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PHOTOCATALYTIC DEGRADATION Cr (VI) BY ZSM-5 IMPREGNATED TiO_2 IN VARIOUS UV-IRRADIATION TIME

Faridah[1), Ana Hidayati Mukaromah[2)] and Ayu Rahmawati Sulistyaningtyas[3)]
[1]Faculty of Nursing and Health Sciences, Universitas Muhammadiyah Semarang
email: faridahrosadi@yahoo.com
[2]Faculty of Nursing and Health Sciences, Universitas Muhammadiyah Semarang
email: anahidamuka@gmail.com
[3]Faculty of Nursing and Health Sciences, Universitas Muhammadiyah Semarang
email: ayurs@unimus.ac.id

Abstract

Chromium is considered as one of the most common ubiquitous pollutants in aquatic environment. There were qualities standard about Chromium content in drinking water and fresh water. Oxidation of Chromium were *Cr (II), Cr (III) and Cr (VI). Among these, Cr (VI) is considered as the most toxic form because it readily passes cellular membranes and then reduced to Cr (III).* TiO_2 *as catalyst can activated and modified zeolites with active metal materials i.e ZSM-5 impregnated* TiO_2*. Main objective of study was to determine decreased percentage of Cr (VI) in water by using ZSM-5 impregnated* TiO_2 *based on UV irradiation time. This study was used Completely Randomized Design i.e length of UV irradiation. Result showed Cr (VI) content was decreasing with various length of UV irradiation in 15;30;45;60;75 minutes, respectively is 17.01; 17.99; 18.99; 28,73; 36, 20%. The highest percentage decrease of Cr (VI) ion content during 75 minute UV irradiation is 39,42%. Chromium (VI) content could be solved with zeolite ZSM-5 impregnated* TiO_2 *by using photocatalytic method. In conclusion, the longer UV irradiation time caused higher of decreased percentage Cr (VI).*

Keywords: *Chromium, Photocatalytic, Zeolite, Impregnated*

1. INTRODUCTION

Water is one of the natural resources needed by all living things. Water must be protected from various factors that cause water degradation to be utilized by all living things. Heavy metal is one of the factors causing water pollution, such as Cr (VI) (Chromium). Cr (VI) includes highly toxic metals. Metal Cr (VI) is highly toxic, corrosive and carcinogenic. Cr (VI) metal can form macromolecular complexes in cells. Its chemical structure can also penetrate cell membranes quickly and undergo reactions in cells. Cr (VI) pollutant sources are derived from the wastewater of Cr (VI) coating, textile, paint, ink, tanning and oil refiners industries (Danarto, 2007). Therefore, it was necessary to decrease the Cr (VI) metal content in water so that water can function properly. According to the Ministry of Health as stated in Health ministry rules RI No. 492/Menkes/Per/2010 about quality of drinking water such as maximum iron content of 0.3 mg/L. In addition, the maximum Cr (VI) content for the benefit of drinking water is 0.05 mg/L. However, maximum Cr (VI) content for the benefit of fresh water is 0.05 mg / L.

One of methods were used to reduce the level of metal in water, it was photocatalytic degradation method. Photodegradation method was requires semiconductor catalyst material and ultraviolet (UV) radiation. Wavelength of UV light was adjusted to the gap semiconductor material possesses. Variations of UV irradiation times have done with assumption that longer of irradiation time should be resulted higher decreased metal content.

Zeolite is an aluminosilicate mineral that forms a 3-dimensional framework and has a cavity, where the surface area in the cavity is much larger than the surface area of the outer crystal zeolite (Rusvirman, 2005). Much research has been done to maximize the work of TiO2 by distributing it into supporting media. One of them is by impregnating it to activated carbon. One example of activated carbon that can be used is zeolite (Agusty, 2012). Zeolites have two types of natural and synthetic zeolites. Synthetic zeolites are better quality than natural zeolites, because they are made from chemicals and natural materials which are then processed from natural ore and have a silica to alumina ratio of 1: 1 while the natural zeolite has a ratio of up to 5: 1(Mukaromah *et al*., 2016; Mukaromah *et al*., 2017).Impregnation is an attempt to maximize the work of TiO_2 utilized as a catalyst by activating and modifying zeolites with active metals (Sriatun & Suhartana, 2002). Titanium dioxide (TiO_2) is a semiconductor material that has a large band gap (3.2 eV), is stable against light, non-toxic, and high oxidizing ability (Nuroppiah & Mukaromah, 2015).

2. THEORY

Water

According to the Government Regulation of the Republic of Indonesia No. 82 of 2001 classified water quality classification into 4 classes, can be seen below:

1.water that can be used for raw water and drinking water.
2.water for which the designation can be used for water recreation facilities / infrastructure, freshwater fish cultivation, water to irrigate crops.
3.water for which the designation can be used for the cultivation of freshwater fish, livestock, and water to irrigate crops.
4.water for which the designation can be used for irrigating, planting, and for others that require water quality with these uses.

Water pollution

Water pollution in environment can be identified through several indicators, can be seen below:

a. Change in water temperature

Industrial activities always need water to operate their machines. So that, water temperature was produced during process of operating machines will become hot. Usually, wastewater was immediately discharged into environment i.e. river without treatment process first. As a result, temperature of water river has increased and disrupted normal biota in water. Oxygen levels dissolved in water was affected by water river temperature. Higher water temperature caused lower dissolved oxygen level.

b. Changing of acidity (pH)

Terms of water which suitable for life are pH 6.5-7.5. If pH of the water below normal has acidic properties, whereas water which has pH above normal value has alkaline properties. This is due to the waste of industrial activities being discharged into the river.

c. Changing of color, smell, and taste water

Normal and clean conditions of water was colorless, it looks clear. However, often water pollution does not cause discoloration in water, but water remains clear with high levels of toxic substances. The appearance of odor of water was significant indicator of water pollution. Whereas smelly water can be caused by industrial waste and microorganisms in water.

d. Appearance of colloidal deposits from dissolved materials

Deposits materials come from presence of industrial waste materials as solid forms. This material cannot be completely dissolved in water. So, it settles on the river bed with some of the deposits becoming colloidal. In addition to originating from solids, sediments and colloids derived from organic waste. Microorganisms have an important role that is to degrade organic matter with the help of oxygen dissolved in water to become a simpler material.

e. Microorganisms

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Microorganisms have an important role in the degradation process. Materials must be degraded. So that, proliferation of microorganisms can not be denied. This pollution is generally caused by food processing industry waste.

f. Radioactivity

Radioactivity can caused changes in genetic composition and even death caused by cell damage. One of the causes of increased radioactivity was residu of burning coal.

g. Heavy metal pollution

Heavy metal pollution in the waters comes from water contaminated by industrial and mining waste. Heavy metals can have health effects on humans depending on which part of the heavy metal is bound in the body (Wardhana, 2004).

Waste

Waste as result of a waste from production process, there were domestic and non-domestic. Usually,it known as waste that has no economic value. Domestic waste is the result of waste from household such as baths, kitchens, laundry, household appliances and so on. Industrial waste that often causes environmental problems, i.e tofu, tempeh, coconut water and soy sauce waste (Sulistyaningtyas & Suprihadi, 2017;Sulistyaningtyas *et al*., 2017; Sulistyaningtyas *et al*., 2018). This has been occurs causes by weakness of management. It was still a lot of traditional and simple so that it causes environmental pollution.Quantitatively, this waste can be either solid or liquid which is dangerous and poisoning if consumed. While non-domestic waste usually comes from pesticides such as fertilizers containing nitrogen, phosphorus, sulfur, minerals and so on. This waste can cause negative health effects if the water used has been polluted, then proper handling must be done (Anitasari, 2016).

Chrom

Chrom is one of the heavy metals, usually in two oxidation states, there were Cr (III) and Cr (VI). These two compounds have differences in chemical properties. Cr (III) is an essential nutrient which that very important for sugar metabolism and some enzyme reactions. Chrom (VI) is very toxic, very active in water at various pH and carcinogenic. Chromium (VI) in chromate and dichromic form is very toxic which can cause skin and respiratory tract cancer (Sunardi, 2011). According to the Minister of Health Regulation number: 492/MENKES/Per/IV/2010 about the maximum Chromium content for drinking water is 0.05 mg/L but for maximum chrome content for the benefit of fresh water is 0.05 mg/L.

Titanium dioxide (TiO_2)

(TiO_2) or also called titania is the most common form of oxide for titanium metal. Titanium dioxide has a white crystalline shape, has a molecular weight of 79.8886 g/mol, a density of 4.23 g/cc, a melting point of 1843ºC in the absence of oxygen and 1892ºC in the presence of oxygen, and has a boiling point of 2972ºC. TiO_2 crystals are acid-insoluble in water, hydrochloric acid, dilute sulfuric acid, and alcohol. However, this crystal dissolves in concentrated sulfuric acid and fluoride acid. TiO_2 has several advantages, namely the economical price, non-toxic and the most important is the stability and activity when subjected to light. Titanium dioxide is widely used as a photocatalyst because it is stable, corrosion resistant, safe, has amphilic properties, and is cheap. Titanium dioxide is stable at pH 4.5-8. Ultraviolet (UV) is an electromagnetic radiation that has a shorter wavelength than violet rays that range from 100-400 nanometers. A lot of research has been done to maximize the work of TiO_2 by distributing it into supporting media. One of them is by impregnating it on Zeolites (Agusty, 2012).

Zeolite

Zeolite is an alumino silicate mineral. It has a cavity, where the surface area in the cavity is much larger than the crystal surface area of the outer zeolite (Rusvirman, 2005). Zeolites have hollow structures that contain interchangeable water and cations. Generally, zeolites function as absorbers, ion exchangers and as catalysts. Chemically zeolites function as ion exchangers that can separate substances contained in water due to alkali metal cations and alkaline earth cations. Synthetic zeolite is better in quality than natural zeolite, because it is made from chemicals and natural ingredients which are then processed from natural ores and have a ratio of silica to alumina which is 1: 1 while natural zeolites have a ratio of up to 5: 1 (Mukaromah *et al*., 2017).

3. METHODS

Tools and Materials

Materials of this study were Chromium powder, TiO_2 powder, ZSM-5, distilled water chromium sample solution, $K_2Cr_2O_7$ powder, TPABr 0.1 M, $NaAlO_2$, ludox HS-40%, diphenylcarbazide solution and absolute ethanol

The tools used are analytic scales, technical scales, UV-Vis spectrophotometer, flask, bowl, filter paper, pH meter, magnetic strirer, sieve, funnel, stirring rod, rotator, stative, burette, mortar, furnace and UV lamp

Data analysis

The result of analysis was tested using Two Way Anova test and all data collected were arranged in tabular form and described descriptively.

Procedures

a. Determination of Cr (VI) Preliminary

The Cr (VI) 50 mg/L sample was piped 5.0 mL, then put into a 50.0 mL measuring flask, added aquadest to the limit and homogenized. In a 5.0 mL sample Cr 10 mg / L inserted into a 50.0 mL measuring flask was added ± 35 mL distilled water, then added 2.5 mL diphenylcarbazide, precisely with aquades to the limit and homogenized, absorbance read using a spectrophotometer at wavelength and stability time optimum. Procedure repeated 5 times (Mukaromah *et al*., 2017).

b. The decrease of Cr (VI) metal using TiO2-ZSM-5 0.75% w / v with variation of UV exposure time 15, 30, 45, 60, 75 min.

A 50 ml Cr (VI) 50 ml L mixed solution was added to a 250 ml erlenmayer plus 0.3750 g of TiO_2-ZSM-5 homogenized for 15 min while irradiated using UV light (3x8 watt) for 15 min, then filtering using whatman paper 42. The filtrate of filtrate is adjusted with aquades to the limit and homogenized, then determined Cr (VI) after treatment. The treatment was repeated for a time variation of 30, 45, 60, 75 minutes (Mukaromah *et al*., 2017)

c. Determination of Cr (VI) content after addition of TiO_2-ZSM-5 0.75% w / v of UV irradiation variation 15, 30, 45, 60, 75 min.

The filtrate resulting from a decrease of Cr (VI) added level of 0.75% w / v TiO2-ZSM-5 was piped as much as 5.0 mL is fed into a 50.0 mL measuring flask, plus aquades to the limit and homogenized. A 5.0 mL sample of Cr 10 mg / L was added to a 50.0 mL measuring flask, plus ± 35 mL of distilled water and 2.5 mL diphenylcarbazide. Adjusted to the limit and homogenized, absorbance is read using a spectrophotometer at the wavelength and optimum wakru stability. The procedure was repeated on the filtrate resulting from the decrease in Cr (VI) levels which had received UV irradiation 15, 30, 45, 60, 75 min. Formula of Decreasing Percentage of Cr (VI) content, there were:

$$x = \frac{y-b}{a}$$

$$x = \frac{y-b}{a} x f p$$

Note:

y = Absorbance, x = Cr (VI) content,

a = Constanta, b = Coefisient

fp = Dilution factor of sample

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$$\frac{Initial\ content - final\ content}{Initial\ content} \times 100\%$$

(Mukaromah *et al*., 2017)

4. RESULT AND DISCUSSION

Based on the results of the research, the addition of 0.75% w / v TiO_2-ZSM-5 powder and UV light exposure variations of 15, 30, 45, 60, and 75 minutes increased the percentage decrease in Cr (VI) levels. The result of comparison of percentage decrease of Cr (VI) with ZSM-5 and TiO_2-ZSM-5 with various duration of UV irradiation, can be seen in Table below.

Table 1. Comparison of Percentage of Decreasing Cr (VI) by using TiO_2-ZSM-5 and ZSM-5 in Various Duration of UV irradiation

Duration of UV irradiation (minutes)	Percentage of Decreasing Cr (VI)	
	ZSM-5 (%)	TiO_2-ZSM-5 (%)
15	13,33	17,01
30	14,73	17,99
45	15,72	18,99
60	16,81	28,73
75	22,07	36,20

Table 1 showed that the highest percentage of Cr (VI) reduction of 36.20% is using TiO2-ZSM-5 with a 75 minute irradiation time, while the percentage decrease in Cr (VI) using the highest ZSM-5 is 22.07% with 75 minute exposure time. TiO2-ZSM-5 powder is proven to decrease Cr (VI) in water. ZSM-5 zeolite is maximized by adding TiO2 catalyst so that its absorbance ability is better in decreasing Cr (VI) content in water than if using Zeolite ZSM-5 only. The optimum UV irradiation time is 75 minutes with the highest percentage decrease of 36.20%.

Zeolite ZSM-5 powder has absorption properties and is an aluminasilical crystal (SiO_2 .Al_2O). ZSM-5 Zeolite has a surface area of 5.1 x 5.5ºA and 5.4 x 5.6ºA so it can absorb heavy metals especially Cr (VI) metal that has been activated and modified with other compounds to improve its absorbs ability (Mundar, 2014). TiO_2 powders have higher photocatalytic activity compared to other photocatalysts, such as: ZnO, CdS, and SnO_2. TiO2 is able to absorb ultraviolet light well, resistant to photodegradation, and has a high oxidation ability (Tarr, 2003).

TiO_2 photocatalysis that is based on the photoinduced interfacial charge transfer has been extensively studied over the past four decades. A great number of modification methods of semiconductor photocatalysts have been developed and investigated to accelerate the photoconversion, to enable the absorption of visible light, or to alter the reaction mechanism to control the products and intermediates. In this regard, various modification methods of TiO_2 are classified according to the kind of surface modifiers (metal-loading, impurity doping, inorganic adsorbates, polymer coating, dye-sensitization, charge transfer complexation) and their effects on photocatalytic reaction mechanism and kinetics are discussed in detail. Modifying TiO_2 in various ways not only changes the mechanism and kinetics under UV irradiation but also introduces visible light activity that is absent with pure TiO_2. Each modification method influences the photocatalytic activity and mechanism in a way different from others and the observed modification effects are often different depending on the test substrates and conditions even for the same modification method (Park *et al*., 2013).

The effect of dissolved oxygen on the photocatalytic reduction of Cr(VI) with illuminated TiO_2 was studied in this work with variation of the solution pH, contact time, and initial Cr(VI) concentration. Oxygen or nitrogen gas was used as a purging gas. Overall, the removal efficiency of Cr(VI) decreased as the solution pH increased. The removal of Cr(VI) by UV/TiO_2 increased by decreasing the solution pH because of the increased potential difference between the conduction band of TiO_2 and Cr(VI)/Cr(III) as well as the anionic-type adsorption of Cr(VI) into the TiO_2 surface (Yang *et al*., 2012). The highest percentage decrease of Cr (VI) ion content during 75 minute UV irradiation is 39,42%. Chromium (VI) content could be solved with zeolite ZSM-5 impregnated TiO_2 by using photocatalytic method.

5. CONCLUSION

Chromium (VI) content could be solved with zeolite ZSM-5 impregnated TiO_2 by using photocatalytic method. The longer irradiation time by Ultraviolet (UV) caused higher of decreased percentage Cr (VI).

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