

PHOTODEGRADATION OF Cr (VI) IN VARIOUS CONCENTRATION OF ZSM-5 IMPREGNATED TiO₂

Yulia Alfiani¹⁾, Ana Hidayati Mukaromah²⁾ and Ayu Rahmawati Sulistyanningtyas³⁾

¹Faculty of Nursing and Health Sciences, Universitas Muhammadiyah Semarang
email: yualf.19@gmail.com

²Faculty of Nursing and Health Sciences, Universitas Muhammadiyah Semarang
email: anahidamuka@gmail.com

³Faculty of Nursing and Health Sciences, Universitas Muhammadiyah Semarang
email: ayurs@unimus.ac.id

Abstract

Nowadays, water could be contaminated by heavy metals such as chromium (Cr). Chromium toxicity depends on its state of valence. Cr (VI) as highly mobile is toxic, while Cr (III) as a less mobile is less toxic. Potentially, Cr (VI) content can be reduced by ZSM-5 impregnated TiO₂. TiO₂ as a catalyst can activated and modified zeolite with active metal materials. The impregnation between ZSM-5 and TiO₂ should be reduce Cr (VI) content in water. The objective of this study was to assess concentration of ZSM-5 impregnated TiO₂ which most effectively for decreasing Cr (VI) content. Decreasing Cr (VI) content in various concentration of ZSM-5/TiO₂ was measured using UV-Vis spectrophotometer. The results showed that variation of zeolite concentration had an effect on decreasing Cr (VI) content in water. Photodegradation of Cr (VI) in various concentrations (0.25%; 0.50%; 0.75%; 1.00%; 1.25% w/v) respectively are 16.99%; 18.84%; 24.83%; 30.82%; 36.14%. Concentration 1.25% w/v of ZSM-5 impregnated TiO₂ as the highest to decrease Cr (IV) content. On the other hand, Using TiO₂ or ZSM-5 only was showing lower percentage of Cr (VI) reduction which compared ZSM-5/TiO₂. In conclusion, More higher concentration ZSM-5/TiO₂ caused faster photodegradation and higher percentage decrease of Cr (VI) content in water.

Keywords: Concentration, Cr (VI), Photodegradation, TiO₂, ZSM-5

1. INTRODUCTION

Water as a natural resource was needed by all living things. Water quality has reviewed physically, chemically and microbiologically. Water chemistry requirements should be no toxins, excessive chemicals, water pH between 6.5 - 8.5 (Ministry of Health, 2002). The development of industrial sector has a significant impact on environmental pollution both air and water, if industrial waste has not treated properly.

Water pollution was caused incidence of pollutants into the aquatic environment. So, water quality would be becomes disrupted. Water can be contaminated by various industrial, agricultural and household waste (Fatimah, 2011). Water contamination can be caused by organic and inorganic materials. One example of organic matter was waste which can be decomposing or degradating by microorganisms. Meanwhile, Inorganic materials such as industrial waste were containing heavy metal ions. Heavy metals was divided into two groups, there are heavy metals (arsenic, mercury, lead, cadmium, and chromium) and essential metals (copper, iron, zinc, selenium) which can be toxic when consumed excessively (Pellerin, 2006).

Chromium is a heavy metal contained which has two oxidation states of Cr (III) and Cr (VI). The two compounds have differences in their chemical properties and toxicity. Chromium was needed by human body in small quantities. Usually, Chromium in the human body as Cr (III) form which is very important for glucose metabolism and some enzyme

reactions. Chromium (VI) is highly toxic, highly active in water at various pH and carcinogenic. Chromium (VI) in the form of dichromate and chromate can cause skin and respiratory tract cancer (Sunardi, 2011). In addition, Chromium metal was often used in the field of industry, such as metal coating industry, paint making and textile dyes, steel hardening, stainless steel manufacture and shaping of many alloys (Pellerin, 2006). The residual waste of this industrial liquid contains chromium which will affect the quality of soil water.

According to Regulation of the Minister of Health No. 32 of 2017, the level of chromium (VI) in water for sanitary hygiene is 0.05 mg/L. According to Minister of Health Regulation No. 492/Menkes/Per/IV/2010 that total chromium content in drinking water is 0.05 mg/L. Various of techniques and processes have been developed to separate heavy metal ions which were very dangerous from water, among others by ion exchange, chemical precipitation, and adsorption. Nowadays, Adsorption was the safest method, has no harmful side effects to health, simple, cheap and easy to do. The application of adsorption technology has been widely developed using biomaterials as well as synthetic materials to reduce the heavy metal content of water bodies (biosorption) such as using rice husks (Utami *et al.*, 2017; Saputri *et al.*, 2017). Other biomaterials can be used as adsorbents, there were silica gel, chitin, chitosan, humic acid, and natural zeolite. Synthetic materials that can be used as adsorbent is synthetic zeolite ZSM-5.

Another method used to reduce chromium contamination (VI) is the photodegradation method (photocatalysis-degradation). The photodegradation method (photocatalysis-degradation) requires semiconductor catalyst material and ultraviolet (UV) radiation. The wavelength of UV light is adjusted to the gap energy of the semiconductor material. The catalysts commonly used for photocatalysis are Fe_2O_3 , SnO_2 , ZnO , CuS , ZrO_2 , and TiO_2 (Hermann, 1999). Titanium dioxide (TiO_2) is a semiconductor material that is widely available in the market and is considered the most superior (Fatimah *et al.*, 2006). TiO_2 is more commonly used in photocatalysis especially waste treatment because it has a large band gap (3.2 eV), is stable against light, non-toxic, and high oxidizing ability (Mukaromah *et al.*, 2010).

Much research has been done to maximize the work of TiO_2 by distributing it into carrier media such as zeolites. Impregnation was an attempt made to maximize the work of zeolites utilized as catalysts by activating and modifying zeolites with active metal carrier materials. Utilization of zeolites as filter because of its porous structure and heat resistance. The porous structure results in a large zeolite surface area so that more catalyst metal can be introduced. Metals introduced on zeolite solids through impregnation will make metals in zeolites as bifunctional catalysts (Sriatun & Suhartana, 2002).

Several studies about ZSM-5, TiO_2 and TiO_2 -Zeolite are among the highest decreases in chromium (VI) content of 64.65% obtained by ZSM-5 zeolite 0.75% w/v in immersion time of 120 minutes (Nurropiah *et al.*, 2015). Research by Mukaromah *et al.*, (2010) about the use of self cleaning photocatalyst TiO_2 20 mg able to degrade Ammonium (NH_4^+) optimally up to 30 ppm with long irradiation time 150 minutes so as to reduce ammonium level of 11.40%. Zeolite impregnated TiO_2 used to degrade congo red dye (Agusty, 2012). Damayanti *et al.*, (2014) on the effect of TiO_2 concentration on methylene blue photodegradation in concentration of TiO_2 from 5 mmol/g zeolite to 10 mmol/g zeolite can be increasing active site of catalyst so that many methylene blue ions has been absorbed on the surface of TiO_2 . So, although the potential of TiO_2 impregnated zeolite has been proven in previous studies. However, it has not yet been applied to chromium (VI), so study of chromium (VI) reduction in water using zeolite ZSM-5 impregnated TiO_2 with concentration variations is needed. Therefore, the combination between ZSM-5 and TiO_2 for reducing Chromium (VI) content in water compared is potential.

2. THEORY

Industrial waste

Industrial waste is all types of waste material or waste material derived from the by-products of an industrial process. Industrial waste can be a waste that is very dangerous for the environment and humans (Palar, 2004).

Industrial Waste Classification

1. Solid waste

According to (Lestiani *et al.*, 2010). The categories for solid waste in industry are:

a. Non B3 solid waste (hazardous and toxic materials)

Non-hazardous solid waste (hazardous and toxic materials) including mud, ash boilers, office waste, household waste, heavy equipment spare parts, gloves, and so on.

b. B3 solid waste (hazardous and toxic materials)

B3 solid waste includes radioactive materials, chemicals, cartridge toner, oil, and so on. According to PP No. 18 of 1999, hazardous and toxic material waste, abbreviated as B3 waste, is the remainder of a business or activity containing hazardous and toxic substances which due to their nature and concentration and their amount, directly or indirectly, can pollute the environment, can endanger the environment, health, survival of humans and other living things. Waste included as B3 waste if it has one or more of the following characteristics: explosive, flammable, reactive, toxic causes infection and is corrosive.

2. Liquid waste

Liquid waste is liquid waste. Liquid waste is dissolved in water, always moves, and never stays silent. Examples of industrial wastewater are chemicals, solvents, used water production, used oil, etc. (Setiawan, 2015).

3. Gas waste

Gas waste is waste material (waste material) which is in the form of gas (Setiawan, 2015). The air condition in the atmosphere is never found in a clean state, but it has been mixed with other gases and particulates that we do not need (Sumantri, 2013). The most common types of pollutants are carbon monoxide (CO), nitrogen dioxide (NO₂), sulfur dioxide (SO₂), organic components, especially hydrocarbons, and particle substances (Darmono, 2001).

Water Quality

Clean water is water that meets the requirements for drinking water supply systems, where the intended requirements are requirements in terms of water quality which include physical, chemical, biological and radiological parameters so that if consumed does not cause side effects that can interfere with human health in accordance with RI PERMENKES / No.492 / MENKES / PER / IV / 2010. Clean water quality parameters are as follows:

a. Physical parameters

Water that meets physical requirements is water that is odorless, tasteless, colorless, not cloudy or clear. In addition, the temperature of clean water should be the same as the air temperature or approximately 25 lebihC, and if there is a difference, the allowed limit is $25^{\circ}\text{C} \pm 30^{\circ}\text{C}$.

b. Chemical Parameters

Chemical parameters of good water are water that is not excessively contaminated by chemicals harmful to health, including mercury (Hg), aluminum (Al), arsenic (As), barium (Ba), iron (Fe), chrome (Cr), acidity level (pH), and other chemical substances.

c. Microbiological parameters

Natural water generally contains bacteria, the number and type of bacteria differ according to the place and conditions that influence it. Water used for daily needs must be free from pathogenic bacteria. Coli class bacteria are not pathogenic class bacteria, but these bacteria are indicators of water pollution by pathogenic bacteria. This parameter is indicated by the absence of E.coli bacteria in water.

d. Radioactivation parameters

The radioactivation parameter, whatever the shape, is the same effect, which causes damage to exposed cells. Damage can be in the form of death and changes in genetic composition. Cell death can be replaced if cells can regenerate and all cells do not die. Genetic changes can cause various diseases such as cancer and mutations.

Chrome (Cr)

The word Chromium comes from Greek (= Chroma) which means color. Chromium chemicals are represented by "Cr" one of the heavy metal elements. Chromium has an atomic number (NA) 24 and has an atomic weight (BA) 51.996. Chromium metal (Cr) was first discovered by Vauquelin in 1797. Pure chromium (Cr) metal has never been found in nature, chrome metal in nature is found in the form of solid or mineral compounds with other elements. Chromium (Cr) mineral material is found mostly in the form of "Cromite" (FeOCr_2O_3) (Palar, 2004).

Chrom is a heavy metal which is contained in two oxidation states namely Cr (III) and Cr (VI). The two compounds have differences in terms of chemical properties and toxicity. Chromium (III) is an essential nutrient that is very important for sugar metabolism and some enzyme reactions. Krom (VI) is very toxic, very active in chromate and dichromic forms which are very toxic which can cause skin cancer and digestive disorders (Sunardi, 2011). The chemical properties of chromium metal (Cr) in its compounds have 2, 3 and 6 oxidation numbers. Chromium (Cr) metal cannot be oxidized by moist air and even in the process of heating the oxidized chromium metal in very little amount. In air containing CO_2 (carbon dioxide) in high concentrations of chromium metal (Cr) can experience oxidation and form Cr_2O_3 . Chromium metal (Cr) can directly react with nitrogen, silica and boron (Palar, 2004).

Impact of Chromium Pollution on the Aquatic Environment

Chromium in the waters can enter in two ways, natural and non-natural. Chromium entry naturally can occur by several physical factors, such as erosion or erosion that occur in mineral rocks. Dust and chrome particles in the air will be brought down by rainwater. The entry of chromium that occurs non-naturally is an impact of human activities. Chromium sources related to human activities can be in the form of waste or industrial waste to household waste (Palar, 2004).

Water organisms that accumulate chrome, if consumed can cause poisoning. Poisoning caused by chromium ion compounds in humans is characterized by a tendency for swelling of the liver. The level of chromium poisoning in humans is measured through levels of chromium content in urine, and chromatic acid crystals (Laksito, 2009).

Zeolite

Zeolite is one of the media used as an ion exchanger that has the ability to absorb heavy metals in liquid waste. Zeolite is classified as a type of mineral composed of silica (SiO_2) and alumina (AlO_3) with cavities in it that contain metal ions, usually alkaline and alkaline earth, and water molecules. Each zeolite has a different rate of ion exchange. This is influenced by the structure of zeolite formation which affects the size of the cavity formed and the effect of zeolite sifting, cation mobility needed, the effect of the electric field generated by the cation and diffusion of ions into the solution of hydration energy. Zeolites have a high absorption capacity, because zeolites can separate molecules based on the size and configuration of the molecule (Poerwadio *et al.*, 2004). Zeolite has several properties, there are dehydration, adsorption, ion exchange, Catalyst, filter / Separator (Amelia, 2003).

There are two kinds of zeolites, natural zeolites and synthetic zeolites such as ZSM-5 zeolites.

1. Natural Zeolite

Natural zeolite is an ingredient that is formed from the results of alkaline hydration with the structure of open frame tissue with the ability to absorb and release water and exchange ions to the environment (Poerwadi *et al.*, 2014). The properties possessed by natural zeolites are dehydration, adsorption, ion exchange, catalyst, and separator (Amelia, 2003).

2. ZSM-5 synthetic zeolite

ZSM-5 Zeolite (Zeolite Secony Mobile-5) is an example of synthetic zeolite which has moderate pores with orthombic cell units. The selectivity of ZSM-5 is very important in catalyst reactions. As a catalyst, it consists of a slightly modified Al and different variations in the increase in catalyst activity. ZSM-5 numeric atomic zeolite pore 5.1 x 5.50 A and 5.4 x 5.60 A, ZSM-5 zeolite is written with the chemical formula $\text{Na}_n\text{Al}_n\text{Si}_{96-n}\text{O}_{192} \cdot 16\text{H}_2\text{O}$ with $n < 27$, ZSM-5 can be synthesized from a liquid gel prepared from sodium aluminate, sol silica, NaOH, H₂SO₄ and tetrapropilalummonium bromide (Kasmui, *et al.* 2010).

Titanium Dioxide

Titanium dioxide (TiO₂) 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 1843 ° C in the absence of oxygen and 1892 ° C in the presence of oxygen, and has a boiling point of 2972°C. TiO₂ crystals are acid-insoluble in water, hydrochloric acid, dilute sulfuric acid, and alcohol. However, this crystal dissolves in concentrated sulfuric acid and fluoride acid. Titanium dioxide is quite abundant in the Earth's crust, which is 0.6% with the main minerals FeTiO₃ (ilmenite) and CaTiO₃ (perovskite). Titanium dioxide is white and has non-toxic and rust resistant properties causing TiO₂ to be widely used as a pigment (white color) in food and cosmetics (Prima, 2012).

ZSM-5 Zeolite Impregnated with TiO₂

ZSM-5 work can be improved by impregnating TiO₂ into supporting media such as ZSM-5 zeolite. Research conducted by Prima (2012) on the use of TiO₂ impregnated zeolites to degrade congo red dyes, 1 gram TiO₂ impregnated on 20 grams of zeolite obtained 81.66% for 120 minutes at pH 4. The difference with the previous research was using zeolite with Congo red samples while this study used ZSM-5 zeolite with water samples containing chromium (VI) metal (Prima, 2012).

Photocatalysis and Photodegradation

Photocatalysis comes from the word photochemistry and catalyst which is defined as a chemical reaction that requires light and catalyst. Catalysts are substances that affect a chemical process without changing chemically. Catalysts can speed up a reaction. Chemical changes caused by light occur on the surface of a catalyst. A reaction without a catalyst will run slowly except with very high temperatures. This causes other difficulties to arise, namely the difficulty in regulating higher temperatures and other reactions that are not desired (Suspeno, 2009). Catalyzed photodegradation reactions require four main components: light source (photon), target compound, oxygen and photocatalyst (Prima, 2012).

3. METHOD

Tools and Materials

Materials of this study were Chromium powder, TiO₂ powder, ZSM-5, distilled water chromium sample solution, K₂Cr₂O₇ powder, TPABr 0.1 M, NaAlO₂, 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 stirrer, 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

1. Preparation of ZSM-5 Zeolite at low temperature (90 °C)

Preparation of ZSM-5 zeolite by mixing 0.136 g NaAlO₂ and 1,390 g NaOH 50% w / v in propylene bottle 1. Dissolved 1,549 g of TPABr with 7.3802 g water into propylene 2 bottle

and stirred with magnetic stirrer for 5 minutes, then put into a propylene 1 bottle, and added 24.940 g of Ludox HS-40%, thus forming a semi-gel and stirring for 6 hours then form a homogeneous gel. Furthermore the propylene 1 bottle is inserted in an oven with a temperature of 90 ° C for 4 days to form a white solid. The white precipitate was washed with water and filtered using Whatman paper No. 42 and inserted into the oven at 60 ° C for 24 h to obtain maximum drying. Solid were heated in furnace at 550 ° C for 6 hours. After that, a solid is crushed and sieved with a mesh size of 100 mesh (Saputri *et al.*,2017).

2. Preparation of Titanium Dioxide Powder

The titanium dioxide (TiO₂) powder was heated at 100 C for 1 hour then sieved with a sieve of 100 mesh.

3. Impregnation of TiO₂ into Zeolite ZSM-5

The TiO₂-ZSM-5 photocatalyst was prepared by mixing 20 grams of ZSM-5 zeolite prepared with 1 gram of TiO₂ and added with 20 mL of absolute ethanol. The mixture was stirred by using a magnetic stirrer for 5 h. After that the mixture was dried in oven at 120 ° C for 5 hours. After dry TiO₂-ZSM-5 was crushed until smooth and calcined at 400 ° C for 5 h (Agusty, 2012).

4. Preparation of Crude Standard of Cr (VI) 100 mg / L

Weighed K₂Cr₂O₇ of 0.5658 grams, put into a 1000.0 mL quantity flask and dissolved with aquadest and then adjusted with aquadest until the marks were bordered and homogenized

5. Preparation of Cr (VI) Standard 10 mg / L

10.0 mL Cr (VI) standard 100 mg/L was fed into a 100.0 mL measuring flask, then adjusted to the limit marker with aquadest and homogenized.

6. Preparation of Cr (VI) 50 mg/L

Taken 500 mL Cr (VI) 100 mg/L solution, incorporated into 1000.0 mL quantity flask, then dissolved with distilled water to the limit and homogenized.

7. Optimization of Maximum Wave Length with Cr (VI)

Prepared 4 pieces of 50.0 mL measuring flask. The first flask was filled with ± 35 mL distilled water while the flasks to 2-4 were each filled with Cr (VI) 10 mg / L 0.5 ml, respectively; 1.5 ml; and 2.5 ml. Each measuring flask was added with distilled water to a solution volume of 35 mL and added 2.5 ml diphenylcarbazide, then adjusted with aquadest to the limit marker and allowed to stand for 10 minutes. Then the absorbance was measured at a wavelength of 520-560 nm. The results of the maximum absorbance obtained using the optimum wavelength.

8. Time Stability Optimization with Cr (VI)

Prepared 4 pieces of 50.0 mL measuring flask prepared. The first flask was filled with ± 35 mL distilled water while the flasks to 2-4 were each filled with Cr (VI) 10 mg / L 0.5 ml, respectively; 1.5 ml; and 2.5 ml. Each measuring flask was added with distilled water to a solution volume of 35 mL and added 2.5 ml diphenylcarbazide, then adjusted with distilled water to a limit marker and sterilized with a stability time of 5.10.15 min. Absorbance is measured at optimum wavelength. The result of maximum absorbance obtained using optimum stability time.

9. Determination of initial Cr (VI) content

A solution of Cr (VI) 50 mg / L sample was 5.0 mL was added to a 50.0 mL measuring flask, added ± 35 mL distilled water and then added 2.5 mL diphenylcarbazide and washed with aquadest until marked and homogenized and sterilized in time optimum stability. Absorbance is read by a spectrophotometer at the optimum wavelength. Procedure repeated 5 times.

10. Decrease of Cr (VI) metal using TiO₂-ZSM-5 with variation of concentration

Provide 5 250 mL erlenmayer pieces and 50.00 ml of Cr (VI) 50 mg / L solution added each, added 0.125 grams of TiO₂-ZSM-5 stirred with a magnetic stirrer and UV irradiated for 75 minutes. After 75 minutes the filtrate was filtered using Whatman 42 filter paper. The filtrate of filtrate was determined Cr (VI) after treatment. The procedure was repeated for a

concentration variation of 0.5% w / v; 0.75% w / v; 1.00% w / v; 1.25% w / v (by adding 0.25 g; 0.375 g; 0.5 g; 0.625 g TiO₂-ZSM-5).

11. Determination of Cr (VI) content after addition of TiO₂-ZSM-5

The filtrate resulted from a decrease of Cr (VI) added level of 0.25% w / v TiO₂-ZSM-5 in a 50.0 ml measuring flask plus distilled water to the boundary mark, then homogenized. The filtrate taken 5.0 mL is fed into a 50.0 mL measuring flask plus distilled to the limit, then homogenized. The filtrate taken 5.0 mL was fed into a 50.0 mL measuring flask. Plus ± 35 ml of distilled water and 2.5 mL diphenylcarbazide. Adjusted until marked and homogenized and sterilized in optimum stability. Absorbance is read by a spectrophotometer at the optimum wavelength. The procedure was repeated on the filtrate resulting from a decrease in Cr (VI) content having received 0.5% w / v treatment; 0.75% w / v; 1.00% w / v; 1.25% w / v TiO₂-ZSM-5 for 75 minutes.

4. RESULT AND DISCUSSION

Adsorbents can absorb heavy metals especially Cr (VI) in wastewater, have high selective properties. Adsorption by zeolite ZSM-5 has an active group of silica alumina (SiO₂, Al₂O₃) and has a certain surface area. So, it can be adsorb through an active group or surface area with other compounds to increase its adsorption (Munandar, 2014). Determination of Cr (VI) content (After Treatment) content showed in Table 1 below.

Table 1. Percentage reducing of Cr (VI) Content

Replication	Various Concentration (% b/v)					
	0 (Control)	0,25	0,50	0,75	1,00	1,25
1	49,76	17,56	18,84	24,77	30,89	36,08
2	49,85	17,17	17,92	23,29	30,51	35,15
3	49,02	16,81	19,02	24,29	29,78	34,77
4	48,84	18,28	18,66	25,14	30,14	36,44
5	49,57	16,99	18,28	22,54	31,07	35,89
Average of decreasing percentage	-	16,99 ± 0,12	18,84 ± 0,12	24,83 ± 0,20	30,82 ± 0,21	36,14 ± 0,20

Based on Table 1 above it can be concluded that the average initial Cr (VI) content in Cr (VI) 50.0 mg / L solution sample before the addition of TiO₂-ZSM-5 was 49.73 ± 0.10 mg / L. After addition of TiO₂-ZSM-5 with variation of concentration 0,25% w / v; 0.50% w / v; 0.75% w / v; 1.00% w / v; 1.25% w / v and the duration of irradiation of 75 minutes Cr (VI) levels decreased. According to Figure 1, the percentage decrease in Cr (VI) concentration using TiO₂-ZSM-5 increases with increasing TiO₂-ZSM-5 concentration, this is because the higher concentration, the more TiO₂-ZSM-5 powder can absorb Cr (VI).

Comparison Percentage Decreasing of Cr (VI) content in TiO₂, ZSM-5 and TiO₂-ZSM-5, it can be seen belows:

Table 2. Comparison Percentage Decreasing of Cr (VI) content in TiO₂, ZSM-5 and TiO₂-ZSM-5

Concentration	Zeolites		
	TiO ₂	ZSM-5	TiO ₂ -ZSM5
0,25	6,16	10,60	16,99
0,50	9,68	13,01	18,84
0,75	12,09	14,59	24,83
1,00	14,39	16,88	30,82
1,25	17,28	21,44	36,14

Based on Table 2 shows the highest percentage decrease of Cr (VI) content of samples with the addition of TiO₂ at a concentration of 1.25% w / v. It is suspected that titanium dioxide (TiO₂) is a semiconductor material often used in photocatalysis especially waste treatment because it has a large bandgap (3.2 eV), is stable against light, non-toxic, and high oxidizing ability .

The highest percentage decrease of Cr (VI) sample with Zeolite ZSM-5 at concentration 1.25% w / v. This is presumably because ZSM-5 zeolite has an active group of silica alumina (SiO₂, Al₂O₃) and has a surface area of 5.1 x 5.50 A and 5.4 x 5.60 A so it adsorbs via an active group or surface area with a compound to increase its adsorption (Munandar, 2014). The adsorption capability of ZSM-5 zeolite can be increased by impregnation with the supporting medium such as TiO₂ so as to decrease Cr (VI) in water more optimally than using only TiO₂ and ZSM-5 Zeolite only. This is because the utilization of zeolites as bearers, among others, because the structure is porous and heat resistant. The porous structure results in a large zeolite surface area so that more catalyst metal can be introduced. Metals introduced on zeolite solids through impregnation will make the metals in zeolites as bifunctional catalysts (Sriatun & Suhartana, 2002).

5. CONCLUSION

More higher concentration of ZSM-5 impregnated TiO₂ caused faster photodegradation and higher percentage decrease of Cr (VI) content in water.

6. REFERENCES

- Damayanti, C. A., Wardhani, S., & Purwonugroho, D. (2014). Pengaruh konsentrasi TiO₂ dalam zeolit terhadap degradasi methylene blue secara fotokatalitik. *Jurnal Ilmu Kimia Universitas Brawijaya*, 1(1), pp-8.
- Ministry of Health RI. (2010). Peraturan Menteri Kesehatan Nomor 494/Menkes/Per/IV/2010. *Persyaratan kualitas air minum*.
- Fatimah, I., Sugiharto, E., Wijaya, K., Tahir, I., & Kamalia, K. (2010). Titanium Oxide Dispersed On Natural Zeolite (TiO₂/Zeolite) And Its Application For Congo Red Photodegradation. *Indonesian Journal of Chemistry*, 6(1), 38-42.
- Mukaromah, A. H., Amin, M., & Darmawati, S. (2010). Penggunaan self cleaning Fotokatalis TiO₂ dalam Mendegradasi Ammonium (NH₄) Berdasarkan lama waktu penyinaran. *JURNAL KESEHATAN*, 3(1).
- Utami, R. A., Mukaromah, A. H., & Yusrin, Y. (2017, October). Sintesis Membran Zeolit Zsm-5 Secara Coating Pada Suhu 90° C Berdasarkan Variasi Jenis Ukuran Kasa Dalam Menurunkan Kadar Gas. In *PROSIDING SEMINAR NASIONAL & INTERNASIONAL* (Vol. 1, No. 1).

- Saputri, M. J., Mukaromah, A. H., & Yusrin, Y. (2017, October). Sintesis Membran Zeolit Zsm-5 Secara Coating Pada Suhu 90° C Berdasarkan Variasi Perlakuan Kasa Stainless Steel Aisi 316 180 Mesh Dalam Menurunkan Kadar Gas CO. In *PROSIDING SEMINAR NASIONAL & INTERNASIONAL* (Vol. 1, No. 1).
- Munandar, A. 2014. *Adsorpsi Logam Pb dan Fe dengan Zeolit Alam Teraktivasi Asam Sulfat*. Skripsi. Fakultas Sains dan Teknologi. UIN Sunan Kalijaga: Yogyakarta.
- Pellerin, C., & Booker, S. M. (2000). Reflections on hexavalent chromium: health hazards of an industrial heavyweight. *Environmental health perspectives*, 108(9), A402.
- Poerwadi, M. R., Zacoeb, A., & Syamsudin, R. (2014). Pengaruh Penggunaan Mineral Lokal Zeolit Alam Terhadap Karakteristik Self-Compacting Concrete (SCC). *Jurnal Mahasiswa Jurusan Teknik Sipil*, 1(2), pp-439.
- Prima, A.I. 2012. *Penggunaan Zeolit Terimpregnasi TiO₂ untuk Mendegradasi Zat Warna Congo Red*. Skripsi Departemen Kimia, Fakultas Sains dan Teknologi. Universitas Airlangga. Surabaya.
- Sriatun dan Suhartana. (2002). *Impregnasi Nikel Klorida pada Zeolit-Y Untuk Katalis Hidrogenkah Minyak Bumi Fraksi 150-230°C*. Skripsi. Fakultas Matematika dan Ilmu Pengetahuan Alam. Universitas Diponegoro, Semarang
- Sulistyaningtyas, A. R., & Supriyadi, A. (2017). Produksi Miselium Jamur Ling ZHI (*Ganoderma lucidum*) Dalam Medium Air Kelapa Tua Dan Tauge Extract Broth Dengan Metode Kultur Terendam Teragitasi. *Bioma: Berkala Ilmiah Biologi*, 19(1), 58-61.
- Sulistyaningtyas, A. R., Prihastanti, E., & Hastuti, E. D. (2017). Performa Green Bean Kopi Robusta (*Coffea robusta* Lindl. Ex De Will) setelah Perendaman Limbah Tahu dengan Jenis dan Konsentrasi yang Berbeda. *Buletin Anatomi dan Fisiologi*, 2(2), 148-152.
- Sulistyaningtyas, A. R., Prihastanti, E., & Hastuti, E. D. (2018). Potential Of Liquid Tofu Waste For Decaffeination Of Robusta Coffee (*Coffea robusta* Lindl. Ex De Will). *Journal of Microbiology, Biotechnology & Food Sciences*, 8(1).
- Sunardi. 2011. *Penurunan kadar krom (VI) dengan Sargassum Sp Saccharomyces Cerevisiae dan kombinasinya pada limbah cair industri pabrik*. Karya Tulis Ilmiah Teknik Kimia. Surakarta. Solo: Universitas Setia Budi