Utilization of ZSM-5/TiO$_2$ Powder and Membrane to Reduce Concentration Cu(II) and Cr(VI) Ions in Water

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Abstract: Cancer is an effect caused by excessive concentrations of Cu(II) and Cr(VI) metal ions in the body. Including health effects of heavy metal ion poisoning industries arise when humans consume fish from various wastes, dyes, electroplating, paint, and battery. Techniques and processes have been developed to separate heavy metal ions which were very dangerous from water by ion exchange, chemical precipitation, and adsorption. Adsorption has no harmful side effects to health, simple, economical and easy to do. Natural materials can be used as adsorbents including ZSM-5, ZSM-5/TiO$_2$ powder, and membrane. The purpose of this study is to determine the initial, final concentration and the percentage decrease concentration of Cu(II) and Cr(VI) ions in water by ZSM-5/TiO$_2$ powder and membrane with variations gauze type and irradiation time. The results showed that the highest percentage reduction Cu(II) ion and Cr(VI) ion with 0.25% w/v ZSM-5/TiO$_2$ powder during UV irradiation 75 minutes were 74.99% and 16.99%. The highest percentage reduction in Cu (II) and Cr (VI) concentration after passing through the ZSM-5/TiO$_2$ membrane with gauze support 304-400 during 90 minute UV irradiation were 57.72% and 54.65%. As the conclusion ability of ZSM-5/TiO$_2$ powder is greater than the ZSM-5/TiO$_2$ membrane in reducing the concentration of Cu(II) and Cr(VI).

Keywords: Cu(II), Cr(VI), ZSM-5/TiO$_2$ powder, ZSM-5/TiO$_2$ membrane, irradiation time

1. Introduction
Cancer is a disease caused by excessive concentrations of Cu (II) and Cr (VI) metal ions in the body. Poisoning, nausea, vomiting, and causing damage to the liver and kidneys also caused by excess Cu (II) and Cr (VI) metal ions because it is carcinogenic, very toxic and very active in water [1, 2]. According to the Minister of Health Regulation No. 492 Menkes /Per /IV /2010 concerning the quality of drinking water, the maximum permissible Cuprum level is 2 mg/L and the maximum chromium of drinking water is 0.05 mg/L [3]. Techniques and processes have been developed to separate heavy metal ions which were very dangerous from water by ion exchange, chemical precipitation, and adsorption. 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. 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 adsorbents were synthetic TiO$_2$, ZSM-5, ZSM-5/TiO$_2$ powder and ZSM-5/TiO$_2$ membrane [1, 4, 5]. Many naturally-derived
polymers have been assessed for application as biomaterials specifically collagen, chitosan, keratin, and silk fibroin [6]. The purpose of this study is to determine the initial concentration of Cu (II) and Cr (VI) ions in artificial water, measure the levels of Cu (II) and Cr (VI) ions and the percentage decrease in the levels of Cu (II) and Cr (VI) ions in water and analyze the effectiveness of decreasing the concentration of Cu(II) and Cr(VI) ions by ZSM-5/TiO₂ powder and ZSM-5/TiO₂ membrane with variations gauze type and irradiation time.

1.1 Cu (II) and Cr(VI) Ion

Cu (II) ion is a component of the enzyme needed to produce energy, anti-oxidation, and synthesis of the hormone adrenaline, as well as for the formation of connective tissue. Cu (II) is an essential metal ion, and if excess will be detrimental to health, resulting in poisoning [1, 7]. Cr (III) is an essential nutrient very important for sugar metabolism and some enzyme reactions. Heavy metals can have health effects on humans depending on which part of the heavy metal is bound in the body. Chromium (VI) in chromate and dichromic form is very toxic which can cause skin and respiratory tract cancer [2, 5, 8].

1.2 Titanium Dioxide (TiO₂)

TiO₂ has a white crystalline shape, has a molecular weight of 79.8886 g/mol, the density of 4.23 g/cc, the 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 insoluble in water, hydrochloric acid, dilute sulfuric acid and alcohol, TiO₂ 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 amphiphilic properties, and is cheap and is stable at pH 4.5-8. TiO₂ is the most effective semiconductor catalyst because it has a relatively large band energy (3.2 eV) suitable for photocatalysts, non-toxic, and has a good absorbency to ultraviolet light [4, 9, 10, 11].

1.4 Zeolite Socony Mobile (ZSM-5)

ZSM-5 is a porous solid crystal with a three-dimensional structure containing aluminosilicate, built from (SiO₄)₄⁻ and (AlO₄)₄⁻ and has a tetrahedral bond with an oxygen atom forming a pentasil chain. ZSM-5 is a zeolite that is synthesized with high silica content, has pores of 2-50 nm and has two types of channels, the namely straight channel with size 5,3 Å × 5,6 Å and winding channel (zig-zag) with size 5.1 Å × 5.5 Å that connects one channel straight to another channel [12, 13, 14, 15].

1.5 ZSM-5 impregnated TiO₂

TiO₂ is the most effective semiconductor catalyst because it has a relatively large band energy (3.2 eV) suitable for photocatalysts, non-toxic, and has a good absorbency to ultraviolet light [9, 10, 11]. Photocatalyst TiO₂ is less than optimal if used in the pure state because it has a relatively low surface area. Thus, TiO₂ needs to be embedded in an adsorbent. The commonly used adsorbent is Zeolite ZSM-5 because it has an active group of silica-alumina (SiO₂·Al₂O₃), a large surface area, has a channel that can filter the ion or molecule to absorb heavy metals especially Cr (VI) metal [2, 5]. ZSM-5/TiO₂ membrane work can be improved by impregnating TiO₂ into supporting media ZSM-5 [1, 2, 4, 7, 8].

2. Research Methods

2.1 Tools and Materials

Materials of this study were Gauze of AISI 316-180, 304-200, 304-400, TiO₂, distilled water, K₂Cr₂O₇, CuSO₄·5H₂O, TPABr 0.1 M, NaAlO₂, ludox HS-40%, diphenylcarbazide, Na diethyl dithiocarbamate, HCl, NaOH, H₂SO₄, NH₄OH, and absolute ethanol. The tools used are analytic Balances, and Technical, UV-Vis spectrophotometer, flask, bowl, filter paper, pH meter, magnetic stirrer, sieve, funnel, stirring rod, rotator, static, burette, mortar, furnace and Reactor with UV lamp.
Object of this study was to use a solution 50 mg/L of Cr (VI) and Cu (II), then a decrease in Cr(VI) and Cu(II) levels in water using ZSM-5/TiO$_2$ powder and membrane with supports were type AISI 316-180, 304-200 and 304-400 and UV irradiation times are 30, 60 and 90 minutes.

2.2 Procedure

2.2.1 Gauze Treatment

Nine gauzes with 3 cm x 3 cm size on AISI 316-180 type is soaked in 15% w/v NaOH for 20 minutes (to remove oil/organic substances), then immersed in 15% v/v HCl solution for 20 minutes (to remove organic substances), then washed with aqua dest in ultrasonic for 20 minutes. Furthermore, it was oxidized electrochemically in H$_2$SO$_4$ 20% v/v with a constant voltage of 3-5 V and a current of 0.01Ampere, then dried at 110°C for 1 hour. The procedure was repeated for 304-400 and 304-200 mesh gauze support [16, 17].

2.2.2 Synthesis of ZSM-5/TiO$_2$ Powder and Membrane

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

Preparation of ZSM-5 zeolite by mixing 0.136 g NaAlO$_2$ and 1.390 g NaOH 50% w/v in propylene bottle 1. TPABr 1.549 g dissolved with 7.3802 g water into propylene 2 bottle and stirred with a magnetic stirrer for 5 minutes, then put into a propylene 1 bottle and added 24.940 g of Ludox HS-40% and stirring for 6 hours. Furthermore, the propylene 1 bottle is inserted in an oven with a temperature of 90 °C for 4 days. The white precipitate was washed and inserted into the oven at 60 °C for 24 h to obtain maximum drying and was heated in a furnace at 550 °C for 6 hours is crushed and sieved with a mesh size of 100 [11, 15].

2.2.2.2 Synthesis of ZSM-5/TiO$_2$ Powder

ZSM-5/TiO$_2$ precursors synthesis with 20 g of ZSM-5 powder is mixed with 1 g of TiO$_2$ and added with 20 mL of absolute ethanol and the mixture was stirred by using a magnetic stirrer for 5 hours, ZSM-5/TiO$_2$ precursors was dried in oven at 120 °C for 5 hours [1, 4, 5, 7, 8].

2.2.2.3 Synthesis of ZSM-5/TiO$_2$ Membrane

After treatment, AISI 316-180, 304-200, and 304-400 mesh gauze are embedded in ZSM-5/TiO$_2$ precursors in polypropylene plastic containers with a surface area to reactor volume ratio of 1.44 [16] and then heated in an oven at 120°C for 5 hours [4]. ZSM-5/TiO$_2$ membrane was washed with distilled water and heated at 60 °C for 3 hours [13, 15, 18, 19].

2.2.3 Decrease of Cr (VI) and Cu(II) Ions Concentration with ZSM-5/TiO$_2$ Powder and Membrane

Cr (VI) and Cu(II) sample solution 50 mg/L were channeled through the ZSM-5/TiO$_2$ powder with UV irradiation for 30 minutes and separated for filtrate. The resulting filtrate was calculated at Cr (VI) and Cu(II) final concentration. The treatment was repeated for time variations of 60 and 90 minutes [1, 2, 5, 6]. This procedure is repeated too or membrane with AISI 316-180 gauze, 304-400 and 304-200 gauze support [14, 15, 18, 19].

2.2.4 Determination of Cr (VI) and Cu(II) Ion concentration with Spectrophotometer

The filtrate solution resulting from a decrease Cr (VI) and Cu(II) concentration which has been flowed into the ZSM-5/TiO$_2$ powder and membrane with irradiation time 30, 60, and 90 minutes was taken 5.0 ml and put into 50.0 ml volumetric flask and then added ± 35 ml of distilled water, Diphenylcarbazide solution 2.5 ml is added Cr(VI) solution sample [2, 5, 8] and 5.0 mL NH$_4$OH 5% and 5.0 mL Na- diethyl dithiocarbamate (Cu (II) solution sample) which is adjusted with distilled water to mark the markers and homogenized, then the absorbance is read using a spectrophotometer at a wavelength of 540 nm (Cr(VI)), 480 nm (Cu (II) sample and a stability time of 5 minutes [1, 7, 18, 19].

2.2.5 Data Analysis

In this study, data were obtained from experiments and analyzed statistically using the Anova One Way test to determine whether there was an effect of variations in gauze type and UV irradiation time with ZSM-5/TiO$_2$ membranes on decreasing Cr (VI) and Cu (II) ion concentration in water.
3. Result and Discussion

3.1 Decrease of Cu(II) and Cr(VI) Concentration (%) with ZSM-5/TiO2 Powder

Decrease percentage of Cu(II) concentration (%) with 0.25 % w/v TiO2, ZSM-5, ZSM-5/TiO2 powder by UV irradiation time in Table 1 and decrease percentage of Cr(VI) concentration by ZSM-5/TiO2 Powder in Table 2.

| UV Irradiation Time (minute) | Percentage Decrease Cu²⁺ Concentration (%) TiO2 | ZSM-5 | TiO2 – ZSM-5 |
|-----------------------------|-----------------------------------------------|-------|--------------|
| 15                          | 46.69                                         | 67.13 | 68.30        |
| 30                          | 47.81                                         | 67.82 | 69.81        |
| 45                          | 49.45                                         | 68.39 | 71.46        |
| 60                          | 51.52                                         | 69.01 | 73.43        |
| 75                          | 54.29                                         | 69.49 | 74.99        |

Table 2. Decrease Percentage of Cr(VI) Concentration (%) with 0.75 % w/v TiO2, ZSM-5, ZSM-5/TiO2 Powder

| Irradiation Time (Minute) | The initial Cr (VI) Ion Concentration (mg/L) TiO2 | ZSM-5 | ZSM-5/TiO2 |
|---------------------------|-------------------------------------------------|-------|------------|
| 15                        | 42.64                                           | 15.21 | 13.33      | 17.01      |
| 30                        | 42.15                                           | 16.31 | 14.73      | 17.99      |
| 45                        | 41.83                                           | 17.40 | 15.72      | 18.99      |
| 60                        | 36.68                                           | 18.59 | 16.81      | 28.73      |
| 75                        | 32.92                                           | 22.76 | 22.07      | 36.20      |

Table 1 and Table 2 show the highest percentage decrease Cu (II) ion concentration with TiO2 ZSM-5, and ZSM-5/TiO2 powder (0.25 %w/v) and Cr(VI) concentration (0.75 %w/v) at UV irradiation time 75 minutes in a row is 74.99 and 36.20 %, The longer contact UV irradiation time of the ZSM-5/TiO2, so the more photon energy is absorbed by TiO2 photocatalysts and the ●OH more formed in photocatalysts and more contact between the ●OH and Cu (II) and Cr(VI) ion substrate also increases. As a comparison, the addition of ZSM-5/TiO2 0.25% w/v during the irradiation time of 75 minutes to decrease the concentration of Cu (II) and Cr (VI) ions was 74.99 and 1699%, respectively (Table 3).

| Concentration Powder (%w/v) | Decrease Cr (VI) Ion Concentration (%) TiO2 | ZSM-5 | ZSM-5/TiO2 |
|-----------------------------|-------------------------------------------|-------|------------|
| 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      |

Table 3 shows that the adsorption capability of ZSM-5 can be increased by impregnation with the supporting medium such as TiO2 to decrease Cr (VI) in water more optimally than using TiO2 and ZSM-5 only. These results are consistent with Agustý’s research (2012) that the greater the concentration of ZSM-5/TiO2 and the UV irradiation time, the greater the decrease in congo red color concentration [4]. The decrease Cu (II) ion concentration with the same ZSM-5/TiO2 concentration (0.25% w/v) is greater than the reduction in Cr (VI). This is due to the radius of Cu (II) ions greater than Cr (VI) ions so that the ability of ZSM-5/TiO2 to adsorption Cu (II) metal ions is higher than Cr (VI) ions concentration.

3.2 Decrease of Cu(II) and Cr(VI) Concentration (%) with ZSM-5/TiO2 Membrane
3.2.1 Decrease of Cu(II) Concentration Ion (%) with ZSM-5/TiO2 Membrane at time

Decrease percentage of Cu(II) concentration (%) with TiO2, ZSM-5, ZSM-5/TiO2 Membrane in Table 4 and Figure 1.

Table 4. Decrease Percentage Cu (II) Ion Concentration with Initial Concentration 47.13±0.53 mg/L

| Type of Gauze | Time (minute) | Gauze (%) | ZSM-5 / TiO2 Membrane (%) | Membrane weight(g) | Membrane zeolite ZSM-5/TiO2 UV (%) |
|--------------|---------------|-----------|---------------------------|-------------------|-----------------------------------|
| AISI 316-180 | 30            | 8.86      | 13.13                     | 0.1252            | 26.47                             |
|              | 60            | 9.46      | 13.54                     | 0.1143            | 33.20                             |
|              | 90            | 12.50     | 15.38                     | 0.1294            | 37.26                             |
| 304-200      | 30            | 9.80      | 15.98                     | 0.0909            | 31.26                             |
|              | 60            | 11.50     | 16.80                     | 0.1024            | 39.49                             |
|              | 90            | 13.13     | 18.23                     | 0.0977            | 41.72                             |
| 304-400      | 30            | 11.09     | 18.01                     | 0.1349            | 40.51                             |
|              | 60            | 13.54     | 20.05                     | 0.1284            | 48.56                             |
|              | 90            | 13.94     | 21.08                     | 0.1330            | 57.72                             |

Figure 1 Decrease of Cu(II) Ion Concentration (%) with ZSM-5/TiO2 Membrane from initial Cu(II) Ion Concentration 47.13±0.53 mg/L [19].

Table 4 and Figure 1 show that the highest percentage of reduction in Cu (II) ion concentration was ZSM-5/TiO2 membrane with 304-400 gauze support with 90 minutes irradiation of 57.72%, This is due to the pore size in the mesh (1 inch = 2.54 cm x 2.54 cm²) there are 400 holes, then in 1 inch the distance between holes in the gauze 304-400 is getting tighter so that the ZSM-5/TiO2 precursors attached stronger to the gauze. Thus, the decrease in Cu (II) ion concentration after getting through ZSM-5/TiO2 membrane with 304-400 gauze is higher than AISI 316-180 and 304-200 gauze supports.

3.3.2 Decrease of Cr(VI) Concentration (%) with ZSM-5/TiO2 Membrane

Table 5 and Figure 2 show that the highest percentage reduction in Cr(VI) ion concentration after getting through ZSM-5/TiO2 membrane with 304-400 gauze supports for 90 minutes irradiation time of 54.65%. The highest decrease in Cr(VI) ion levels was obtained with a UV irradiation time of 90 minutes. The longer the irradiation time the more photon energy is absorbed by the TiO2 photocatalyst so that the •OH greater formed in the photocatalyst. Contact between •OH and Cr (VI) ion substrate can increase the effectiveness of decreasing Cr (VI) ion levels.

Decrease of Cr(VI) Concentration (%) with ZSM-5/TiO2 Membrane in Table 5 and Figure 2.

Table 5. Decrease of Cr(VI) Concentration (%) with ZSM-5/TiO2 Membrane

| Type of Gauze | Time (%) | Gauze (%) | ZSM-5 / TiO2 Membrane (%) | Membrane weight(g) | ZSM-5/TiO2 Membrane with UV irradiation (%) |
|--------------|----------|-----------|---------------------------|-------------------|---------------------------------------------|
| AISI 316-180 | 30       | 11.96     | 15.53                     | 0.2459            | 16.51                                       |
|              | 60       | 12.30     | 16.42                     | 0.2390            | 22.92                                       |
|              | 90       | 12.49     | 16.78                     | 0.2182            | 29.65                                       |
Figure 2. Decrease of Cr(VI) Concentration (%) with ZSM-5/TiO₂ Membrane from initial Cr(VI) Concentration 50.73±0.18 mg/L [18].

The results of this study are consistent with the results of Azizah et al. (2016) research study. The effectiveness of ZSM-5 membrane size and contact time to decrease carbon monoxide gas levels from cigarette smoke with a time of 5, 10, 20 and 30 minutes also increased. In this study using ZSM-5/TiO₂ membrane with variations, the gauze supports and UV irradiation time also increased [20]. Decrease Cu(II) ion concentration with ZSM-5/TiO₂ powder and membrane is higher for Cr(VI) ion concentration because the Cu (II) ion radius is greater than the Cr (VI) ion radius so that the ZSM-5 TiO₂ membrane's ability to adsorb Cu (II) ions is also increased. The ability of ZSM-5/TiO₂ powder is greater than ZSM-5/TiO₂ membrane in reducing the concentration of Cu (II) and Cr (VI) ions because ZSM-5/ TiO₂ powder has a larger surface area so that when exposed to UV light then the amount of radicals OH is also more produced, so the ability to adsorb is also greater.

4. Conclusion
The highest percentage reduction in Cu (II) ion and Cr(VI) ion levels with 0.25% w/v ZSM-5/TiO₂ powder during UV irradiation for 75 minutes was 74.99% and 16.99%. The highest percentage of reduction in Cu (II) and Cr (VI) levels after passing through the ZSM-5/TiO₂ membrane with gauze buffer 304-400 during 90-minute UV irradiation is 57.72% and 54.65%. The ability of ZSM-5/TiO₂ powder is greater than ZSM-5/TiO₂ membrane in reducing the concentration of Cu (II) and Cr (VI).

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