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# Simultaneously photocatalysis of rhodamine-B and Cr(VI) by activated natural zeolite-$TiO_2$/ZnO under visible light irradiation

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## Abstract

Photocatalysis of the mixture of rhodamine-B and Cr (VI) by activated natural zeolite (ZA) loaded $TiO_2$ and ZnO semiconductor materials has been carried out. This study aims to determine the ability of ZA-$TiO_2$/ZnO photocatalyst in degradation of rhodamine-B and reduction of Cr (VI) simultaneously under the visible light irradiation. The photocatalyst is synthesized using the ceramic method. The photocatalyst is analyzed to determine the success of the synthesis process, namely functional groups analyzed by infrared spectrophotometer (FTIR) and surface acidity by acid-alkalimetry titration method. The analysis result of the functional groups of ZA-$TiO_2$/ZnO photocatalyst showed that the specific peaks of Ti-O appeared at wavenumbers of 2368.69 $cm^{-1}$ and 678.11 $cm^{-1}$ as well as the peaks of Zn-O appeared at 884.4 $cm^{-1}$, 501.01 $cm^{-1}$ and 438.46 $cm^{-1}$. The peaks of O-Si-O and O-Al-O bonds in the aluminosilicate of zeolite framework were appeared at 788.91 $cm^{-1}$ and 1055.1 $cm^{-1}$. In addition, the active sites tend to be acidic with the number of active sites was 16.9515 x $10^{20}$ sites/g. The photocatalytic process showed that the highest value of degradation of rhodamine-B and reduction of Cr (VI) simultaneously at pH 3, with an irradiation time of 10 minutes and a photocatalyst mass of 300 mg, which reached 99.91% and 99.92%, respectively. The photocatalyst activity of ZA-$TiO_2$/ZnO for rhodamine-B degradation and Cr (VI) reduction simultaneously under the visible light irradiation, so that it is important considered.

**Keywords:** cr(vi), photocatalyst, rhodamine-b, activated natural zeolite-$tio_2$/zno

## Introduction

Rhodamine-B has an amino group and a benzene well known as a basic dye which difficult to decompose naturally (Setiyanto *et al*., 2015) [18]. This condition will affect the pH and oxygen availability in water, so that the activity of biota decreases and even becomes toxic at certain levels. According to WHO, chlorine in rhodamine-B makes it react to bind to compounds in the body (protein, fat and DNA), trigger liver and kidney dysfunction, cancer even mutagen. This makes the presence of rhodamine-B in water, food and beverages strictly prohibited (Dewi *et al*., 2020) [4].

Chromium in wastewater is generally in the form of Cr (VI) which is classified as a highly carcinogenic and toxic inorganic heavy metal pollutant. The solubility and mobility of Cr (VI) are very high, making it toxic to the body and all organisms. Cr (VI) anions ($HCrO^{4-}$, $CrO_4^{2-}$ and $Cr_2O_7^{2-}$) are able to penetrate blood cell membranes, bind to globin and cause oxidation (Wahyuni *et al*., 2002) [22]. The Cr (VI) is also carcinogenic and causes skin and eye irritation, metabolic disorders due to stomach and intestinal irritation, and even death (Khairani *et al*., 2007) [8].

Based on the impact of the two compounds (rhodamine-B and Cr (VI)), the photocatalytic process using catalysts that are sensitive to light can be the right choice at this time. Photocatalysis is easier to apply, more economical than the activated sludge method, and more efficient than the adsorption method (Negara *et al*., 2018) [12]. Photocatalysis utilizes photon energy (light) and semiconductor material catalysts to decompose pollutant into simpler and safer compounds in the environment (Dewi *et al*., 2020) [4]. Photocatalysis enable degradation and reduction processes simultaneously, so that textile waste treatment becomes more effective. Titania ($TiO_2$) and zinc oxide (ZnO) semiconductor materials are widely used to produce high-performance photocatalysts, due to their narrow band gap (3.2 eV).

Natural zeolites can improve the performance of $TiO_2$ in photocatalytic process (with UV light) up to 9.4%, because the adsorption power increases and the possibility of the photocatalyst getting saturated is decreased, so that the lifetime becomes longer (Safni *et al*., 2019) [17]. Oktapiani *et al*., (2020) [14] stated that the addition of ZnO was able to improve the performance of the photocatalyst to degrade rhodamine-B (with visible light) up to 99.3%. A similar photocatalyst used by Negara *et al*., (2018) [12] is able to reduce Cr (VI) up to 94.73%. Meanwhile, Fang *et al*. (2019) [6] conducted research on photocatalysis Cr (VI) and rhodamine-B simultaneously using hybrid $Al_4SiC_4$/rGO catalysts, but were only able to reduce Cr (VI) by 96% and degrade rhodamine-B by 45%. The percentage of both is much lower compared to a single compound photocatalyst.

The objective of this study is to examine the ability of activated zeolite-$TiO_2$/ZnO to degrade dyes and to reduce heavy metal. The material is utilized as a photocatalyst in degradation of rhodamine-B and reduction of Cr (VI) simultaneously under the visible light.

## Materials and Methods

### Materials

Natural zeolite, $TiO_2$, ZnO, rhodamine-B, $K_2Cr_2O_7$, diphenylcarbazide (DPC), distilled water, ethanol, HCl, BaCl, NaOH, $H_2SO_4$, BaCl, penolpthalein, pH indicator and filter paper.

## Methods

### Preparation of activated natural zeolite (ZA)

100 g of natural zeolite (100 mesh), washed with distilled water and dried at 110ºC. Added 1000 mL of $H_2SO_4$ 2M and stirred for 14-16 hours, then rinsed with distilled water until it sulfate ions-free (negative test with 0.1M $BaCl_2$ solution). Dried out the ZA at 120ºC, then grind and sieved it with a 100 mesh (Setiyawati *et al*., 2020) [19].

### Photocatalyst synthesis

5 mg of $TiO_2$ was added to 100 mg of ZA and stirred for 5 hours with 10 mL of a 96% ethanol (Fauzi *et al*., 2018; Oktapiani *et al*., 2020) [7, 14], decanted, heated at 120ºC for 5 hours and then sieved it again with a 100 mesh. Then calcined, the product at 500ºC for 5 hours (Setiyawati *et al*., 2020) [19], cooled to a room temperature, added 35 mg of ZnO (3:1) and stirred for 5 hours with 10 mL of 96% ethanol. Decanted and finally heated the mixture at 450ºC for 1.5 hours. For comparison and to get a further information, the synthesis products were analyzed for functional groups by FTIR and surface acidity and number of acid active sites by acid-alkalimetry titration method.

### Photocatalyst Mass Optimization

Added ZA/$TiO_2$-ZnO photocatalyst (100; 200; 300; 400 and 500 mg) into 5 pieces 100 mL Beaker glass, contained 25 mL of a mixture of 400 mg/L rhodamine-B dye solution and 400 mg/L Cr (VI) solution each (1:1). Put it into a pfotocatalytic reactor, stirred under the visible light irradiation (445 nm) for 2 hours, then centrifuged for 10 minutes (3500 rpm). To determine the concentration of the remaining solution, the filtrate was divided into two then measured by UV-Vis spectrophotometry at the maximum wavelength of rhodamine-B and Cr(VI).

Then substituted the absorbance into the linear regression equation of the calibration curve, so that the percentage of degradation (%D) and the percentage of reduction (%R) can be calculated using the following equation (Agusriyanti and Pedy, 2015; Oktapiani *et al*., 2020) [1, 14]:

$$\%D \text{ and } \%R = \frac{Co - Ct}{Co} \times 100\% \qquad (1)$$

Where, $C_o$ = initial concentration of rhodamine-B and Cr (VI) and $C_t$ = concentration of residual rhodamine-B and residual Cr (VI).The %D and %R was used to determine the optimum mass of ZA/$TiO_2$-ZnO photocatalyst in the photocatalytic process, y plotting the percentage and the photocatalyst mass into a curve.

### Irradiation time optimization

Added an optimum amount of mass of the ZA/$TiO_2$-ZnO photocatalyst into 8 pieces 100 mL Beaker glass, contained 25 mL of a mixture of rhodamine-B dye solution and Cr (VI) solution each (400 mg/L, 1:1). Stirred and irradiated under the visible light (445 nm) for a time variation of 2.5; 5; 10; 20; 30; 45; 60 and 90 minutes. Centrifuse for 10 minutes (3500 rpm), give the same treatment for the filtrate as the previous procedure, and determined the linear regression equation, calibration curve, %D and %R. Plotting the percentage and the irradiation time to get the optimum irradiation time.

### pH optimization

Added an optimum amount of mass of the ZA/$TiO_2$-ZnO photocatalyst into 7 pieces 100 mL Beaker glass. Added 25 mL of a mixture of rhodamine-B dye solution and Cr(VI) solution (400 mg/L, 1:1) and 0,5M HCl each glass, adjust to pH 1; 2; 3; 4; 5; 6 and 7. Stirred and irradiated under the visible light (445 nm) for an optimum irradiation time. Centrifuse for 10 minutes (3500 rpm), given the same treatment for the filtrate as the previous procedure, and determined the linear regression equation, calibration curve, %D and %R. Plotting the percentage and the pH to get the optimum pH of the solution mixture.

### Photocatalyst activity

Added an optimum amount of mass of the ZA/$TiO_2$-ZnO photocatalyst into 6 pieces 100 mL Beaker glass. Added 25 mL of a mixture of rhodamine-B dye solution and Cr(VI) solution (400 mg/L, 1:1) at optimum pH. Three Beakers glass were stirred under the visible light irradiation (445 nm) for an optimum irradiation time. The other three Beakers glass are wrapped in black plastic and stirred for an optimum irradiation time without the irradiation process. Given the same treatment for the filtrate as the previous procedure, and determined the linear regression equation, calibration curve, %D and %R.

## Results and Discussions

### Characteristis of photocatalyst

The FTIR analysis identified compounds into spectra certain peaks at specific wavenumbers ($cm^{-1}$), as shown in Figure 1.

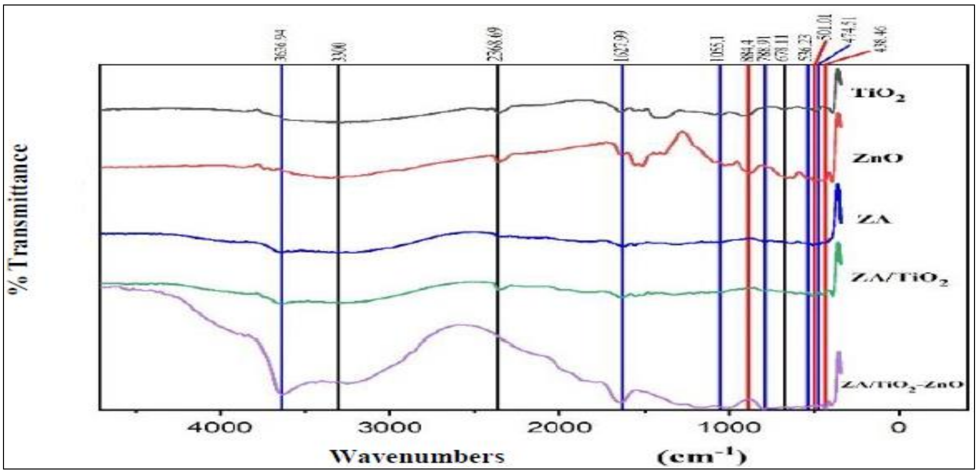

**Fig 1:** Comparison of FTIR spectrum of $TiO_2$, ZnO, ZA, ZA-$TiO_2$ and ZA-$TiO_2$/ZnO

The $TiO_2$ compound spectra which are a specific peak of Ti-O were identified at 2368.69 $cm^{-1}$ and 678.11 $cm^{-1}$. Meanwhile, peaks around 3600 $cm^{-1}$ are -OH stretching (Setiyawati *et al.*, 2020) [19], wide bands around 3300 $cm^{-1}$ are H-O-H vibration (Ritonga, 2015) [16], and at the range of 1600-1650 $cm^{-1}$ is the region of the -OH bending vibration which is a functional group of the absorbed $H_2O$ on the zeolite and deformed (Dewi *et al.*, 2020) [4]. These statements indicate that the peaks at 3636.94 $cm^{-1}$, wide bands at 3300 $cm^{-1}$ and 1627.99 $cm^{-1}$ are specific peaks of the functional group of the water molecule.

The peaks of O-Si-O and O-Al-O bonds in the aluminosilicate of zeolite framework were appeared at 788.91 $cm^{-1}$ and 1055.1 $cm^{-1}$. This data was supported by Utubira *et al.* (2006) [21] which stated that the external symmetric and asymmetric strain absorption of O-Si-O or O-Al-O was around 700 $cm^{-1}$ and 1050 $cm^{-1}$. Around 500 $cm^{-1}$ is the region of the Si-O-Al bending, around 520 $cm^{-1}$ is very sensitive to Al in the octahedral layer (Komadel, 2003; Madejova, 2003) [9, 10], and at the range of 430-470 $cm^{-1}$ is the OT4 group bending. Based on these statements, it is known that the peaks 536.23 $cm^{-1}$ and 474.51 $cm^{-1}$ are the peaks of the Si-O-Al and $SiO_4/AlO_4$ groups.

The specific peak of O-Zn-O was detected at 884.4 $cm^{-1}$, which was also mentioned by Dony *et al.* (2003) [5] that the range 800-1200 $cm^{-1}$ is closely related to O-Zn-O vibrations. Anžlovar *et al.* (2012) [2] and Mahalaksmi *et al.* (2019) [11] state that at the range of 420-510 $cm^{-1}$ is specific to Zn-O stretching. Other sources mention that Zn-O-Si bonds appeared in the range of 430-470 $cm^{-1}$. Then this can be concluded that the peak at 501.01 $cm^{-1}$ is the peak of Zn-O vibration and the peak at 438.46 $cm^{-1}$ could be the peak of Zn-O or Zn-O-Si.

The average surface acidity and the acid active sites on natural zeolite (Table 1), increased after activation which indicates successful activation, so that the impurities in the zeolite pores were reduced (Na, Ca and K) through the substitution with $H^+$ ions. Substitution with $H^+$ also increases the Bronsted acid sites which makes it to be more acidic and binds the electropositive compounds strongly. Al dealuminated which forms the Lewis acid site $Al^{3+}$, also increases the surface acidity and the active sites (Widihati, 2008) [23].

**Table 1:** The Photocatalyst Surface Acidity and Acid Active Sites

| Samples | Surface acidity (mmol/g) | Number of Acid Active Sites (x $10^{20}$ sites/g) |
|---|---|---|
| Natural zeolite | 1.4170 | 8.5303 |
| ZA | 1.6761 | 10.0898 |
| ZA-$TiO_2$ | 2.1423 | 12.8969 |
| ZA-$TiO_2$/ZnO | 2.8159 | 16.9515 |

After $TiO_2$ and ZnO were added into ZA, the surface acidity and the active sites are also increasing, reaching 2.8159 and 16.9515 x $10^{20}$. The increase occurred because of the loaded $TiO_2$ and ZnO, which are amphoteric in nature tend to be acidic when it's interacting to an acidic material. The presence of this acid active site, affects the kinetics of the reaction forming of the most important parts in the photocatalytic process, which is the formed of hydroxyl radicals (•OH) and superoxide radicals (•$O_2$) (Dewi *et al.*, 2020) [4]. Due to the importance of the presence of an acidic active site, ZA-$TiO_2$/ZnO photocatalyst with the high acid active sites was selected for the next process.

## Photocatalytic Activity

### Photocatalyst mass optimization

The lowest photocatalyst mass required to obtain the highest rhodamine-B degradation and Cr (VI) reduction percentage, is referred as the optimum mass. Figure 2 shows the mass of 300 mg photocatalyst as the mass optimum.

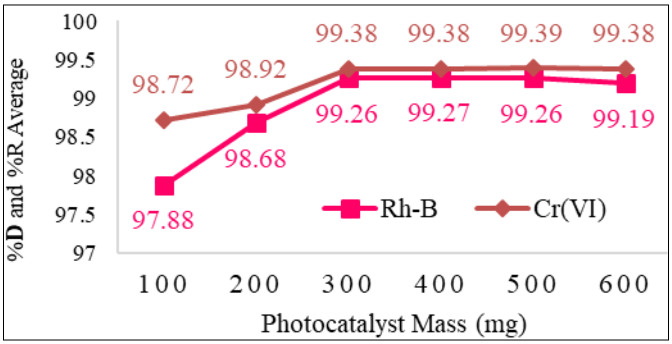

**Fig 2:** Relation Curve of Photocatalyst Mass with %D and % R Average

Compared to the 100 and 200 mg photocatalyst mass, at a mass of 300 mg photocatalyst showed an increase performance in photocatalytic process. It is happening because the mass of the photocatalyst affects the number of active sites, which was the initial trigger for the formation of OH and $O_2$ which play an active role in photocatalytic process (Setiyawati *et al.*, 2020) [19]. However, too much mass of photocatalyst are actually increasing the potential for suspension due to the formation of bulk, so that the irradiation is not optimal, as happened with a mass of 600 mg photocatalyst (Riskiani *et al.*, 2019; Setiyawati *et al.*, 2020) [15, 19]. Based on this explanation, 300 mg of photocatalyst was chosen as the optimum mass.

### Irradiation time optimization

The optimum irradiation time is the highest photocatalytic percentage in a shorter time, which the results are shown in Figure 3.

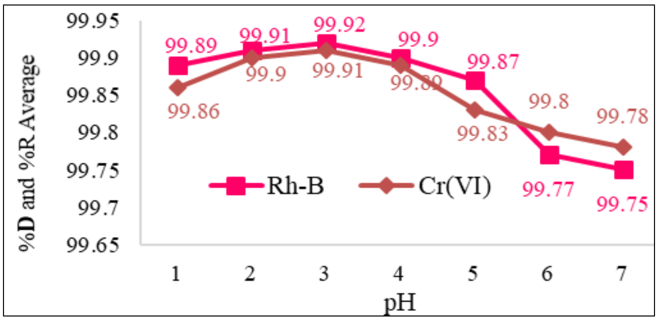

**Fig 3:** Relation Curve of Irradiation Time with %D and %R Average

The percentage at 2.5 minutes experiment is relatively low. The short irradiation time minimizes the contact between the solution mixture and the photocatalyst. It will reduce the amount of •OH and •$O_2$ that formed, which is described by the following equation (Arfan *et al.*, 2009) [3]:

$TiO_2 + hv \rightarrow TiO_2\ (e^- + h^+)$

$TiO_2\ (e^-) + O_2 \rightarrow \bullet O_2$

$TiO_2\ (h^+) + H_2O \rightarrow OH^- + H^+$

$TiO_2\ (h^+) + OH^- \rightarrow \bullet OH$

$\bullet OH + \text{dye} \rightarrow \text{dye oxidation}$

$\bullet O_2 + Cr^{6+} \rightarrow 2Cr^{3+}$

Sibarani *et al.*, (2016) [20] describes the reaction of ZnO under irradiation through the following equation:
$ZnO + hv \rightarrow ZnO\ (e_{cb}^{-} + h_{vb}^{+})$
$h_{vb}^{+} + H_2O \rightarrow H^{+} + OH^{-}$
$h_{vb}^{+} + OH^{-} \rightarrow \bullet OH$
$\bullet OH + Rh\text{-}B \rightarrow CO_2 + H_2O + \text{other compounds}$
If the irradiation time isn't enough, this reaction can't be started.

The photocatalyst performance started to be constant from the time of 10 minutes (99.62% and 99.70%), which was the minimum time required for a 300 mg photocatalyst to formed •OH and •$O_2$. Photocatalytic process decrease that occurs at the 90 minutes experiment, was because of the active site deactivation makes the photocatalyst to be saturated and the photocatalytic rate is slower. Based on these results, 10 minutes was chosen as the optimum irradiation time (Oktapiani *et al.*, 2020) [14].

**pH optimization**

Photocatalysts are also affected by pH, so does rhodamine-B and Cr (VI) which are degraded and reduced optimally at acidic pH (Negara *et al.*, 2018; Fauzi *et al.*, 2019; Oktapiani *et al.*, 2020) [7, 12, 14]. Based on these sources, the pH optimization test was carried out at an acidic pH, which is shown in the Figure 4 that the pH 3 as the optimum pH (99.91% and 99.92%).

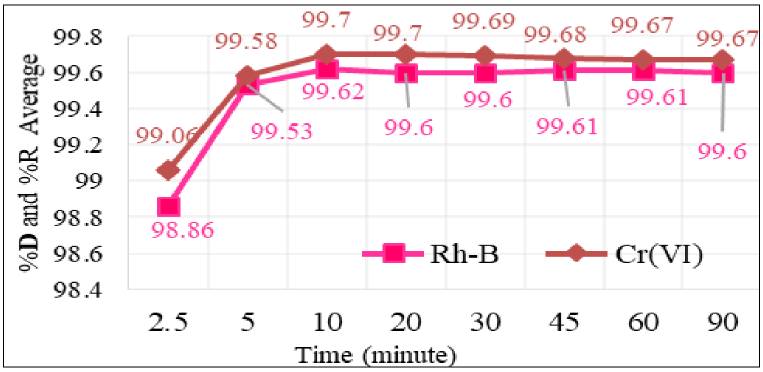

**Fig 4:** Relation Curve of pHwith %D and % R Average

Rhodamine-B is easily soluble in water, in acidic conditions tends to be negatively charged, which facilitating the electrostatic interaction of rhodamine-B with the positively charged surfaces of $TiO_2$ and ZnO (Nurmasari *et al.*, 2014; Sibarani *et al.*, 2016) [13, 20]. At pH < 1, Cr (VI) tends to form into $CrO_4^{2-}$, at pH 2-6 formed $Cr_2O_7^{2-}$ and $HCrO_4^{-}$ which are in equilibrium and easily reduced, above pH 6 $CrO_4^{2-}$ are formed which are less oxidizing. The ionization is described by the following reaction equation (Wahyuni *et al.*, 2002) [22]:
$H_2CrO_4 \leftrightarrow HCrO_4^{-} + H^{+}$
$HCrO_4\text{-} \leftrightarrow CrO_4^{2-} + 2\ H^{+}$
$Cr_2O_7^{2-} + H_2O \leftrightarrow 2HCrO_4^{-}$

Under alkaline conditions, the following hydrolysis occurs:
$Cr_2O_7^{-} + OH^{-} \leftrightarrow HCrO_4^{-} + CrO_4^{2-}$
$HCrO_4^{-} + OH^{-} \leftrightarrow CrO_4^{2-} + H_2O$
This statement explains the high percentage of photoreduction at acidic pH.

**Photocatalyst activity at optimum conditions with and without irradiation**

The contact activity test at the optimum conditions, to catalyze 25 mL of a mixture of rhodamine-B (Rh-B) and Cr (VI) solution was carried out in the two different conditions. The first one was contact activity with HPL 30W ($\lambda$ = 445 nm, I = 14,28 mW/cm$^2$) irradiation and the other one was contact activity without irradiation. Figure 5 shows that the contact activity test for Rh-B and Cr (VI) with irradiation values of 99.91% and 99.92%, while without irradiation the values are 94.81% and 97.92%, respectively.

As previously explained, photocatalytic process utilized for photon energy in light irradiation to degrade and reduce any compound. The presence of acid active side helped electrons and holes excited, and interacted with $H_2O$ molecule will be optimal, so that •OH and •$O_2$ can be formed and the photocatalytic process takes place. This statement explained the low percentage of the contact activity without irradiation. The absence of such irradiation automatically negating the contact that might be happen between the semiconductor materials and the photon energy, so that the next processes are all canceled. Although the photocatalytic process doesn't occur, the percentage is quite high due to the adsorption process which keeps going even without irradiation.

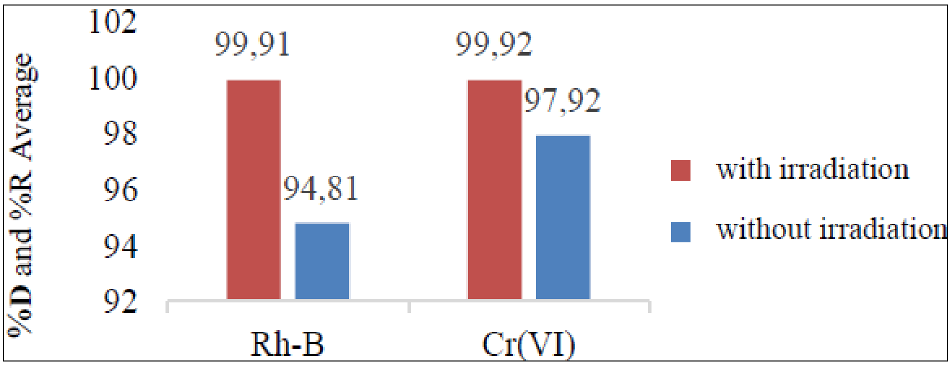

**Fig 5:** Photocatalytic Percentage at Optimum Condition

## Conclusion

Based on these results and disccusions, it was concluded that the optimum condition for ZA-$TiO_2$/ZnO photocatalyst to photocatalysis 25 mL of a mixture of rhodamine-B and Cr (VI) simultaneously was 300 mg, with an optimum irradiation time of 10 minutes at pH 3. %D rhodamine-B and %R Cr (VI) simultaneously under visible light irradiation at optimum conditions were 99.91% and 99.92%, respectively.

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