

Study Degradation of 4-(2-Pyridylazo)Resorcinol Dye in Circulating Fluidized Bed Photo Reactor Using ZnO Nanoparticles

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Background & Aims of the Study: In this study, 4-(2-pyridylazo) resorcinol (PAR) as model azo dye was used. In spectroscopic measurements and studies of PAR reagent as a ligand are used to formation a complex with toxic metals. So, removal and degradation these compounds of wastewaters are necessary. The aim of this study is the degradation of PAR from aqueous solutions in circulating fluidized bed photo reactor (CFBPR) using ZnO powder. The UV/O₂ system was used for dye degradation.

Materials & Methods: ZnO powder used a catalyst for the degradation of dye in aqueous solution. ZnO powder has been characterized by scanning electron microscopy (SEM) and Fourier transform infrared (FT-IR). The effect of operational parameters such as: pH, catalyst dosage and temperature were studied. The effect of UV irradiation, UV/O₂ and UV/O₂/ZnO on photocatalytic degradation of PAR were studied. The reaction kinetic was studied. The optimum conditions were determined using design of experimental based one factor at the time (OFAT) method.

Results: The optimum conditions for this reaction were obtained at pH=10, catalyst dosage=20 mg/L, and temperature=40°C. The pseudo first order reaction with rate constant ($k=0.0105 \text{ min}^{-1}$) in T=40°C was observed for the photocatalytic degradation of PAR. Activation energy (E_a) for the degradation of PAR was obtained as 48.12 (kJ/mol). These experiments demonstrated that UV/O₂ and ZnO catalyst were needed for the effective degradation of dye.

Conclusions: The results showed that the photocatalytic process can be suitable to degradation PAR dye from aqueous solutions using ZnO catalyst.

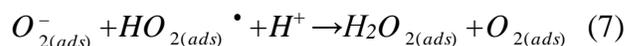
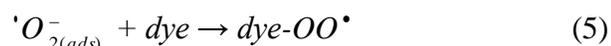
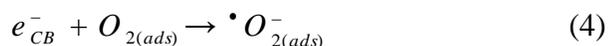
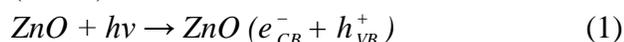
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Background

Dyes and pigments used in industries for applications such as textiles, leathers, papers, foodstuffs, additives, etc (1,2). In spectrophotometric methods of PAR reagent as a ligand are used to formation a complex with toxic metals (3,4). Zinc oxide is a semiconductor having many applications, such as being photocatalyst and transparent conductor (5,6). The degradation of dye wastewaters in aqueous

solution with heterogeneous semiconductor such as ZnO catalyst was studied by many investigators (7-9). The techniques for the synthesis of ZnO powder including chemical deposition (10), sol-gel process (11), chemical vapor decomposition (12), hydrothermal method (13,14) and precipitation method. In this study, of precipitation method for synthesis ZnO was used with simple, fast, low cost process. The UV/ZnO process is due to the well-known electron promotion from the valance band to the

conduction band of the semiconducting oxide to give electron-hole pairs. The valance band hole (h_{VB}^+) potential is positive enough to generate hydroxyl radicals at the surface. Also, the conduction band electron (e_{CB}^-) is negative enough to reduce the oxygen molecules, present in the solution. The generated hydroxyl radicals are powerful oxidizing agents and attack organic pollutants, present at the surface of ZnO and of course the reaction rate of hydroxyl radicals with pollutants decreases as the distance from surface increases. The mechanism degradation of dye usually described by the following (Eqs. 1-8) (15-17):



Aims of the study:

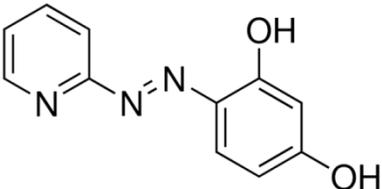
In this study, ZnO catalyst was characterized by SEM and FT-IR. The reaction kinetic was studied. The effects of operational parameter such as pH, catalyst dosage and temperature on the process were studied and optimized. The results indicated that the UV/O₂/ZnO could be used as process to degrade PAR.

Materials & Methods

Materials

The azo dye, PAR obtained from Sigma-Aldrich Company and was used without further purification. The structure and characteristics of PAR is shown in Table 1. The pH values were adjusted at desired level using dilute NaOH and H₂SO₄. Zn(CH₃COO)₂ and ethanol were all Merck products (Germany). Double distilled water was used for preparation of requisite solutions.

Table 1) The structure and characteristics of PAR.

Name	Formula	Structure	λ_{max} (nm)	MW (g/mol)
4-(2-Pyridylazo) Resorcinol (PAR)	C ₁₁ H ₉ N ₃ O ₂		390	215.21

Apparatus

Fig. 1 shows the schematic diagram of circulating fluidized bed photo reactor (CFBPR) which was used for photocatalytic decomposition method of PAR. In this equipment, capacity 0.5 L with a low mercury pressure lamp Philips 15W (UV-C) was used in photo reactor. UV/Vis Spectrophotometer, Jenway (6505) was employed to measure the absorbance using glass cells of path length 1 Cm. For the chemical oxygen demand (COD)

measurement, COD meter analyzer model AL250 AQUALYTIC was used. The morphologies of the catalyst were taken by SEM model (Philips XL30 microscope). The FT-IR spectroscopy was measured on PerkinElmer Spectrometric Analyzer using KBr pellets. pH values were measured with Horiba M12 pH meter.

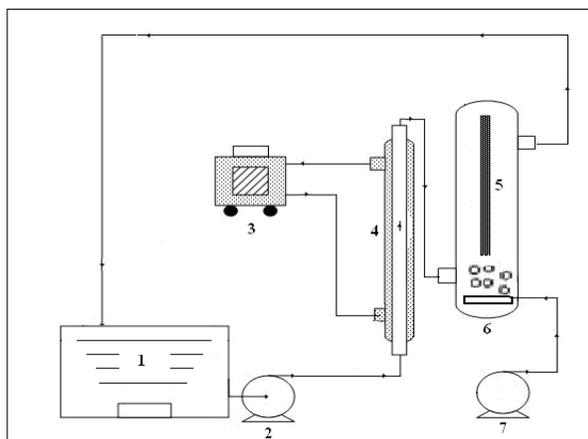


Figure 1) Schematic diagram of photo reactor
 1) tank (Pyrex), 2) pump, 3) temperature controller,
 4) condenser, 5) UV lamp, 6) reaction flask, 7) air
 pump.

Synthesis of ZnO powder

ZnO powder was prepared by precipitation method (18). In this procedure, 50 mL of 4 M NaOH was added drop by drop into 50 mL of 2.5 M $\text{Zn}(\text{CH}_3\text{COO})_2$ aqueous solution under magnetic stirring at 80 °C. Then, the reaction mixture was further stirred for 120 min constantly, and naturally cooled to room temperature. The resultant solid products were filtered and washed with ethanol for several times. Finally, the obtained white precipitate ZnO was dried in an oven at 100 °C for 1 h, and then calcined at 400 °C for 2 h. The precipitation was sieved using 100 mesh standard sieve.

Procedures

For the photodegradation of PAR, a solution containing known concentration of dye (35 ppm) and catalyst was prepared. The suspension pH values were adjusted at the desired level using dilute NaOH 0.1N and H_2SO_4 0.1N and were allowed to equilibrate for 30 min in darkness. Then, the prepared suspension was transferred to reaction flask. The degradation reaction took place under the radiation of a mercury lamp. The aeration operation was used an air pump with constant flow rate into reaction flask. The temperature was adjusted using the temperature controller. The concentration of the samples was determined (at 25 min intervals) using a Spectrophotometer(UV-Vis Spectrophotometer,

Jenway (6505) at $\lambda_{\text{max}}=390$ nm. The degree of photodegradation (X) as a function of time is given by (Eq.9)

$$X = \frac{C_0 - C}{C_0} \quad (9)$$

where C_0 and C are the concentration of PAR at $t = 0$ and t , respectively.

The optimum conditions were determined using design of experimental based one factor at the time (OFAT) method.

Results

The characterization of ZnO powder

Fig. 2 shows the SEM image of ZnO particles. Regarding to the specified scale in the Fig. 2 size of the particles is nanometer. The size and morphology of ZnO powder were characterized. FT-IR spectrum of ZnO particles was recorded in the wave number range from 400 of 4000 cm^{-1} is shown in Fig. 3.

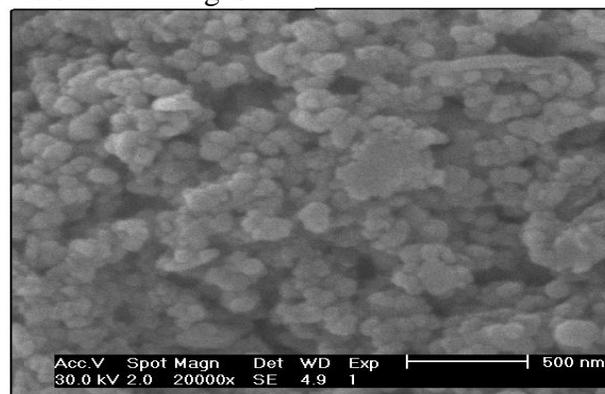


Figure 2) SEM image of ZnO

The band observed at 3490 cm^{-1} was due to vibration stretching mode of O-H group. The absorption band at 1686 cm^{-1} corresponds to H-O-H bending vibration of free or absorbed water (19,20). The two peaks observed at 1524 cm^{-1} and 1015 cm^{-1} were due to stretching mode of vibration of C=O and C-O respectively (21,22). The peak corresponding to the stretching vibration of ZnO is observed at 419 cm^{-1} (22).

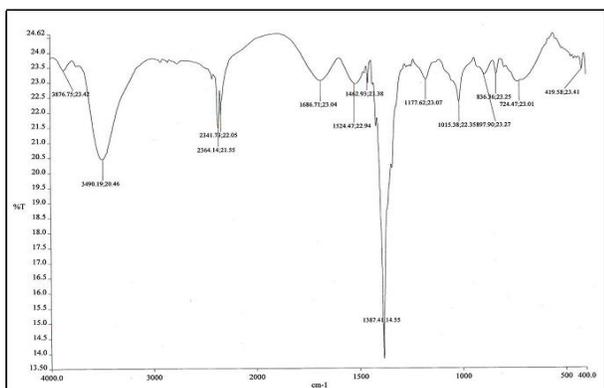


Figure 3) FT-IR spectrum of ZnO

The kinetic of photocatalytic degradation of PAR

Photocatalytic degradation reaction kinetic of PAR completely correspond the kinetic of pseudo-first-order reaction model reaction (23, 24). In the kinetic equation of pseudo-first-order relationship between COD and time (t) is in Eq.10:

$$\frac{-d[COD]}{dt} = k[COD], \quad (10)$$

the integral Eq.10 is in Eq.11:

$$\ln\left(\frac{[COD]_0}{[COD]}\right) = k.t, \quad (11)$$

in which k is the apparent pseudo-first-order rate constant (that is affected by COD) and t the reaction time.

A plot of $\ln\left(\frac{[COD]_0}{[COD]}\right)$ versus t for optimum

condition of photocatalytic degradation of PAR is shown in Fig. 4. The linear plot suggests that the photodegradation reaction approximately follows the pseudo-first-order kinetic with rate constant $k = 0.0105 \text{ min}^{-1}$ in $T=40^\circ\text{C}$.

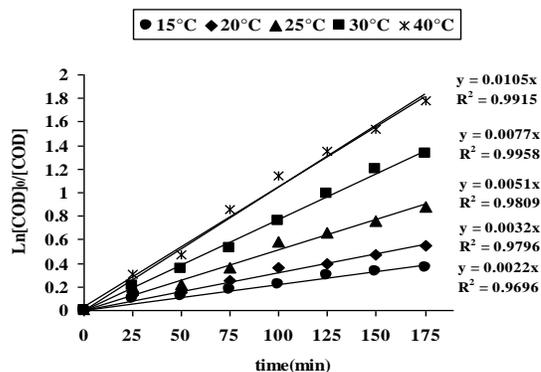


Figure 4) Kinetic for degradation of PAR (pH=10, catalyst dosage=20 mg/L, dye concentration=35 ppm, irradiation time=175 min).

The effect of pH

pH is one of the main factors influencing the rate of degradation of organic compounds in the photocatalytic process. The effect of pH on degradation rate was studied from pH 4 to 12. The results pH using photocatalytic process is shown in Fig. 5. It can be seen that the best results obtained in alkaline solution, (pH=10, X=70.12%). The degradation rate in alkaline solution is higher than that in acidic condition.

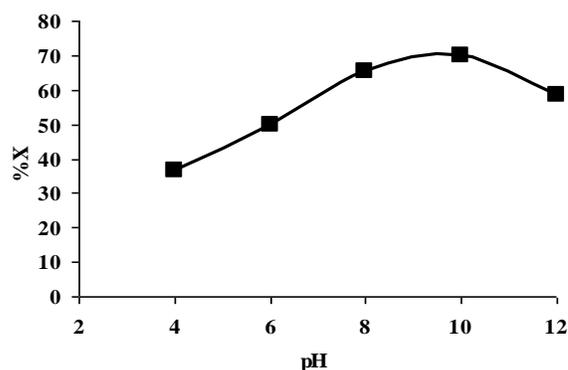


Figure 5) Effect of pH on the degradation of PAR (catalyst dosage=20 mg/L, dye concentration=35 ppm, T=40°C, irradiation time=175 min).

The effect of catalyst dosage

Fig. 6 showed the effects of catalyst dosage on dye degradation percent. At this stage, the effect of different catalyst dosage between 10 to 30 mg/L was tested. The results in Fig. 6 shows that increasing the catalyst dosage to 20 mg/L

degradation percent increased and with the increase more than this dosage, degradation percent decreased.

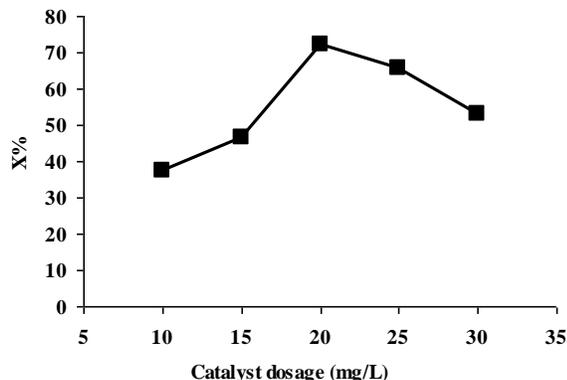


Figure 6) Effect of catalyst dosage on the degradation of PAR (pH=10, dye concentration=35 ppm, T=40°C, irradiation time=175 min).

The effect of temperature

Effect of temperature on the degradation process was tested in the range of 15-40 °C is shown in Fig. 7. The positive influence of the temperature can be observed. It can be seen that the best results obtained in (T=40°C, X=69.93%). Thus, increasing temperature of 15-40°C indicated that the degradation rate of PAR increased with increasing temperature.

A correlation between k and the process temperature (T) can be expressed by the Arrhenius is Eq.12:

$$k = A \cdot \exp^{-Ea/RT}, \quad (12)$$

the Eq.12 can be linearized by taking logarithms as:

$$-\ln k = -\ln A + \frac{Ea}{R} \left(\frac{1}{T} \right), \quad (13)$$

where k is pseudo-first-order rate constant min⁻¹, A is frequency factor, T temperature (K), Ea (kJ/mol) the activation energy and R the gas constant 8.314 J/(mol K)). Activation energy (Ea) was obtained through fitting the rate

constants into the Arrhenius equation. Fig. 8 is a plot of -ln k versus 1/T at 15–40 (°C) when the obtained Ea value was 48.12 (kJ/mol). The results shown in Fig. 8, indicates that the reaction rate increases when the photocatalytic reaction temperature rises. Table 2 shows the calculated Ea value and A for PAR.

Table 2) The Ea value and A for PAR.

Name	Catalyst	Ea(kJ/mol)	A
4-(2-Pyridylazo) Resorcinol (PAR)	ZnO	48.12	1.26×10 ⁺⁶

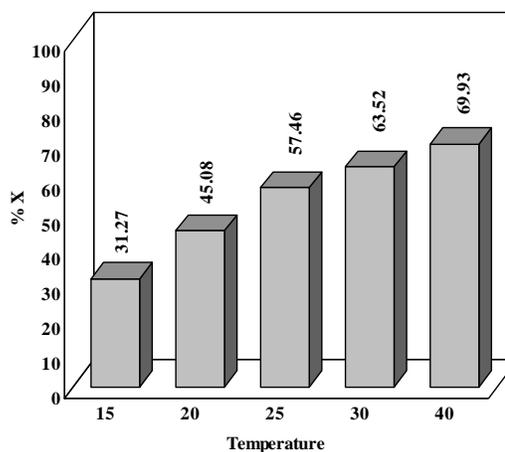


Figure 7) Effect of temperature on the degradation of PAR (pH=10, catalyst dosage=20 mg/L, dye concentration=35 ppm, irradiation time=175 min).

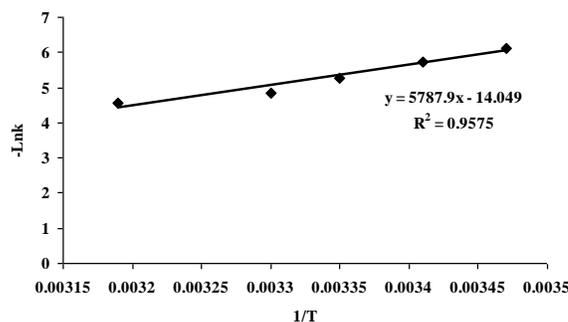


Figure 8) Arrhenius plot for photocatalytic degradation of PAR (pH=10, catalyst dosage=20 mg/L, dye concentration=35 ppm, irradiation time=175 min).

The effect of UV irradiation, UV/O₂ and UV/O₂/ZnO

The effect of UV irradiation, UV/O₂ and UV/O₂/ZnO in degradation process PAR are shown in Fig. 9. This figure indicates that in the presence of UV/O₂/ZnO 71.2% of PAR was degraded at the irradiation time of 175 min while it was 44% for UV/O₂. This was contrasted with 13.3% degradation for the same experiment performed under only UV irradiation. It is observed that the simultaneous use of UV irradiation, ZnO catalyst and O₂ were needed for the effective degradation of dye.

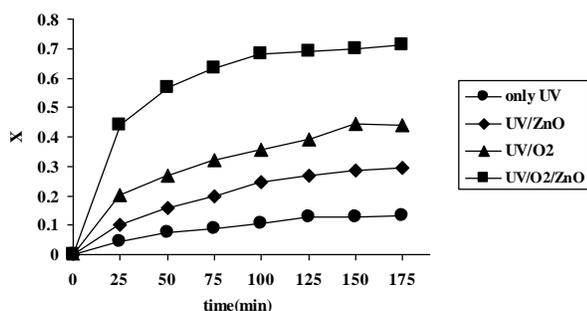


Figure 9) Effect of UV irradiation, UV/O₂ and UV/O₂/ZnO on the degradation of PAR (pH=10, catalyst dosage=20 mg/L, dye concentration=35 ppm, T=45°C, irradiation time=175 min).

Discussion

In this study, the degradation of dye in water solutions in photocatalytic process applied using CFBPR. In this process the effect of operational parameters such as: pH, catalyst dosage and temperature were studied.

pH is one of the effective parameter in this process. Fig. 5 shows the degradation of dye with ZnO catalyst which, first increases and then decreases with increasing pH. There is also the photocatalytic degradation of dye in alkaline solution, which is probably due to the formation of hydroxide radical as it can be inferred from the reactions (14–15) (25).



So, maximum dye degradation was obtained in pH= 10.

The catalyst dosage results in Fig. 6 shows that increasing the catalyst dosage to 20 mg/L reaction rate increased and with the increase more than this dosage, reaction rate decreased. The reduction in photocatalytic activity in amount more than 20 mg/L it is that with increasing the catalyst particles, the light scattering phenomenon occurred in a collision with catalyst particles in solution and lose the number of light photons energy and thus decreases the photocatalytic reaction rate (26–28).

The positive influence of the temperature is shown in Fig. 7. The best results obtained in T=40°C. The increasing temperature of 15–40°C indicated that the degradation rate of dye increased with increasing temperature (29,30). It is necessary to cause the temperature more than 40°C was not selected was that at higher temperatures possible vaporization of the dye solution increases and caused change the concentration of dye. However, an increase in temperature helps the degradation reaction to compete more effectively with valance band hole (h_{VB}^+) and conduction band electron (e_{CB}^-) recombination. On the other hand, the increase in temperature decreases the solubility of oxygen in water which is not desirable for photocatalytic processes (31). Therefore, the temperature of 40°C can be applied as a mild temperature with significant conversion of substrate.

Conclusion

Azo dyes and pigments have been extensively are used in various industries. The industries

color wastewater cause environmental pollution problems. So, wastewater treatment these industries are necessary. ZnO particles have been characterized by SEM and FT-IR. In this study, degradation of dye was investigated by photocatalytic process (UV/O₂/ZnO). Various factors affecting in the degradation process such as: pH, catalyst dosage, and temperature were analyzed and optimized. The results showed that pH=10, catalyst dosage=20 mg/L, and temperature 40°C was optimum conditions for this reaction. Also the results showed that simultaneous utilize of UV irradiation, ZnO catalyst and O₂ oxidation were needed for the effective degradation of dye. The results showed that in the presence of UV/O₂/ZnO 71.2% of dye was degraded at the irradiation time of 175 min. Pseudo-first-order model reaction corresponds to the experiment data of photocatalytic degradation of dye. Activation energy (E_a) and frequency factor (A) values for the degradation of dye respectively, 48.12 and $1.26 \times 10^{+6}$ was.

Footnotes

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Conflict of Interest:

The authors declared no conflict of interest.

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