Photocatalytic Degradation of Remazol Brilliant Blue R and Remazol Yellow FG using TiO₂ doped Cd, Co, Mn

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Abstract

TiO₂ and TiO₂ doped Cd, Co, Mn (TiO₂-M) were synthesized with a sol-gel method, and the photocatalytic activity of Remazol Brilliant Blue R and Remazol Yellow FG has been conducted. TiO₂-M (Cd, Co, Mn) was synthesized with the mol Ti:M ratio of 3:1, and the materials were calcined at 300, 400, and 500 °C. The materials were characterized by X-ray Diffraction (XRD), Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX), and UV-Vis Reflectance. The XRD result shows that at the temperature of 300 °C TiO₂ and TiO₂-M formed tend to be amorphous. At 400 °C the anatase phase is formed, while at 500 °C the rutile phase begins to form. And overall, the crystallinity of TiO₂ is higher than metal-doped TiO₂. The UV-Vis Reflectance result showed that the bandgap energy of all doping materials (TiO₂-M) decreased. The larger the metal ion radius of dopant, the larger the crystal size obtained and then the higher the bandgap obtained. The results of SEM-EDX showed that the morphology of TiO₂ was spherical and regular, whereas the morphology of TiO₂-M had a smoother surface due to the influence of metal doping. Photocatalytic activity of TiO₂-M on Remazol Brilliant Blue R and Remazol Yellow FG was greater than TiO₂. The optimum pH of the solution was obtained at pH 5 and the optimum catalyst phase was obtained at the anatase phase. The percentages degradation for 30 min of Remazol Brilliant Blue R were 67.34% (TiO₂), 92.12% (TiO₂-Co), 85.47% (TiO₂-Mn), and 83.91% (TiO₂-Cd), while for Remazol Yellow FG they were 58.84% (TiO₂), 74.61% (TiO₂-Co), 67.93% (TiO₂-Mn) and 64.19% (TiO₂-Cd), respectively.

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Keywords: Degradation; Remazol Brilliant Blue R; Remazol Yellow FG; TiO₂; TiO₂-M (Cd, Co, Mn)

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1. Introduction

The textile industry is one of the biggest sources of water pollution, with a large amount of dye waste [1]. The negative impacts of textile production are primarily derived from the dyeing process resulting in dye wastewater, which has a chromophore groups [2]. Dye waste disposed by the textile industry is a pollutant that may contaminate the environment. The waste is extremely harmful to the environment, especially the river ecosystem in Indonesia. They are stable, difficult to degrade, toxic, mutagenic, and carcinogenic [3,4]. Some of the dyes frequently applied in the textile industry are anionic dyes of Remazol Brilliant Blue R and Remazol Yellow FG. The two dyes provide bright colors on textile but due to the complex structure, reactive, and difficult to be biologically degraded. Dye

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waste has to be managed to prevent environmental pollution. To date, such a method of dye waste management as photodegradation has been developed. Photodegradation utilizes photocatalyst and ultraviolet rays whose energy is equivalent to or higher than the energy of the photocatalyst bandgap [5]. Some of the textile industry wastewater treatment that continuously developed to minimize waste pollution is photocatalyst and photoelectrocatalyst [6, 7]. Several photocatalysts have been used to degrade Remazol Brilliant Blue R and Remazol Yellow FG. However, the degradation process often takes much time and a large amount of light energy, such as UV lamps, making it less effective and efficient. Photocatalytic degradation of Remazol Brilliant Blue R under ultraviolet irradiation (UV light) was examined and ~80% degradation was achieved but in 120 min (2 h) by using Nanostructured biophotocatalyst hydroxyapatite (HAp) [8]. Cd-doped TiO₂ photocatalyst did not only achieve discoloration of Remazol Brilliant Blue R but also removed 70% of organic carbon but in 6.5 hour [9]. The nickel-based catalyst (EGNiO₃₀₀₀) shows excellent photoactivity which degraded around 90.0% of Remazol Brilliant Blue R but in 1.5 hour using florescent lamp [10]. Catalyst of Fe₂O₃ intercalated bentonite has degraded remazol brilliant blue 98.02% but in 2 hours using UV light [11]. The iron oxide nanoparticle that was synthesized from leaf extract of Carica papaya plant showed efficient degradation ability against remazol yellow RR dye in the presence of sunlight about 77% but in 6 hours [12]. Removal of Remazol Yellow using Sn/SBA-15 catalyst was 58.2% [13]. The degradation of Remazol Yellow was reached 96% within 1 h using catalyst Polyaniline (PANI)-doped tin oxide-diatomite and UV lamp [14].

And today, TiO₂ is one of the most prospective catalyst with such advantages as long-term stability, easy to modify, cost-effectiveness, and non-toxicity [15]. However, the success of TiO₂ is still traded off by the large energy of the band gap (3.2 eV) and rapid recombination valence of electron-hole that decreases the photocatalytic activity [16]. Therefore, modification is needed to improve the photocatalytic activity of TiO₂. The limitation of TiO₂ can be improved by developing a TiO₂ composite with other semiconductor materials so it can absorb the visible light and avoid recombination [17,18]. Modification with transitional metal doping can decrease the energy of the band gap and reduce the process of electron-hole recombination so that the process of catalytic reaction at the TiO₂ surface can last longer [19]. Some applicable transitional metals include Cd, Co, and Mn.

The addition of metal ions to the TiO₂ crystal lattice results in changes in the crystal structure, crystal size and electronic properties of TiO₂. The addition of metal ions can reduce the crystallinity of TiO₂ because of the difference in radii and charge between metal ions and Ti⁴⁺ ions. Metal ions can inhibit crystal growth, causing the crystal size to become smaller. The addition of metal ions is also possible to reduce the band gap energy of TiO₂ which has an impact on increasing light absorption into the visible region [19]. It is possible for metal ions to enter the crystal lattice and substitute for Ti⁴⁺ ions which causes the formation of new energy levels so that it has an impact on decreasing the width of the band gap. The decrease in the band gap width will cause the photon energy used for electron excitation to be lower so that the band gap energy decreases. In addition, the addition of metal ions to TiO₂ acts as an electron trapper that can prevent electron-hole recombination so that it can increase its photocatalytic activity [20]. The addition of Co into TiO₂ causes a decrease in crystal size and a decrease in band gap energy thereby increasing its photocatalytic activity [21]. Changes in the crystal structure and electronic properties of TiO₂-M (M= Cd, Co, Mn) can be identified through characterization using XRD, SEM-EDX, and UV-Vis Reflectance spectrophotometer. And then, it’s photocatalytic activity can be studied further.

To date, there has been no application of TiO₂-M (Cd, Co, Mn) catalyst for the degradation of anionic dyestuffs such as Remazol Brilliant Blue R and Remazol Yellow FG. Therefore, there needs to be a study to see the ability of the catalytic activity of TiO₂-M (Cd, Co, and Mn) in degrading the anionic dyes Remazol Brilliant Blue R and Remazol Yellow FG.

2. Materials and Methods

2.1 Equipment and Materials

The equipment had been used in the research were glassware (Pyrex), X-Ray Diffraction Spectrophotometer (Bruker D8 Advance), Spectrophotometer UV-Vis (Perkin Elmer Lambda 25), Scanning Electron Microscopy-Energy Dispersive X-Ray (JOEL JED-2300). While the materials used were Titanium (IV) Isopropoksida (TTIP) (Merck), glacial acetate acid (Merck), CdSO₄·8H₂O (Merck), CoSO₄·7H₂O (Merck), MnSO₄·1H₂O (Merck), aquades, Remazol Brilliant Blue R and Remazol Yellow FG.
2.2 Synthesis of TiO₂

TTIP was hydrolyzed with glacial acetate acid solution (at 14 °C) with a ratio of 1:10 (v/v). The solution was stirred and heated at 90 °C. The formed gel was then heated in the oven at 150 °C for 24 hours and calcined at different temperatures of 300, 400, and 500 °C for 2 hours.

2.3 Synthesis of TiO₂-M (Cd, Co, Mn)

TTIP was hydrolyzed with glacial acetate acid solution (14 °C) with a ratio of 1:10 (v/v). The solution was stirred and heated at 90 °C. The formed gel was then added to CdSO₄, MnSO₄, and CoSO₄ that have been solved with gradual drops of aquadest with mol Ti:M (M=Cd, Co, Mn) ratio of 3:1. TiO₂-M gel was then heated at 150 °C for approximately 24 hours and calcined at different temperatures of 300, 400, and 500 °C for 2 hours.

2.4 Determination of Optimum pH for Solution

Some 0.1 gram of TiO₂ and TiO₂-M (T= 400 °C) was added to 10 mL solution of Remazol Brilliant Blue R and Remazol Yellow FG 10 ppm at different pH of 3, 5, 7, 9, and 11. The solution was stirred and raid with visible light for 30 minutes at the black box reactor. The solution was filtered with Whatmann 42 and tested with a UV-Vis spectrophotometer.

2.5 Determination of Optimum Catalyst Phase

Some 0.1 gram of TiO₂ and TiO₂-M at different temperatures of 300, 400, and 500 °C was added to 10 mL solution of Remazol Brilliant Blue R and Remazol Yellow FG 10 ppm at the optimum pH. The solution was stirred and raid with visible light for 30 minutes at the black box reactor. The solution was filtered with Whatmann 42 and tested with a UV-Vis spectrophotometer.

Figure 1. Patterns of XRD (a) TiO₂, (b) TiO₂-Cd, (c) TiO₂-Co, and (d) TiO₂-Mn at different calcination temperatures (300, 400, and 500 °C).
3. Results And Discussion

3.1 Characterization of XRD

The structure and size of the crystal obtained from the material can be identified through characterization with XRD. Calcination temperature and dopant will affect the formation of the crystal phase. The patterns of XRD TiO₂, TiO₂-Cd, TiO₂-Co, and TiO₂-Mn at different calcination temperatures of 300, 400, and 500 °C are shown in Figure 1.

TiO₂ and TiO₂-M diffractogram for different calcination temperatures resulted in different diffraction patterns. Diffraction patterns showed the transformation from amorphous to anatase and from anatase to rutile in line with the increase of calcination temperature. At the calcination temperature of 300 °C, the formed TiO₂ and TiO₂-M (Cd, Co, Mn) were more likely to be amorphous. At the calcination temperature of 400 °C, it was shown that in TiO₂, an anatase phase was formed. It was characterized by the appearance of a peak at 2θ = 25.4604°; 37.2899°; and 47.9482°. At TiO₂-Cd, the peak appeared at 2θ = 24.8747°; 37.5241°; and 47.9482°. At TiO₂-Co the peak appeared at 2θ = 25.2261°; 37.2899°; and 47.9482°, and at TiO₂-Mn the peak appeared at 2θ = 25.3432°; 38.2269°; and 47.9482°. The peaks resulted from the anatase in line with the ICSD Anatase No.9852. At calcination temperature of 500 °C, besides the formation of anatase phase, the rutile phase appeared as characterized by the appearance of a peak at TiO₂ at 2θ = 27.4765°; 36.9517°; and 41.2682°. At TiO₂-Cd the peak appeared at 2θ = 27.6739° and 36.8227°. At TiO₂-Co a peak appeared at 2θ = 27.258° and 36.3029°, and at TiO₂-Mn a peak appeared at 2θ = 27.362° and 36.1989°. The result of XRD showed that the calcination temperature of 400 °C was the optimum temperature in the formation of the anatase phase. Therefore, when calcination temperature is lower, the amorphous form is likely to be formed and when calcination temperature is higher, the anatase phase starts to be unstable and transformation to rutile phase occurs. Besides that, diffraction patterns of TiO₂ and TiO₂-M (Cd, Co, Mn) show higher calcination temperature leading to a higher and sharp peak, because higher calcination temperature affects the development of the formed crystal and affect the crystallinity of TiO₂ as reported by Behnazady et al. [22]. The resulting diffraction pattern matches the standard, but the peak pattern shows a slight shift due to the doping effect [23]. Crystallinity is also can be affected by radius of ion metal. Ions metal Ti²⁺; Co²⁺; Mn²⁺; and Cd²⁺ consecutively have a radius of 0.745 Å; 0.79 Å (ls) or 0.885 Å (hs); 0.81 Å (ls) or 0.97 Å (hs); and 1.09 Å. And overall, the crystallinity of TiO₂ is higher than metal-doped TiO₂. This is because the presence of metal dopant ions disrupts the formation of TiO₂ polymers and decrease crystal regularity or crystallinity of the catalyst. It can be seen from decreasing peak at 2θ = 25.4604° dan increasing amorphous at 2θ = 25.4604° until 37.8755°. The sizes of TiO₂ and TiO₂-M crystals can be identified through the calculation using Debye-Scherrer’s equation. The sizes of the resulted crystals are shown in Table 1.

Metal doping results in the decreased size of crystal because the addition of dopant has resulted in the inhibition of TiO₂ crystal growth [24]. With different temperatures of calcination, the size of the crystal increases along with the increase of calcination temperature. Higher calcination temperature results in the formation structure of Ti−O−Ti and O−Ti−O become longer. This results in a larger volume of crystal that results in a larger size of a crystal. Crystal size is also can be affected by radius of ion metal. Ions metal Co²⁺; Mn²⁺; and Cd²⁺ consecutively have a radius of 0.79 Å (ls) or 0.885 Å (hs); 0.81 Å (ls) or 0.97 Å (hs); and 1.09 Å. The larger the metal ion radius, the larger the crystal size obtained. If the radius of the doping ion increases, the crystal lattice changed. The modified lattice changes the volume of the crystal cell. The larger the radius of the doping ion, the wider the lattice spacing and causes 2θ to smaller. In overall, the crystal size of TiO₂ is larger than metal-doped TiO₂. This is because

| Material | Size of Crystal (nm) at 300 °C | Size of Crystal (nm) at 400 °C | Size of Crystal (nm) at 500 °C |
|----------|-----------------------------|-----------------------------|-----------------------------|
| TiO₂     | 7.155                       | 11.918                      | 12.891                      |
| TiO₂-Cd  | 5.590                       | 11.577                      | 11.639                      |
| TiO₂-Mn  | 5.312                       | 10.646                      | 10.930                      |
| TiO₂-Co  | 4.298                       | 6.221                       | 9.456                       |

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the presence of metal dopant ions disrupts the formation of TiO₂ polymers and causes the size of TiO₂ macromolecules to become smaller.

The mechanism of metal ion doping into TiO₂ crystals as shown in Figure 2. The metal ion doping mechanism can be through substitutional doping (a,b) and/or Interstitial doping (c).

3.2 Characterization of SEM-EDX

Results of SEM and EDX analysis are shown in Figure 3. Results of SEM analysis in Figure 3(a) show that TiO₂ has a homogenous and regular spherical structure. The result of SEM analysis of TiO₂-M (M=Cd, Co, Mn) is shown in Figure 3(b), (c), and (d). The result of SEM shows that morphologically, TiO₂-M (M=

![Figure 2. Mechanism of metal ion doping into TiO₂ crystals: (a), (b). substitutional doping [25], (c). Interstitial doping [26]. Blue color (M = Co, Mn, or Cd).](image)

![Figure 3. Morphology of (a) TiO₂ (b) TiO₂-Cd (c) TiO₂-Co (d) TiO₂-Mn.](image)
Cd, Co, Mn) has a smoother surface than the TiO$_2$, because the addition of metal ion to TiO$_2$ may cover some parts of the surface of TiO$_2$-M and make them smoother.

The result of EDX shows that the material of TiO$_2$ comprises Ti and O, while TiO$_2$-M (Cd, Co, Mn) comprises Ti, O, and metal dopant. This shows that the synthesis of TiO$_2$-M (Cd, Co, Mn) has been successfully carried out due to the existence of the Cd, Co, Mn in the material of TiO$_2$-M. The percentage of Cd; Co; and Mn in the material of TiO$_2$-M (Cd, Co, Mn) are 10.11%; 3.42%; and 4.71%, respectively.

### 3.3 Energy of Band Gap

The energy of the band gap ($E_g$) is required by an electron to experience an excitation from the valence band to the conduction band [27]. The energy of the band gap can be calculated with the Tauc Plot method by extrapolating the correlation graph between $h\nu$ as the abscissa of axis x and $(a\nu)^2$ as the ordinate of axis y. Tauc Plot graph for TiO$_2$ and TiO$_2$-M (M= Cd, Co, Mn) at the calcination temperature of 300, 400, and 500 °C is shown in Figure 4. Metal ion doping results in the decreased energy of the band gap. The scores of the energy of the band gap for TiO$_2$ and TiO$_2$-M at different calcination temperatures are shown in Table 2.

The radius of the metal ion affects the resulted energy of the band gap. The larger the metal ion radius of dopant, the larger the crystal size obtained and then the higher the bandgap obtained. Band gap energy of TiO$_2$-Co<TiO$_2$-Mn<TiO$_2$-Cd. Ion Ti$^{4+}$ has a radius of 0.745 Å, while ion Co$^{2+}$; Mn$^{2+}$; and Cd$^{2+}$ consecutively have a radius of 0.79 Å (ls) or 0.885 Å (hs); 0.81 Å (ls) or 0.97 Å (hs); and 1.09 Å. When the radius of metal dopant ion reaches a radius of ion Ti$^{4+}$, the formation of inter band gap level becomes much easier, so that it

![Figure 4. Tauc Plot Graph of TiO$_2$ and TiO$_2$-M (M=Cd, Co, Mn) (a) T = 300 °C, (b) 400 °C, (c) T = 500 °C](a)

![Figure 4. Tauc Plot Graph of TiO$_2$ and TiO$_2$-M (M=Cd, Co, Mn) (a) T = 300 °C, (b) 400 °C, (c) T = 500 °C](b)

![Figure 4. Tauc Plot Graph of TiO$_2$ and TiO$_2$-M (M=Cd, Co, Mn) (a) T = 300 °C, (b) 400 °C, (c) T = 500 °C](c)

#### Table 2. Scores of the energy of band gap for TiO$_2$ and TiO$_2$-M at the calcination temperature of 300, 400, and 500 °C.

| Sample     | Energy of band gap (eV) at |
|------------|---------------------------|
|            | T = 300 °C | T = 400 °C | T = 500 °C |
| TiO$_2$    | 3.48 eV | 3.28 eV | 3.39 eV |
| TiO$_2$-Cd | 3.31 eV | 3.18 eV | 3.26 eV |
| TiO$_2$-Mn | 3.30 eV | 3.10 eV | 3.23 eV |
| TiO$_2$-Co | 3.26 eV | 3.04 eV | 3.18 eV |
results in the decrease of band gap energy of the material as reported by Chen et al. [28].

The radius of metal ion Co$^{2+}$ is more close to the radius of ion Ti$^{4+}$, so that it results in the smallest bandgap energy. Calculination temperature also affects the magnitude of band gap energy. At the calcination temperature of 300 °C the band gap energy is largest because, at the temperature, an amorphous phase is likely to be formed. Amorphous TiO$_2$ does not have a regular valence band and conduction band. Therefore, the bandgap energy is large. Band gap energy at the calcination of 500 °C is higher than at 400 °C because at 500 °C, the rutile phase is formed and it results in irregularity of TiO$_2$ or non-uniform TiO$_2$. In addition, the greater the calcination temperature, the size of the catalyst crystals formed is larger so that the band gap becomes larger.

### 3.4 Determination of Optimum pH of a Solution

According to Goswami et al. [21], photocatalytic degradation is divided into two stages, namely adsorption and degradation. In the initial stage, TiO$_2$ absorbs dye molecules and in the second stage the dye decomposes after irradiation. The photocatalytic reaction of TiO$_2$ consists of photoreduction and photooxidation reactions initiated by the adsorption of the substrate on the surface. The degradation mechanism of Remazol Brilliant Blue R and Remazol Yellow FG using TiO$_2$–M (Co, Cd, Mn) is written as follows:

\[
\begin{align*}
\text{TiO}_2\text{–M} + h\nu & \rightarrow e^-\text{CB} + h^+\text{VB} \\
\text{O}_2^- + e^- & \rightarrow \text{O}_2^{2-} \\
\text{O}_2^{2-} + \text{H}^+ & \rightarrow \text{HO}_2^- \\
2\text{HO}_2^- & \rightarrow \text{O}_2 + \text{H}_2\text{O}_2
\end{align*}
\]

If TiO$_2$ is given the appropriate energy there will be an excitation of electrons from the valence band (VB) to the empty conduction band (CB) and leaves a hole ($h^+$) in the valence band as a positive charge. Electrons react with O$_2$ to form superoxide radicals ($\cdot$O$_2^{2-}$) and the holes formed react with H$_2$O in solution to form hydroxyl radicals ($\cdot$OH). Hydroxyl radicals and superoxide radicals continue to be formed during the irradiation process and degrade the dye into simpler components.

Different pH in solutions can affect the charge of TiO$_2$ surface and affect the structure of dyes that have impacts on the process of photodegradation. At the acid pH, surface TiO$_2$ have a positive charge, while at alkaline pH, it have a negative charge. Anionic dyes of Remazol Brilliant Blue R and Remazol Yellow FG in acid condition have a strong anionic character. Therefore, the two dyes experience a stronger degradation.

\[
\begin{align*}
e^- + \text{H}_2\text{O}_2 & \rightarrow \text{OH}^- + \cdot\text{OH} \\
\text{OH}^- + \text{H}^+ & \rightarrow \cdot\text{OH} \\
\text{h}^+ + \text{H}_2\text{O} & \rightarrow \text{H}^+ + \cdot\text{OH}
\end{align*}
\]

\[
\begin{align*}
\text{Remazol Brilliant Blue R} + \cdot\text{OH} & \rightarrow \text{smaller degradation product} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{SOx} + \text{NOx} \\
\text{Remazol Yellow FG} + \cdot\text{OH} & \rightarrow \text{smaller degradation product} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{SOx} + \text{NOx} \\
\text{Remazol Brilliant Blue R} + \cdot\text{O}_2^{2-} & \rightarrow \text{smaller degradation product} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{SOx} + \text{NOx} \\
\text{Remazol Yellow FG} + \cdot\text{O}_2^{2-} & \rightarrow \text{smaller degradation product} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{SOx} + \text{NOx}
\end{align*}
\]

Figure 5. Degradation Percentage for (a) Remazol Brilliant Blue R (b) Remazol Yellow FG using TiO$_2$, TiO$_2$–Co, TiO$_2$–Mn, and TiO$_2$–Cd at different pHs.
electrostatic interaction at acid pH due to the different charges between the dyes and the surface.

Based on the result of the analysis in Figure 5, it is known that the optimum pH of both dyes is obtained at pH 5. This shows that Remazol Brilliant Blue R and Remazol Yellow FG have effective degradation at the acid pH and decreases along with the increase of pH. At acid pH, the hydroxyl radical resulting from the photocatalyst system becomes even higher.

In acidic conditions there is an increase in H\(^+\) ions in the solution. At acidic pH the hydroxyl radicals produced by the photocatalyst system increase with the following equation:

\[
e^- + O_2 \rightarrow \cdot O_2^- \quad (12)
\]

\[
\cdot O_2^- + H^+ \rightarrow HO_2^- \quad (13)
\]

\[
2HO_2^- \rightarrow O_2 + H_2O_2 \quad (14)
\]

\[
e^- + H_2O_2 \rightarrow OH^- + \cdot OH \quad (15)
\]

\[
h^+ + OH^- \rightarrow \cdot OH \quad (16)
\]

As reported by Sibarani et al. [29], at an acidic pH the decomposition process of H\(_2\)O\(_2\) in producing hydroxyl radicals occurs quickly, because OH\(^-\) will bind to H\(^+\) so that it will increase the number of hydroxyl radicals that play a role in the degradation process of Remazol Brilliant Blue R and Remazol Yellow FG. Besides that, at acid pH, hydrogen radical (\(\cdot\)H) will also be formed. Hydrogen radicals can degrade dyes. The reaction of \(\cdot\)H formation is shown in the following equation:

\[
e^- + H^+ \rightarrow \cdot H \quad (17)
\]

The formation of hydroxyl radical and hydrogen radical results in higher effectivity of degradation of Remazol Brilliant Blue R and Remazol Yellow FG at acid pH than the alkaline pH. Under alkaline conditions, the decomposition of H\(_2\)O\(_2\) is inhibited due to the concentration of \(\cdot\)OH\(^-\) from the solution. A similar study was also reported by El-Bahy et al. [30] where the degradation process of Direct Blue 53 anionic dye using TiO\(_2\)-Gd in the pH range of 2-9 resulted in the greatest degradation efficiency at pH 4 which then decreased with increasing pH.

The degradation percentages of Remazol Brilliant Blue R at pH 5 are 67.34% (TiO\(_2\)), 92.12% (TiO\(_2\)-Co), 85.47% (TiO\(_2\)-Mn), and 83.91% (TiO\(_2\)-Cd), while for Remazol Yellow FG they are 58.84 % (TiO\(_2\)), 64.19% (TiO\(_2\)-Cd), 74.61% (TiO\(_2\)-Co), and 67.93% (TiO\(_2\)-Mn). Photocatalytic activity of TiO\(_2\)-M is better than TiO\(_2\). This is correlated to the bandgap energy of TiO\(_2\)-M that is smaller than TiO\(_2\), where the smaller bandgap energy of material will lead to a larger percentage of degradation.

3.5 Determination of Optimum Catalyst Phase

The catalyst phase affects the degradation of Remazol Brilliant Blue R, where it is known that the anatase phase has high photocatalytic activity. According to Kiswanti & Pratapa [31], the formation of the crystal phase is affected by calcination temperature. The result of the degradation of Remazol Brilliant Blue R and Remazol Yellow FG with different catalyst phases is shown in Figure 6.

Figure 6 shows that the degradation of Remazol Brilliant Blue R and Remazol Yellow FG reach the highest level at the anatase phase, because the anatase phase is the most photoactive phase and the formation of free radicals is higher in the crystal at the anatase

![Figure 6](image-url)
phase than in rutile phase [32]. At the amorphous phase, the lowest result is found because at the amorphous phase, an active site from the catalyst has not been perfectly formed. Accordingly, the photocatalytic activity is low. The anatase phase is the most photoactive phase, because it has a larger surface area when compared to the rutile phase [33]. In the rutile phase, lower yields were obtained when compared to the anatase phase. This is because the rutile phase has a lower photocatalytic activity and causes a decrease in the degradation product. In the amorphous phase, the lowest yield was obtained, because in the amorphous phase the active site had not been completely formed, so the photocatalytic activity was low. The results of a similar study were also reported by Subagia et al. [34], where TiO$_2$ in the anatase and rutile phases was obtained with a calcination temperature of 400 °C to 600 °C and resulted in the highest percentage of Methyl Orange degradation in the dominant anatase phase and decreased along with the formation of the rutile phase.

Results of degradation of Remazol Brilliant Blue R and Remazol Yellow FG show that Remazol Brilliant Blue R has a higher percentage of degradation. This is closely related to the different structures of the two dyes. Remazol Brilliant Blue R has a molecular mass of 626.53 gram/mol, while Remazol Yellow FG has 659 gram/mol. The different molecular mass results in an easier process of degradation of Remazol Brilliant Blue R because it has a smaller molecular mass than Remazol Yellow FG and consequently, it is more easily degraded and has a higher percentage of degradation.

This is also caused by the different structures of the two dyes. The structure of the two dyes. Analysis of the structure of both dyes shows that the structure of Remazol Brilliant Blue R has more phi (π) and double bonds than Remazol Yellow FG. Double bonds at the base structure of a compound contribute to resulted color. The double bonds are unstable. Accordingly, the bonds are easily attacked by hydroxyl radical (•OH), which is strong oxidation to become a simple component. A larger number of double bonds of a dye result in a higher sensitivity to the oxidation to the carotenoid compound as reported by Susilowati & Januar [35]. Besides that, Remazol Brilliant Blue R has an amine cluster at the orto and meta position so that the steric hindrance effect is larger and more reactive. This has resulted in higher degradation of Remazol Brilliant Blue R than Remazol Yellow FG. Hydroxyl radical is the primary radicals that initiate the degradation of dye compounds. The proposed of the degradation reaction of Remazol Brilliant Blue R

![Figure 7. Mechanism of the degradation reaction of (a). Remazol Brilliant Blue R and (b). Remazol Yellow FG.](image-url)
and Remazol Yellow FG as shown in Figure 7, while the graphical abstract of the research is shown in Figure 8.

4. Conclusion

Catalyst TiO$_2$ and TiO$_2$ doped Cd, Co, Mn (TiO$_2$-M) were synthesized with a sol-gel method, and the photocatalytic activity of Remazol Brilliant Blue R and Remazol Yellow FG has been conducted. The radius of the metal ion (Co$^{2+}$ = 0.79Å; Mn$^{2+}$ = 0.81Å; Cd$^{2+}$ = 0.109Å) affects the crystallinity, crystal size, and band gap the catalyst. Overall, the crystallinity of TiO$_2$ is higher than metal-doped TiO$_2$. The larger the metal ion radius, the larger the crystal size obtained. The larger the metal ion radius, the higher the band gap obtained, which is band gap energy of TiO$_2$-Co<TiO$_2$-Mn<TiO$_2$-Cd.

TiO$_2$ and TiO$_2$-M at the calcination temperature of 400 °C have the best characteristics since their optimal anatase phase is formed and has lower band gap energy. The optimum degradation of Remazol Brilliant Blue R and Remazol Yellow FG is reached at acid pH (pH 5) with anatase phase. The percentages degradation of Remazol Brilliant Blue R were 67.34% (TiO$_2$), 92.12% (TiO$_2$-Co), 85.47% (TiO$_2$-Mn), and 83.91% (TiO$_2$-Cd), while for Remazol Yellow FG they were 58.84% (TiO$_2$), 64.19% (TiO$_2$-Cd), 74.61% (TiO$_2$-Co), and 67.93% (TiO$_2$-Mn), respectively.

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Figure 8. Graphical abstract of the research.
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