RB5 for 120 min.

![Figure 7](image)

(a) Decolorization efficiency of 5 mg/L RB5 dye at different pH and time treatment. (b) Comparison of decolorization efficiency using 5 mg/L RB5 dye at pH 7 and 120 min.
3.2.3. Effect of RB5 dye initial concentration

The different initial concentration of RB5 (3, 5 and 10 mg/L) was used to evaluate its effect to the decolorization efficiency. These experiments were conducted using optimum pH condition (pH 11) which was obtained from previous experiments. This experiment revealed that photocatalytic activity will greatly increase by the decreasing of RB5 dye initial concentration. 3 and 5 mg/L of RB5 dye achieved 100% of decolorization efficiency at 90 and 120 min respectively.

![Figure 8](image)

**Figure 8.** Effect of different initial concentration of RB5 at optimum pH condition (pH.11)

![Figure 9](image)

**Figure 9.** The visual image of color gradation of 3 mg/L RB5initial concentration (at pH 11) as the function of Photocatalytic duration.

4. Conclusion

The new type of ceramic/ZnO NPs has been successfully synthesized in this study using gelatine as dispersive agent for ZnO NPs powder in the dip solution, although some of ZnO NPs tend to form agglomerates. Extreme acid and alkaline condition in RB5 dye solution will greatly enhance the photocatalytic activity of ceramic/ZnO NPs due to its ability in promoting higher radical ion concentration under UV irradiation. The optimum condition for this study was achieved at pH 11 and RB5 initial concentration of 3 mg/L (100% of decolorization efficiency at 90 min treatment time).

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