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PHOTOCATALYTIC DEGRADATION OF INDUSTRIAL DYE WASTEWATER USING ZINC OXIDE-POLYVINYLPYRROLIDONE NANOPARTICLES

(Penguraian Fotopemangkinan Air Sisa Pewarna Industri Menggunakan Nanopartikel Zink Oksida-Polivinilpirolidon)

Dilaeleyana Abu Bakar Sidik[1,2], Nur Hanis Hayati Hairom[1]*, Nur Zarifah Zainuri[1], Amira Liyana Desa[1], Nurasyikin Misdan[3], Norhaniza Yusof[4], Chin Boon Ong[5], Abdul Wahab Mohammad[6], Nur Shahirah Mohd Aripen[2]

[1]Department of Chemical Engineering Technology, Faculty of Engineering Technology
[2] Department of Science and Mathematics, Center of Diploma Studies
[3]Department of Mechanical Engineering Technology, Faculty of Engineering Technology
Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Batu Pahat, Johor, Malaysia
[4]Advanced Membrane Technology Research Centre (AMTEC),
Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia
[5]Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment
[6]Centre for Sustainable Process Technology (CESPRO), Faculty of Engineering and Built Environment
Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

**Corresponding author: nhanis@uthm.edu.my*

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Abstract

Due to the lack of studies regarding the potential of polyvinylpyrrolidone (PVP) as capping agent in precipitation of zinc oxide (ZnO) nanoparticles, this research focused on the performance of ZnO nanoparticles with presence of PVP loading on photocatalytic degradation treatment for industrial dye wastewater. Three different samples of ZnO-PVP were successfully synthesized via precipitation method. The degradation rate of dye approached 90.61% under pH7 in the presence of ZnO-PVP (0.025g/L of PVP). The chemical bonds in ZnO-PVP was analysed using Fourier Transform Infrared Spectroscopy (FTIR).

Keywords: zinc oxide, polyvinylpyrrolidone, photocatalytic, nanoparticles, wastewater treatment

Abstrak

Oleh kerana kekurangan kajian mengenai potensi polivinilpirolidon (PVP) sebagai ejen penutup dalam mendakan nanopartikel zink oksida (ZnO), kajian ini memberi tumpuan kepada prestasi nanopartikel ZnO dengan kehadiran muatan PVP dalam rawatan penguaraian fotopemangkinan air sisa industri pewarna. Tiga sampel ZnO-PVP yang berlainan telah berjaya disintesis melalui kaedah pemendakan. Kadar degradasi pewarna menghampiri 90.61% di bawah pH 7 bagi ZnO-PVP (PVP sebanyak 0.025 g/L). Ikatan kimia ZnO-PVP telah dianalisis menggunakan spektroskopi inframerah transformasi Fourier (FTIR).

Kata kunci: zink oksida, polivinilpirolidon, fotopemangkinan, nanopartikel, rawatan air sisa

Introduction

In recent studies, zinc oxide (ZnO) nanoparticles have been prove as effective photocatalyst due to their properties such as strong excitation binding energy, higher reactivity, surface area, photosensitivity, non-toxic nature and chemical stability [1-3]. Furthermore, ZnO nanoparticles have stable wurtzite structure and wide bandgap (3.4eV) which is suitable to act as catalyst, primarily for degradation of Congo red dyes [4].

To date, there are several methods have been implemented to synthesize ZnO including sonochemical [5, 6], sol gel process [7, 8], hydrothermal synthesis [9] and precipitation [1]. Since the synthesis method of nanoparticles is very sensitive and may influence their performance, precipitation is believed to be one of the promising method due to its simpler route, economic and operates at moderately low temperature [10]. However, there is severe drawback encounter in the synthesis of nanoparticles which is agglomeration. Agglomeration occurred due to Van der Waals and Ostwald ripening interactions which leads to the production of aggregation of the particles. In 2015, Hairom et al. [4] claimed that the agglomeration of ZnO nanoparticles could be stabilized by the addition of polyvinylpyrrolidone (PVP) in the precipitation method. Moreover, they also reported that the ZnO-PVP showed better photocatalytic activity in compared to absence of PVP, due to the less agglomeration of ZnO-PVP. Therefore, this study investigated the optimum loading of PVP on precipitation of ZnO nanoparticles and its photocatalytic activity in industrial dye wastewater treatment. These details are very useful as the preliminary study for the synthesis of nanoparticles in order to improve the performances of a photocatalyst in wastewater treatment.

Industrial dye wastewater is difficult to treat satisfactorily due to highly variable in compositions, flow and volume which contains various chemicals and coloring compounds. Therefore, a proper treatment is required before it was discharged into any water bodies. The industrial dye wastewater discharged is a major source which contributed wide range of pollutions on the earth. In terms of wastewater management, it does not favorable from a view of ecological point since the wastewater are heavily colored. It also cause severe health problem and toxic to the aquatic organisms by reducing photosynthetic activity due to less penetration of light. The influent of industrial dye wastewater is very important to be managed and degraded in order to prevent any diseases spread out over the world. Due to their toxic and recalcitrance properties, colored particles can also contribute to the failure of biological processes in wastewater treatment plants. Further, the regulations imposed for the discharged colored effluents have become more stringent and thus motivated the industries to improve their effluent de-colorization technology [11].Commonly, industrial dye wastewater has high degree chemical, highly variable in compositions and photolytic stability which is one of the sources of wastewater that give bad impacts to the environment [12].

There are many present methods are being used in these days for treating industrial dye wastewater. However, they only offered for phase transfer or partial degradation of water pollutants [13]. In recent years, photocatalysis process has been suggested as an alternative treatment for dye wastewater due to the completion degradation rate [14]. This method also involved the inexpensive photocatalyst, non-toxic photocatalyst and environmental safety compared to the other methods [1]. Photocatalytic degradation has great characteristics to investigate since it is essential and useful for decolorization of dye wastewater. This potential method has become research interest in order to create clean and fresh environment. Consequently, the other purpose of this study is to examine the optimum condition of several parameters including pH and ZnO-PVP loading on photodegradation efficiency (measured by color intensity, turbidity and dissolve oxygen (DO)) of industrial dye wastewater which collected from the newspaper printing factory.

Materials and Methods

Synthesis of ZnO nanoparticles

0.15 M solution of oxalic acid dehydrates (R&M Marketing, Essex, UK) was added slowly into 0.1M solution of zinc acetate dehydrated (R&M Marketing, Essex, UK) with molar ratio of 3:2 under room temperature (25 °C). Different loading of PVP (0.015g/L, 0.020g/L or 0.025g/L) was then added in each of the mixture after 5 minutes of the reactions. The mixture was stirred for 12 hours to increase the production of ZnO. The precipitate obtained will be filtered and consequently dried in oven under100 °C for 1 hour to remove water. Next, the precipitate was calcined in the furnace (Nabertherm model, Germany) under 550 °C for 3 hours to remove impurities. After calcination process, the white powder of ZnO-PVP has been formed and proceed for characterization.

Characterization of ZnO-PVP nanoparticles

The characterization has been conducted by using FTIR spectrophotometer was performed using a Perkin-Elmer FTIR (Spectrum RX-I) model (Nicolet FT-IR Avatar 360) in the wavelength range 400-6000 cm^{-1}. Chemical bonds in the samples were analysed by producing an infrared absorption spectrum in order to ascertain the purity and nature of the ZnO-PVP.

Photocatalytic degradation

In this study, 500 mL of beaker used as the photocatalytic reactor in batch method. The photocatalysis process has been conducted under UV light (UV light source at 253 nm with definite power of 6 W) for activation of the photocatalyst as indicated in Figure 1. Then, ZnO-PVP nanoparticles (0.015, 0.020 and 0.025g/L of PVP) were added into the reactor which filled with 200 ml industrial dye wastewater which collected from newspaper printing industry located at Selangor, Malaysia. The mixture has been agitated at 150 rpm under room temperature (25 °C). The operation temperature was controlled by water recirculating in a water bath. At the interval of 5 minutes, 10 ml of degraded wastewater were sampled and the samples of domestic wastewater with ZnO were separated by using centrifuge for 20 minutes. Next the quality of samples were analysed after the separation process. For treated water quality analysis, color intensity of the samples has been determined by using UV-Vis Spectrophotometer (LABOMED, INC, Spectro UV-2650). Dissolve oxygen (DO) of the samples measured by using DO meter (HACH, H280G). While for turbidity was analysed by using turbidity meter (EUTECH Instrument, TN100, 1000NTU) respectively.

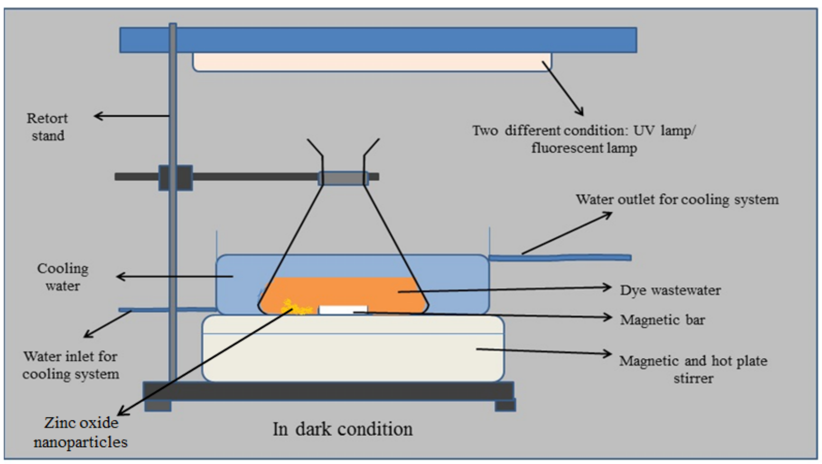

Figure 1. The schematic diagram of photocatalysis process

Results and Discussion

The findings presented in this research demonstrate the potential of the ZnO-PVP nanoparticles in photocatalytic degradation of dye wastewater. There are three different ZnO with the different loading of capping agent of PVP (0.015 g/L, 0.020 g/L and 0.025g/L) has been successfully synthesized via precipitation method. Figure 2 exhibits the FTIR spectra of ZnO-PVP nanoparticles with 0.025 g/L of PVP. The ZnO-PVP nanoparticles bands revealed several characteristics of the absorption bands in the range of 600-4000 cm^{-1}. The strong intensity of adsorption band from 1068 and 612 $cm^{-1}$was due to the larger magnitude of dipole change during the vibration process, which can be elucidated by the covalent bonds of PVP [15]. The peaks in the area from 1068 and 612 cm^{-1} were assigned to the C-C stretching of pyrrolidone. The result revealed that C=O bond existed in the range from 2327 until 2420 cm^{-1} was a group of carboxylic derivatives which may be present due to the residue of zinc acetate used in reaction. It may happened because of the precursor material and reaction product. The presence of absorption from 3000 to 4000 cm^{-1} related to O-H vibration of the moisture which make the bond arises and proved that ZnO-PVP samples has absorbed the existence water from surroundings [16].

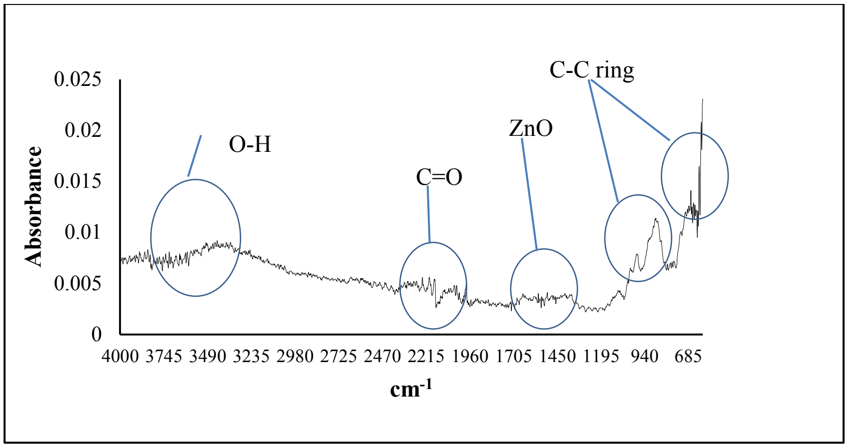

Figure 2. IR spectra of ZnO-PVP (0.025g/L)

Mechanism of photocatalytic degradation

According to Hairom et al. [10], mechanism of photocatalytic degradation for industrial dye wastewater has been started by the photo excitation of the ZnO which followed by the creation of an electron-hole pair on the nanoparticles surface. The high oxidative potential of the hole (hVB^+) in ZnO which leads the direct oxidation of dyes occurred. Through decomposition of water during the reaction between hydroxide ion and hole caused a formation of reactive hydroxyl radicals. Furthermore, due to the extremely unstable of hydroxyl radicals may lead to the degradation of organic chemicals. Then, the molecular oxygen continued for reduction to superoxide anion by electron in conduction band (eCB^-). The radical may formed into organic peroxides in the presence of organic scavengers or hydrogen peroxide (H_2O_2). Electrons in the conduction band are also included in the production of hydroxyl radicals, which have been indicated as the primary cause or organic matter mineralization.

Effect of photocatalytic activity of dye wastewater under different pH

Figure 3 shows the percentages of dye degradation in presence of ZnO-PVP (0.015 g/L of PVP) under three different pH condition which represented as acidic, neutral and alkaline wastewater. This can lead to obtain the ideal pH of the wastewater in order to ensure the best performance in treated wastewater. Based on the result, pH 7 was found as the optimum solution pH due to the higher percentage of dye degradation at 82.15% compared to pH 4 and pH 10 which are 54.84% and 71.76% respectively. In 2016, Mondal and Sharma [17] claimed that at certain concentration of dyes in both acidic and alkaline tends to lower degradation efficiency of some dye wastewater. The greater photodegradation at pH7 can be explained by the point of zero change (PZC) of the photocatalyst since the PZC value of ZnO has been found at pH 6.25 and pH 8.9. PZC refer to the condition which the surface charge of nanoparticles is zero or neutral. The impact of pH toward the performance of photocatalytic oxidation process can be explained through PZC. Where at PZC the interaction between nanoparticles and water contaminant is minimal due to the absence of electrostatic force. Consequently, the adsorption of dye wastewater is extremely good at pH7 and hence photocatalytic degradation activity is significant at neutral pH value.

Subsequently, the changes on dye degradation has been grown rapidly after 5 minutes of experiment conducted. The degradation rate of dye wastewater is very fast due to the involving PVP as capping agent in ZnO nanoparticles. It is correlative to Hairom et al. [1] statement in 2014 which stated that ZnO-PVP has good condition in morphology and smallest particle sizes which can lead to the faster degradation rate of dye wastewater. In 2013, Sudha and Rajarajan [18] claimed that the degradation efficiency by ZnO-PVP for Rhodamine B (RhB) increased with the increment of pH exhibiting maximum degradation efficiency at pH 8. Based on result obtained; the percentage of degradation at pH 10 rapidly increases from 23% to 45.88% and continued increases to 65.30% but it stay constant when it achieved at 71.76%. They also stated that the degradation rate found to be decreased when it was achieved at pH 8 beyond [18]. However, the reaction under alkaline conditions could be attributed to the increase of hydroxyl ions which leads to the formed of ·OH radicals. Thus, the degradation rate for condition of alkaline is much higher compared to the acidic but lower than neutral condition. As reported by Zahrim et al. [19] acidic and alkaline condition would promote self-aggregation phenomena of nanoparticles in solution which caused the reduction of the dye degradation. The observed trend from this study correlated with electrostatic interaction between substract and photocatalyst surface which depending on the pH of wastewater. This phenomena caused by the effect of pH on the surface properties of photocatalyst and physical properties of dye solution including aggregation or dispersion of dye.

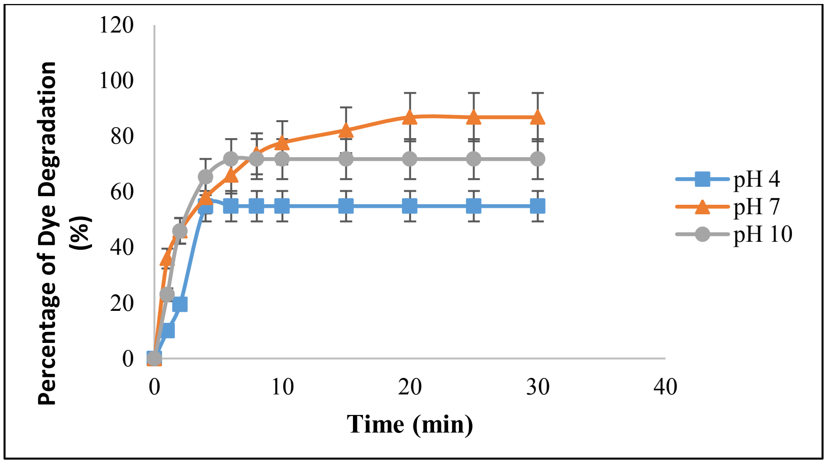

Figure 3. Percentages of dye degradation for photocatalysis process in the presence of ZnO-PVP (0.015 g/L of PVP)

Figure 4 shows the turbidity for three different pH of dye wastewater. It was observed that pH 7 is less cloudy at percentage of 54.49%, in comparison to the dye wastewater for pH4 and pH10 which has turbidity reduction at percentage of 36.67% and 52.17% respectively. The percentage different of the turbidity reduction between pH 4, 7 and 10 is minimal maybe due to varies of the real dye wastewater concentration. The percentage of dye degradation indicated in Figure 3 shows significance correlation with the turbidity reduction where the higher of degradation rate leads to the higher reduction of turbidity of the treated dye wastewater. According to Li et al. [20] revealed that photocatalytic degradation has ability to remove colours of dyeing effluent efficiently. In 2012, Huber and Carre [21] also claimed that UV photons excite ZnO, which then reacts with water molecules or hydroxide ion to produce hydroxyl radicals. Then, the dye molecules were degraded, and the degradation leads the breaking at least one of the conjugated bonds since the colour of dyes formed by conjugated molecules.

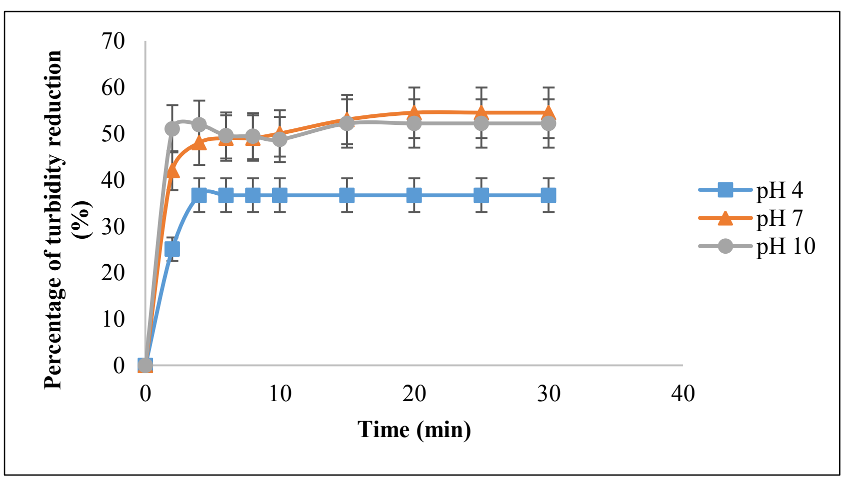

Figure 4. Percentage of turbidity reduction for photocatalysis process in presence of ZnO-PVP (0.015 g/L of PVP)

Based on Figure 4, pH 4 of wastewater was more turbid compared to others pH since the higher percentage of turbidity reduction that can be achieved at 36.67%. This was due to the photodegradation of the dye is retarded by the high concentration of proton, resulting in lower degradation efficiency [22]. Hence, the percentage of dye removal for pH 4 was lower compared to pH 7 and pH 10 of wastewater.

Figure 5 demonstrates the behavior of dissolved oxygen (DO) for different condition pH of wastewater after undergo the treatment. The results have been obviously stated that pH 4 lead for higher value of DO, followed by pH7 and continued by pH 10. It can be seen that certain value of DO shown to be decreased while the others has been increased than the initial value for DO of wastewater which is 3.36 ppm. The increment of DO occurred may be due to the presence of oxygen in photocatalytic degradation which acts as electron acceptor that used to trap the photo induced e^- [23]. According to the National Water Quality System (NWQS), the acceptable range of DO value after wastewater treatment is in the range 0.02 to 20 ppm. Therefore, the treated wastewater could be discharged to environment and safe to aquatic life. From the analyzed results, it could be deduced that the treated wastewater is safe to discharge to environment since their DO value is in the acceptable range.

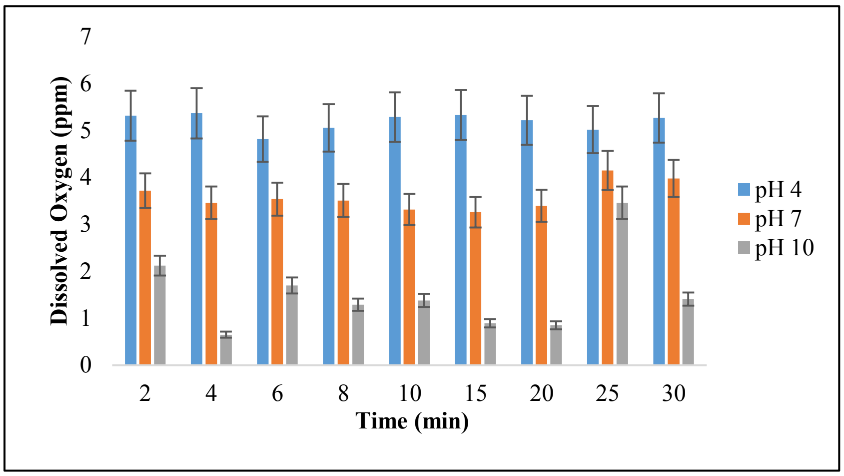

Figure 5. The amount of dissolve oxygen for photocatalysis process in the presence of ZnO-PVP (0.015 g/L of PVP

Photocatalytic activity under different loading of ZnO-PVP photocatalyst

The experiments were carried out with varying photocatalyst loading from 0.015, 0.020 and 0.025 g/L of PVP in precipitation of ZnO-PVP at pH 7. Figure 6 revealed that the ZnO-PVP (0.025 g/L of PVP) is the best performer regarding the highest degradation of dye which about 90.61% compared to the ZnO-PVP (0.015 and 0.020 g/L) were 86.81% and 86.75% respectively. PVP has been used to protect the nanoparticles from growing and agglomerating [24]. The introduction of optimum loading of PVP may leads to higher percentage of dye degradation due to the increasing of ZnO surface area which enhance the accessibility of photocatalyst sites [17,18]. Consequently, the number of hydroxyl radicals will increase and promote the increment of the degradation percentage of dye. In fact, the hydroxyl radicals is a powerful oxidizing agent and attacks to organic compounds and formed intermediates compounds [25].

Wang et al. also stated that the optimum loading of PVP may led to the modulation of viscosity and diffusion coefficient of the solvent which promote better dispersion of dye removal [24]. Thus, it can be deduced that the optimum loading of PVP in ZnO-PVP precipitation was 0.025 g/L of PVP. The efficiency of photocatalytic degradation rate was depend on the saturation of nanoparticles used. Chong et al. [26] reported that excess amount of nanoparticles operate in photocatalytic reactor will create a light screening effect which reduce the surface area of nanoparticle being expose to light illumination and subsequently will affect the photocatalytic efficiency.

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The turbidity of treated wastewater is very relative to the percentage of dye degradation. It can be found as in Figure 6 and Figure 7 which are described that the higher of dye degradation may led to the less turbid of treated wastewater. Figure 7 shows the percentage of turbidity reduction on three different loading of PVP (0.015, 0.020 and 0.025 g/L of PVP) in the precipitation of ZnO-PVP. As illustrated, the treated wastewater by using ZnO-PVP (0.025 g/L of PVP) has less turbid as 58.99% of percentage for turbidity reduction than ZnO-PVP (0.020 and 0.015g/L of PVP) were 53.37% and 54.49%, respectively. The trend of sudden increment in the percentage of turbidity reduction for 0.015g/L of ZnO-PVP loading may be due to the tendency of the particles to aggregate in acidic condition. According to literature [1, 2], they claimed that the degradation efficiency increases along the catalyst dose of PVP due to the absorption of the maximum UV light and effective surface of ZnO-PVP. Hence, it could be concluded that ZnO-PVP (0.025 g/L of PVP) was the best photocatalyst for photocatalytic degradation of industrial dye wastewater due to the maximum adsorption of UV and less turbid of the treated wastewater.

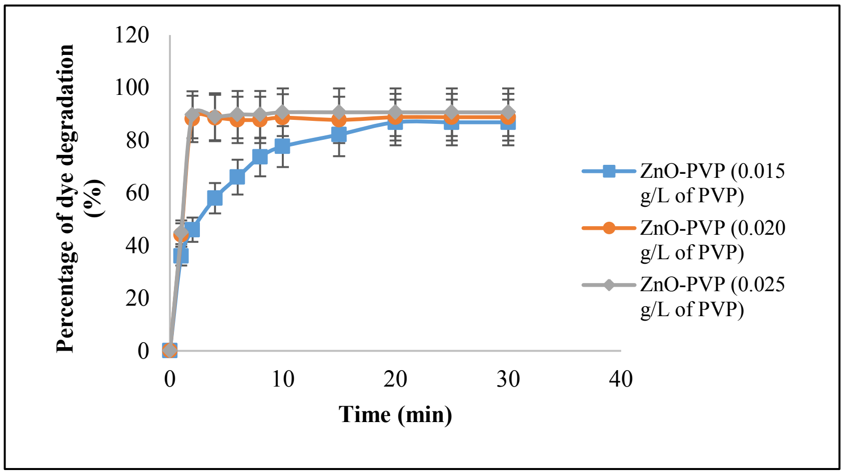

Figure 6. Percentages of dye degradation for photocatalysis process in presence of different loading PVP in ZnO-PVP

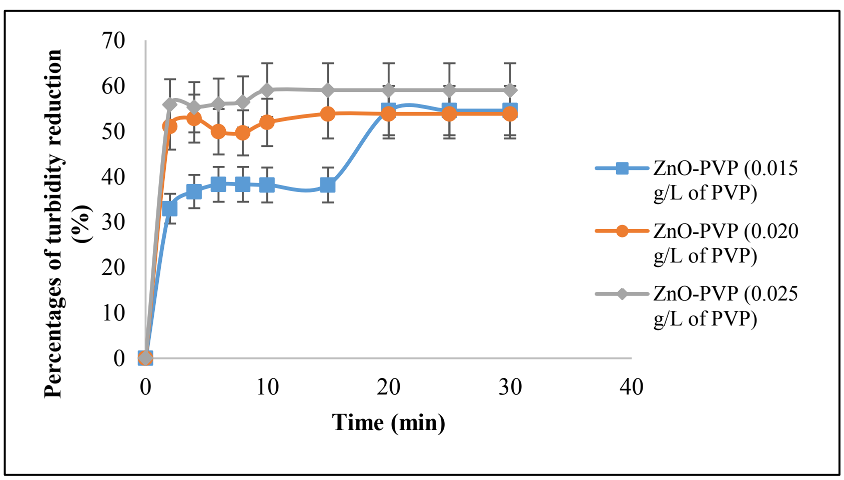

Figure 7. Percentage of turbidity reduction for photocatalysis process in presence of different loading PVP in ZnO-PVP

Based on the Figure 8, it obviously found that there is variation amount of DO that has been obtained by three different of photocatalyst. However, all the reading value of DO that has been obtained were lower to the initial amount of DO which is 3.36 ppm. This is due to the generated oxygen has been involved in the mineralization of dye wastewater since the presence of oxygen contributed to the photocatalytic degradation [23]. This might happen due to the exposure of treated wastewater to the environment.

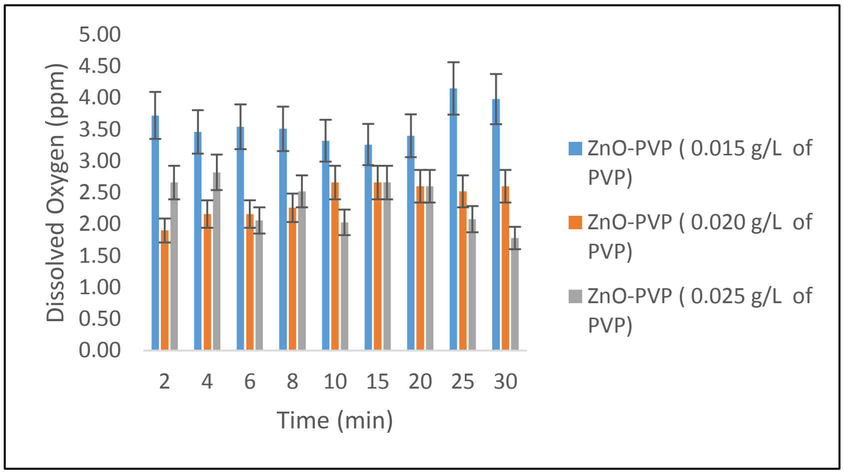

Figure 8. The amount of dissolved oxygen for photocatalysis process in presence of different loading PVP in ZnO-PVP

Conclusion

The optimum operational condition of photocatalytic degradation for the newspaper printing industrial dye wastewater was found under pH 7 of dye wastewater in the presence of ZnO-PVP (0.025 g/L of PVP) nanoparticles. This is due to the maximum dye degradation of 90.61% and turbidity reduction of 58.99%. It can be concluded that the photocatalytic degradation of industrial dye wastewater by ZnO-PVP nanoparticles has great potential as alternative treatment in order to preserve the potable water since it is an eco-friendly treatment due to the non-harmful by-products formed. Furthermore, this study demonstrates the feasibility of ZnO-PVP nanoparticles in photocatalytic treatment of newspaper printing wastewater

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