Harmful Heavy Metals and Liquid Organic Waste Membrane Based on Fly-Ash/TiO$_2$-rGO Composite

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Abstract. This study utilized fly-ash and TiO$_2$/rGO as raw materials to produce membrane for absorbing harmful heavy metals and liquid organic waste. Graphene oxide (GO) was synthesized by using modified Hummer’s method and then transformed into reduced Graphene Oxide (rGO) by means of hydrothermal reduction at 160°C for 4 hours. The objective of this research was to identified the structure and morphology as well as the ability of the produced membrane to absorb heavy metals. The x-ray diffraction (XRD) examination showed the high purity of GO and rGO nanoparticles. Scanning electron microscopy (SEM) images for each TiO$_2$ concentration showed that membrane added with 1% TiO$_2$ result in homogenous distribution of TiO$_2$ and rGO on the surface of geopolymer. Atomic Absorption Spectroscopy (ASS) showing significant differences of Fe heavy metal of the contaminant concentration before and after filtration. Fe concentration in the first concentration was 1.226 ppm and become 0.239 ppm after filtration process was performed. The results of this study indicate that the membrane based on geopolymer/TiO$_2$-rGO contain 1% of TiO$_2$ and rGO relative to the mass of the starting fly-ash can be used as a membrane of heavy metal absorption.

1. Introduction

Water is an essential source of living for all creatures in our world [1]. Polluted water due to heavy metals has become a tremendous problem due to their toxicity, not degradable, and accumulation of heavy metals properties through food chain. Although heavy metals such as copper, selenium, and zinc are important for human being, their excessive usage will endanger the existence of living creatures [2]. Therefore, heavy metals and liquid organic compound must be overcome before channeling into the environment in order to prevent health and environmental risk [3, 4].

Polymeric membrane is an excellent type of membrane for liquid waste management but the manufacture cost is expensive and difficult to handle [5]. Pointed out that the performance of geopolymer in reducing heavy metals and colorant is comparable to those of membranes. Geopolymer is a friendly and widely use material due to its high mechanical strength, able to withstand heat and fire, high resistance to acid attack, and high definition of surface [6, 7]. Geopolymer is an excellent binder for fibers or inorganic and organic particulates to form functional composite [8]. One of the main source of aluminosilicate mineral for geopolymer production is fly ash resulted from coal burning in power plant [9, 10].
The performance of membranes for separating and purifying water can be improved by the addition of nanomaterials such as TiO$_2$, MgO, Al$_2$O$_3$, AgO, C-nanotube, graphene, Fe$_2$O$_3$, zeolites, and CuO into the network of membrane material [11]. TiO$_2$ has important optical properties, non-toxic, high refraction index, high dielectric constant and transmission [12-14]. The advantages of using TiO$_2$ are able to prevent corrosion, easy to clean, cheap and anti-bacteria [15-17].

Reduced Graphene Oxide (rGO) is a modified form of graphene oxide (GO) to reduce to oxygen content [18]. According to [19] the addition of graphite into TiO$_2$ is a method to improve its photocatalytic efficiency due to the enhancement of specific surface area and its carrier mobility [20]. During the transformation of GO into rGO nanopores are created which suitable to be designed as thin film membrane [21]. Previous research showed that material based on rGO produced membrane with high selectivity, and permeable which suitable for water purification. Wang et al. [22] investigated the influence of carbon nanotube-rGO (CNT-rGO) structure on the selectivity and permeability of the membrane for water purification. The addition of TiO$_2$ or ZnO will enhance the photocatalytic properties of rGO [23].

2. Methodology

2.1 Reduced Graphene Oxide (rGO) Synthesis using Hummer’s Method

An amount of 5 g of graphite particle was mixed with 600 ml H$_2$SO$_4$ and 80 ml H$_3$PO$_4$ into a beaker glass. The solution was stirred for 1 hour at room temperature. Next, 15 g was added into graphite solution, H$_2$SO$_4$, and H$_3$PO$_4$ while stir continuously at constant temperature for 15 hours with a speed of 340 rpm. The solution was cooled with 400 ml ice block. The reaction was terminated by the addition of 5 ml H$_2$O$_2$. GO suspension was centrifuged for 4 hours with a speed of 5000 rpm. The final solution was filtered, washed with HCl, ethanol and deionized water until neutral pH was reached. The resulting material was dried and leave in a vacuum chamber at 40°C for 24 hours and graphene oxide (GO) particles was obtained.

An amount of 0.5 GO particle was put inside an autoclave which contained 220 ml distilled water and then stir continuously until the mixture was homogenous. Autoclave was sealed and put in an oven at 160°C for 4 hours. The autoclave was cooled at room temperature for 24 hours. The solution was decanted leaving rGO particles at the bottom of the autoclave. rGO particles was washed with acetone and poured into a small container. Finally, the resulting rGO was left at room temperature for 24 hours.

2.2 The Production of Geopolymer Membrane

Geopolymer paste was produced through alkali (NaOH + Na$_2$SiO$_2$ + H$_2$O) activation method of fly ash. The mixture was stirred manually until homogenous paste was obtained. An amount of predetermined mass of rGO was mixed with geopolymer paste and stir continuously. TiO$_2$ particles was then added and stir until the mixture was homogenous, and poured into a sealed mold. The sample was then cured at 50°C for 4 hours and the sample was demolded 24 hours later.

2.3 Absorption Test of Geopolymer Fly-Ash/TiO$_2$-rGO Membrane

Vickers hardness is one of a method to measure the hardness of a material. Vickers test procedure as per [7] standard specifies making indentation with a range of loads using a diamond indenter which is then measured and converted to a hardness value.

3. Results and Discussion

3.1 X-Ray Diffraction (XRD)

Figure 1 shows the XRD result of the ball milling TiO$_2$ for 10 hours at 200 rpm. The main phase of TiO$_2$ was anatase and it is well known that pH in sol-gel method of TiO$_2$ influence the size and crystallinity level of TiO$_2$. Low pH will result in rutile phase, while high pH will produce anatase phase.
Figure 1. Diffractogram of TiO$_2$ nanoparticles.

Figure 2 shows the diffractograms of GO and rGO synthesized through modified Hummer’s method. The result confirmed the transformation of GO into rGO due to hydrothermal process. The diffractogram of the produced rGO is similar to those reported by [24] whose investigated the crystallinity level, photocurrent respon and optical properties due to the reduction of rGO in each concentration of ZnO.

Figure 2. XRD Pattern of GO and rGO particles.

Diffractogram of membrane specimens produced in this study is plotted in Figure 3 showing different concentration of TiO$_2$. The addition of both rGO and TiO$_2$ did not change the structure of geopolymer except that the peak of TiO$_2$ become more discernible as its concentration increase. The presence of rGO is identified as the peak of carbon (C).
3.2 Heavy Metal (Fe) Contaminant

The example of heavy metal (Fe) contaminants is showed in Figure 4. There were three different concentration of Fe used in this study, namely contaminant 1, 2, and 3. The samples were produced by dissolving Fe compound into distilled water.

3.3 Fourier Transform Infra-Red (FTIR) Characterization

FTIR technique was used to examine the functional groups of atoms or molecules formed in the network of geopolymer/TiO$_2$-rGO as shown in Figure 5. The broad band centered around 3300 cm$^{-1}$ is a vibration of of water OH- and the band at 1090 cm$^{-1}$ is a identified a stretching of Si – O – Al confirming the structure of geopolymer [25]. A weak band between 1400 – 1500 cm$^{-1}$ is due to the vibration of Al-OH and Si – O.
3.4 Scanning Electron Microscopy (SEM) Examination

Figure 6 showed surfaces morphology of rGO, geopolymer paste, and geopolymer/TiO$_2$-rGO membranes examined by using Tescan Vega3 SEM.

Figure 5. FTIR spectrum of geopolymer/TiO$_2$-rGO membrane.

Figure 6. SEM images of (a) rGO particles (b) geopolymer paste, (c) geopolymer/0.5%TiO$_2$-1%rGO, and (d) geopolymer/1.5% TiO$_2$-1%rGO.
3.5 Atomic Absorption Spectroscopy Result

Figure 4 shows the picture of liquid contain Fe contaminant before and after filtration process was conducted. It can be seen clearly the difference in color between the two, indicating the membrane was working very good to absorb Fe. Figure 7 is a graph of AAS result for liquid waste before and after filtration.

![Figure 7. The results of AAS examination.](image)

The concentration of Fe in contaminant 3 before filtration was 8.224 ppm and 0.909 after filtration process took place using geopolymer/TiO$_2$-rGO membrane. This result indicate that the membrane produced in this study contained micro pores which able to absorb Fe atom during filtration process.

The results of this study suggest that the membrane based on geopolymer/TiO$_2$-rGO has a big potential to be applied in our daily life or in industrial scale for water purification due to heavy metals pollutant in water stream.

4. Conclusions

Membrane inorganic based on geopolymer/1%TiO$_2$-1% rGO nanocomposite offer high potential to be applied for water purification by absorbing heavy metals contaminant from water source. The AAS results showed that geopolymer/TiO$_2$-rGO membrane were able to absorb Fe from water stream from 8.224 ppm into 0.909 ppm after filtration process took place.

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