Removal of Methylene Orange and Procion Blue with Integrated Adsorption-Photocatalytic Method

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Abstract. One of the non-biodegradable organic contaminants is methylene orange and procion blue. These dyes contain benzene groups that are very difficult to degrade, carcinogenic and mutagenic. Therefore, adsorption-photocatalytic method is used to reduce the concentration of these dyes. TiO_2 as a photocatalyst was introduced into a natural zeolite of Sukabumi as adsorbent will resulting adsorption-photocatalytic property. Synthesis of TiO_2-Zeolite composite has been performed with a ratio 40:60 ($\%\,{}^{w}/_{w}$). Initial concentration, variation of pH, condition and source of irradiation were studied. XRD and FTIR characterization results show that TiO_2 is successfully introduced into the zeolite. Optimum photocatalytic activity at dye concentration of 100 ppm with pH 4, UV light irradiation 11 watt and 17 cm penetration distance, resulted percentage degradation were 32,2% and 54,7% for methylene orange and procion blue respectively. Based on the calculation, the dissolved CO_2 concentration resulting from the photocatalytic process of methylene orange is 0,589 ppm and procion blue is 0,687 ppm.

1. Introduction

Dye wastes represent one of the most problematic groups of pollutants because they can be easily identified by the human eye and are not easily biodegradable [1]. Methylene orange and procion blue are one of organic dye that are non biodegradable. These dyes contain benzene groups that are very difficult to degrade, have carcinogenic and mutagenic properties. The dyes potentially reduce the entry of sunlight, thus preventing photosynthesis. This will lead to a decrease in the quality of the waters. Therefore, it is necessary to reduce the concentration of the dyes, one of them by the adsorption-photocatalytic method.

Adsorption is an interaction between two phases that causes the accumulation of particles on the surface of adsorbat [2]. While Photocatalysis is one of the advanced oxidation processes, is a new method used to mineralize dye compounds. One of the major advantages of the photocatalytic degradation over existing technologies is that there is no further requirement for secondary disposal methods [3]. Photocatalytic process will produce hydroxyl radicals (●OH) as oxidizing agents that strongly oxidize organic compounds [4].

Mineralization of organic compounds with formation of CO_2, H_2O and mineral acids, is not always easy to be achieved using only a photocatalysis process. In an adsorption–photocatalysis combined process, an appropriated adsorbent, *e.g.* silica, alumina, zeolites or activated carbon, will selectively adsorb the pollutant present in the wastewater, overcome this problem

Research on reducing dyes concentration using photocatalytic methods has been studied. Fajriati *et al*. (2014) resulted that optimum degradation of methylene orange with initial concentration of 20 ppm by TiO_2 was 90% [5]. Soni *et al*. (2015) showed that TiO_2 nanocatalyst was able to degrade 99,9% methylene orange with initial concentration of 40 ppm [6].

Hybrid processes (Integrated adsorption-photocatalytic method), which couple the adsorptive properties with the photocatalytic properties of TiO_2, offer the potential to significantly enhance the photodegradation of a range of hazardous organics in water by concentrating dyes at the TiO_2 surface.

In this research, removal of methylene orange and procion blue using adsorption-photocatalytic method (Natural zeolit of Cikembar Sukabumi as adsorben and TiO_2 as photocatalyst) with variation of UV irradiation condition.

2. Research Method

2.1 Tools and Materials

The tools used in this research were analytical balance, magnetic stirrer, furnace, photoreactor, UV lamp, oven, UV-Vis spectrophotometer LW-200 Series, X-ray Diffractor (XRD) Shimadzu 7000, and FTIR Burker.

The materials used in this research were Titanium dioxide (TiO_2), natural zeolite of Cikembar Sukabumi, 96% p.a ethanol, HCl, aquadest, $Ba(OH)_2$, methylene orange (MO), and procion blue (PB).

2.2 Synthesis of TiO2-Zeolite

The TiO_2-Zeolite composite was synthesized with a ratio of TiO_2: Zeolite of 40:60 (% $^{w}/_{w}$) using 96% ethanol. The mixture was stirred for 5 hours, then dried at 120°C for 5 hours. TiO_2-Zeolite was calcined at 500ºC for 5 hours. The characterization of TiO_2-Zeolite was performed using XRD and FTIR [7].

2.3 Photocatalytic Activity Test of TiO2 to Dyes

2.3.1 Optimation of Dyes Concentration

The TiO_2-Zeolite composite was added each dye (MO and PB) pH 7 with concentration of 150 ppm, 125 ppm, and 100 ppm. Then stirred and performed irradiation using ultraviolet (UV) power of 11 watts and penetration distance of 24 cm for 120 minutes. After the result was filtered, the obtained filtrate was then measured absorbance using a UV-Vis spectrophotometer at λ 480 nm (MO) and 580 nm (PB).

2.3.2 Optimation of Dyes pH

Composite TiO_2-Zeolite was added each dye (MO and PB) with pH variations 10, 7, and 4. Then radiation was done using 11 watt ultraviolet (UV) with penetration distance of 24 cm. After that filtered, then measured its absorbance using a UV-Vis spectrophotometer.

2.3.3 Optimation power and Radiation Distance

The TiO_2-Zeolite composite was added each dye (MO and PB), then irradiated using ultraviolet (UV) light in the reactor with a powerful variation of 13 watts, 11 watts, and 9 watts. After the best result obtained variations of irradiation distance 24 cm, 17 cm, and 10 cm. Then the result was filtered, the obtained filtrate was measured absorbance using UV-Vis spectrophotometer.

2.3.4 Effect of Irradiation Sources

The TiO_2-Zeolite composite is added to each dye (MO and PB), then irradiated using ultraviolet (UV), visible, and no light (dark). After it was filtered, the obtained filtrate was measured in absorbance using a UV-Vis spectrophotometer.

2.4 Determination of Dissolved CO_2 Concentration Photocatalytic Results

The photocatalytic carbon dioxide is captured with an excess of $Ba(OH)_2$ solution. Excess $Ba(OH)_2$ is titrated with 0,1 M HCl solution using phenolptalein indicator to obtain the end point of the titration (pink becomes colorless) [8].

3. Results and Discussion

3.1 Synthesis of TiO_2-Zeolite Composites (TZ) and their Characterization

The TiO_2-Zeolite composite was synthesized with a ratio of TiO_2: Zeolite of 40: 60 (% $^{w}/_{w}$) using 96% ethanol solvent. Subsequently the composites were characterized using XRD and FTIR. The XRD results in the diftractogram form are shown in Figure 1.

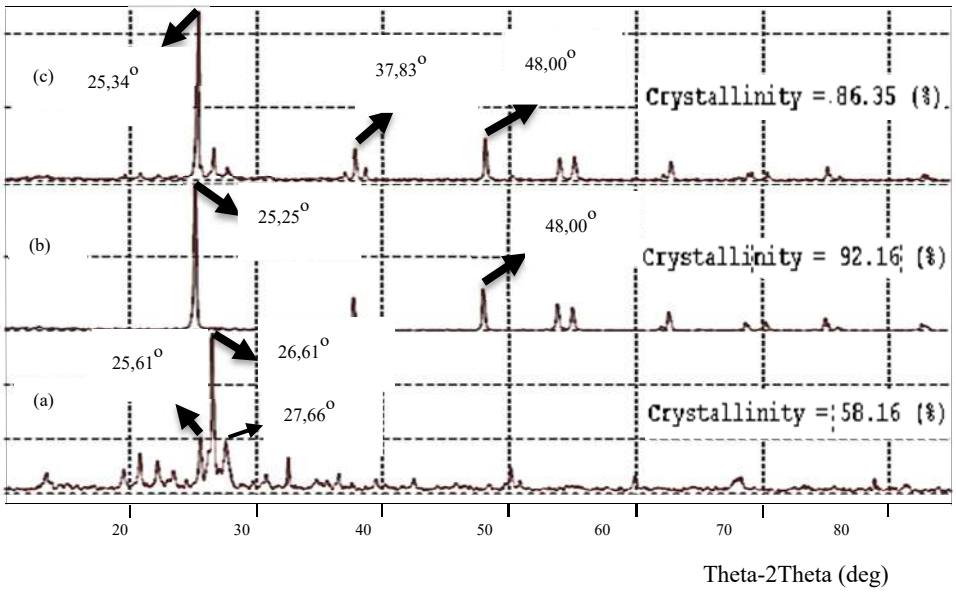

Figure 1. Difftractogram of (a) activated zeolite, (b) TiO_2, (c) T:Z (40:60)

The result of difractogram shows that TiO_2 used is anatase type, it is seen in area of 2θ = 25,25° and 48,00° according to anatase standard no 21-1272 [9]. While in Sukabumi's zeolite give some peak at 2θ = 25,61°; 26,61°; and 27,66° were identified as zeolite type mordenite no 06-0239 [10]. In the diffraction pattern it is seen that the crystallinity of TiO_2-Zeolite is 86.35%, indicating TiO_2 has been dispersed into the pores of zeolite. The result of FTIR analysis of TiO_2-Zeolite composite in the form of spectrum is shown in Figure 2.

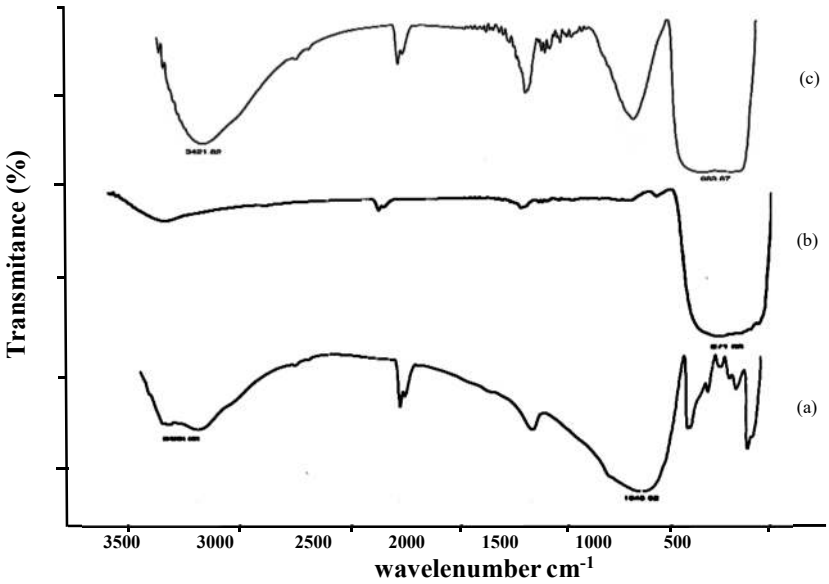

Figure 2. Spectrum (a) activated zeolite, (b) TiO_2, (c) T:Z (40:60)

In activated natural zeolites, the absorption of functional groups is present in the 3436,6 cm^{-1} wave number indicating the presence of a stretch OH group. The absorption at wave number 1043,8 cm^{-1} shows the bonding characteristics of O-Si-O/O-Al-O. In fig 3 (b) shows the typical uptake of Ti-0_2 by wave number 671 cm^{-1}. While on TiO_2-Zeolite, there is greater vibration in wave number 3421,8 cm^{-1} and 683,27 cm^{-1} showing TiO_2 has been successfully composed into Zeolite

3.2 Photocatalytic Activity Test of TiO_2 to Dyes

3.2.1 Effect of Dyes Concentration

This condition is carried out at pH 7, lamp power 11 watts and penetration distance of 24 cm. The results of the effect of concentration on dyes are given in Table 1.

Table 1. the optimation of concentration on dye degradation

Concentration (ppm)	Degradation (%)	
	Methylene Orange	Procion Blue
100	8,176	11,609
125	6,042	8,992
150	4,422	7,169

From table 1 the optimum result at a concentration of 100 ppm. The degradation value of the dyes will decrease as the dyes concentration increases. This is due to the high concentration of dye will inhibit the absorption of UV rays by photocatalyst. In addition, high dye concentrations lead to greater interaction between dye molecules, thus decreasing photocatalytic activity [11]

3.2.2 Effect of pH to dyes

The methylene orange and procion blue dyes are anionic dye (negatively charged), along with the chemical structure of the two dyes (Figure 4) and the optimum result of pH to dye degradation are given in Table 2.

Table 2. The Optimation of pH to dye degradation

pH	Degradation (%)	
	Methylene Orange	Procion Blue
4	15,463	47,645
7	3,037	13,72
10	0	0

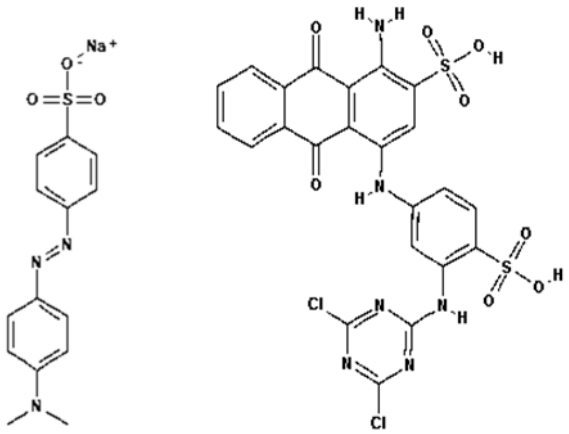

Figure 3. methyleneorange and procion blue dye

In solution, TiO_2 is amphoteric, positively charged in acidic condition and negatively charged in an alkaline condition. According to the reaction [12]:

$$>TiOH_2^+ \rightleftharpoons >TiOH + H^+ \quad pKa_1 = 4,5 \text{ and } >TiOH \rightleftharpoons >TiO^- + H^+ \quad pKa_2 = 8$$

From table 2 the optimum degradation of dyes at pH 4. This is due to the electrostatic interaction between TiO_2 with the dye making it easier for TiO_2 to degrade the compound.

At pH 10 obtained the value of zero degradation, caused by the negative charge of dye molecules refuse to reject with TiO_2 surface so that no degradation process occurs. In addition to the basic atmosphere of low Si/Al ratio, the zeolite surface becomes more negative, due to the formation of AlO^{4-} [13]. The negative charge of the zeolite will refuse with the dye molecule which is also negatively charged, so the adsorption process does not occur.

3.2.3 Effect of Power and Radiation Distance

This condition is carried out at concentration of dye 100 ppm, pH 4, and penetration distance of 24 cm. The results of the strong irradiation effect are given in Table 3, and the result of variation of radiation distance to dye degradation is given in Table 4.

Table 3. Optimation strong of irradiation for dyes degradation

Power (watt)	Degradation (%)	
	Methylene Orange	Procion Blue
9	15,221	29,901
11	18,929	34,391
13	11,159	17,853

Table 4. Optimation of radiation distance to dye degradation

Distance (cm)	Degradation (%)	
	Methylene Orange	Procion Blue
10	16,147	49,835
17	32,243	50,602
24	12,908	48,288

From table 3 the optimum result on the strong 11-watt irradiation. It can be explained that at 9 watt lamp power produces wavelength of about 400 nm, 11 watts about 380 nm and 13 watt about 360 nm. So that the most effective 11 watt lamp power degrades the dye as it approaches the wavelength of TiO_2 at 387 nm [14]

Variations in radiation distance were performed to determine the effect of UV light penetration on the TiO_2 photocatalyst in generating ●OH. From table 4 the optimum result are known at a distance of 17 cm. So it can be said that the variation of distance can affect the UV rays received by the photocatalyst.

3.2.4 Effect of Irradiation Sources

This condition is carried out at a concentration of dye 100 ppm, pH 4, with a lamp power of 11 watts and a penetration distance of 17 cm. The results of the effects of irradiation sources on the degradation of dyes are given in Table 5.

Table 5. Optimation the source of irradiation to dyes degradation

Irradiation Sources	Degradation (%)	
	Methylene Orange	Procion Blue
Visible	7,559	99,672
UV	32,243	54,764

From table 5 the procion blue optimum result were obtained at visible light sources. This is because the molecular structure of procion blue has more chromophores than methylene orange, so the procion blue dye absorbs more visible light. Therefore, methylene orange degradation values become larger in UV rays because photocatalysts produce more ●OH [15]. In dark (no ray), no tension is generated ●OH so that the degradation value is obtained from the adsorption process only.

3.3 Dissolved CO_2 Concentrate Photocatalytic

Based on the calculation, the dissolved CO_2 concentration resulting from the photocatalytic process of methylene orange is 0,589 ppm and procion blue is 0,687 ppm

4. Conclusion

Photocatalysts of TiO_2-Zeolite were synthesized by a ratio of 40:60 (% w/w). XRD results showed that TiO_2 was successfully introduced into the zeolite surface resulting in a degree of crystallinity of 86,35%. On the FT-IR spectrum showed a greater vibration in the uptake of 3421,8 cm^{-1} and 683,27 cm^{-1} which indicates that TiO_2 was successfully composed in the zeolite pore resulting in photocatalytic adsorption properties. Photocatalytic activity test was done on methylene orange and procion blue dyes to obtain optimum condition at 100 ppm and pH 4. Methylene orange and procion blue dyes gave optimum degradation results on UV light with 11 watt lamp and 17 cm, respectively 32,2% and 54,7%. These results explain that the photocatalytic process is less effective at high concentrations.

Acknowledgments

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5. References

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