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Synthesis and Photocatalytic Activity of Silica-based Sand Quartz as the Supporting TiO_2 Photocatalyst

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Abstract

TiO_2-SiO_2 photocatalyst was prepared by immobilizing TiO_2 on natural quartz sand SiO_2. The Scanning Electron Microscope-Energy-Dispersive X-ray Spectroscopy (SEM-EDS) and X-Ray Diffraction (XRD) were used to characterize the morphology and structure of the photocatalyst. The photocatalytic activity of the synthesized catalyst was evaluated by applying the catalyst for photocatalytic decomposition of chromium (VI). The concentration of chromium (VI) before and after the photocatalytic decomposition was determined using atomic absorption spectroscopy (AAS). SEM-EDS results of TiO_2-SiO_2 photocatalyst showed homogenous aggregate. XRD characterization result of the synthesized catalyst showed that TiO_2 was in anatase crystalline state, while SiO_2 was in amorphous state. The results of the present study indicate that 20% (w/w) TiO_2-SiO_2 photocatalyst has the highest activity by reducing 92.24% chromium (VI) in the photocatalytic decomposition test.

Keywords: quartz sand, natural resource, photocatalyst, SiO_2, TiO_2

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1. Introduction

Quartz sand material entrenchment is composed of silica crystals (SiO_2) and other impurities which carried away during deposition process. Quartz sand, which also known as white sand, is the weathering rocks containing minerals mainly quartz and feldspar. The result of weathering then leached and carried away by water or wind, and settles at the edges of rivers, lakes or sea. Quartz sand is mainly composed of SiO_2, Fe_2O_3, Al_2O_3, TiO_2, CaO, MgO, and K_2O[1].

Natural quartz sand is mixed with impurities and other oxide groups which blended during the weathering process and natural sand formation and also very long interaction process with the environment. Extraction methods at low temperature have been used for obtaining silica from rice husk ashes. This method was developed based on the nature of solubility of amorphous silica. High solubility of amorphous silica at alkaline condition lead to extractable silica from siliceous materials. Silica extraction from rice husk ashes produce high concentration of silica xerogel (91%)[2].

Structure, density and mechanical force of silica xerogel are strongly influenced by pH and concentration of silica gel. Overall, the utilization of siliceous quartz sand using extraction at low temperatures is very potential for fabrication of silica xerogel. High silica content in quartz sand can be utilized as enabler in TiO_2 photocatalyst and applied to decrease heavy metal concentration such as chromium[3].

Photocatalysis is a technology for treating toxic and dangerous waste. Photocatalysis, an effective and in-expensive process, is a combination of a photochemical process and catalysis. The photocatalytic process treats waswater and removal toxic and dangerous substances[4]. Kajitvichyanukul et al. (2005)[5], observed that catalyst immobilization in the substrate could increase photocatalytic efficiency. The photocatalytic process is inefficient if TiO_2 is used in powder form. This form disperses homogenously in water and produces milky dispersion. Therefore, the catalyst is difficult to recover. To measure the residue from the photocatalytic process, the solution must be clear. Ultraviolet light cannot activate a catalyst in a turbin solution. Consequently, catalyst immobilization in a substrate, in granule form, chould produce a clear, easy-to-handle solution.

When the light ($h\nu$) from photon light interact with a catalyst article, electrones and holes form according to the reaction $TiO_2 + h\nu \rightarrow e^- + h^+$. Electrons exist in the conduction band, and the hole is in the valence band. Hole produced by TiO_2 are very active and oxidize many compounds. Electrons in the presence of oxygen can also produce an active form of oxygen that runs in

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the reduction process. Joshi and Shrivastava. (2011)[6] stated that the charges can react directly with adsorbed pollutants, but reactions with water are more likely since the water molecules are far more numerous than contaminant molecules. Oxidation of water or OH by the hole produce the hydroxyl radical (·OH), an extremely powerful oxidant.

In this study, a photocatalytic reactor was designed in which the type of catalyst used in the degradation process varied. Thiruvenkatachari et al. (2008)[7], showed that the photocatalytic process was directed by the catalyst, source of light, and reactor configuration. The amount of TiO_2-SiO_2 used in the photocatalytic process was measured by determining of Cr(VI).

2. Experimental

2.1. Silica extraction

A sieving machine was used to get 325 mesh quartz sand particles followed by soaking in 2 M HCl for 12 h. The residue was washed using distilled water until no yellowish color detected on the filtrate, followed by drying at 110°C and reacted with 3 M NaOH at 95°C with stirring for 4 h. The solution was filtered using a fine filter paper. When the filtrate reached room temperature, 6 M HCl was added gradually until gel was formed. The gel was left for 18 h, followed by washing with distilled water and dried at 110°C until no moisture detected. Silica powders were tested using SEM - EDS.

2.2. Preparation of TiO_2 - SiO_2 Photocatalyst

TiO_2 - SiO_2 photocatalyst was prepared by immobilization of TiO_2 on SiO_2 with varying concentrations of TiO_2 (10, 20, and 50% w/w) on SiO_2. To a sonicated TiO_2 in distilled water, SiO_2 was added and further sonicated. Subsequently, the mixture of water - TiO_2 - SiO_2 was then heated on a hot plate until paste was formed. Finally, the paste was dried using oven and calcinated using furnace at 100°C and 500°C, respectively.

2.3. Photocatalytic Test

Photocatalytic test was performed using mercury lamp. In this test, 2.6 ppm chromium (VI) solution was used to determine the photocatalytic degradation. The solution was placed into a quartz tube and the photocatalyst was added followed by irradiation under mercury lamp for 4 hours. Samples were taken every 1 hour interval up to 4 h and the chromium (VI) was determined using AAS. Photocatalytic test was performed for all composition variation of TiO_2 - SiO_2 photocatalyst synthesized and TiO_2 was used as control.

3. Results and Discussion

The sample tube was made of quartz glass, because of the quartz glass transmits UV light. A 100 W UV-lamp was used as the photon source and placed on the up of the tube[6]. The wavelength of the lamp ranged from 315 to 400 nm, wheares the peak appeared at 352 or 368 nm with E_{bg} 3.37 and 3.52 eV.

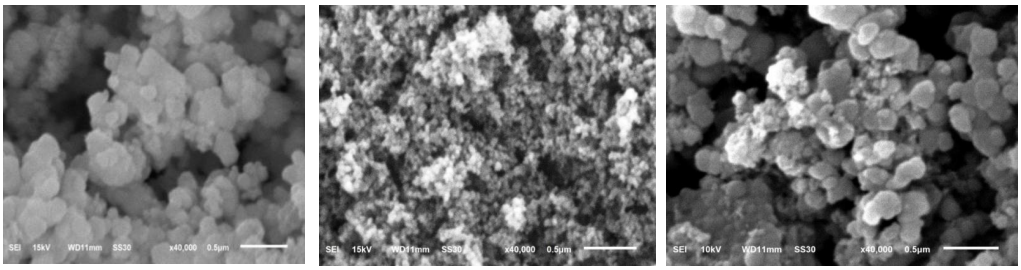
The irradiation process was carried out in a closed system (enclosed in containers made of wood). The closed system kept the radiation inside the reactor, to make catalyst absorb the maximum UV light. Irradation for 4 h increases the system temperature. Therefore, the reactor was equipped with a blower. The catalyts were put in a sample tube that contained the sampel solution and constantly stirred to produce a homogenous catalyst system.

Immobilization of TiO_2 on SiO_2 followed the slurry precipitation method/dip coating method (Thiruvenkatachari et al., 2008)[8] with a specific composition. The catalyst was mixed with silica, and then the mixture were sonicated. After the water evaporated, calcination was carried out at 100°C and 500°C.

Table 1 presents the composition of quartz sand used in the present study. The SiO_2 content of the sand was 78.28%. The extraction process increase SiO_2 purity to 91.19%. Reduction of metal oxide levels lead to an increase in SiO_2 content from 78.28 to 91.19%. This indicates that the quartz sand with acid leaching dissolved other metal oxide.

Table 1. Composition of quartz sand

Metal oxide	Composition (%)	
	Quartz sand	Extraction results
SiO_2	78.28	91.19
Re_2O_7	21.72	-
Na_2O	-	3.66



(a) (b) (c)

Fig. 1. The SEM image of SiO_2 (a), TiO_2 (b), and 20% TiO_2-SiO_2 (c)

Figure 1 shows the morphology of SiO_2 [Fig. 1 (a)], TiO_2 (Figure 1 (b), and 20% w/w TiO_2 - SiO_2 [Figure 1 (c)]. Figure 1 (a) and (b) shows that SiO_2 and TiO_2 are forming overlap aggregates. The morphology of the TiO_2 photocatalyst are nano-sized particles that have a wide sufrace. The size of the SiO_2 particles is not uniform in the profile obtained. The presence of TiO_2 immobilized on SiO_2 was obvious by the presence of white spots around the SiO_2 surface, even in small quantities [Figure1 (c)].

Characterization of the TiO_2 – SiO_2 photocatalyst by XRD was performed to determine whether TiO_2 already propped up on SiO_2. The XRD pattern is shown on Figure 2, XRD results of TiO_2 - SiO_2 photocatalyst showed very high intensity peak at 2θ = 25.04°, a characteristic area of anatase TiO_2 crystals types. This is similar to the identity of anatase phase of TiO_2 Degussa P25 as a comparison (2θ = 25.29) and 2θ = 27.4° which is a rutile TiO_2 crystal region type.

The rutile crystal on TiO_2 Degussa P25 disappeared in the immobilized catalyst due to the calcination process. Then a stable anatase crystalline phase appeared in these condition. According to Joshi and Shrivastava. (2011)[6], this situation indicates that calcination techniques can change amorphous TiO_2 to become crystalline anatase, not rutil crystals (Kajitvichyanukul et al., 2005)[5]. The presence of amorphous SiO_2 can be detected by low intensity sharp peak at 2θ = 20.98°. However, no peak detected at this region on the XRD pattern, which indicate there were no SiO_2 crystalline regions.

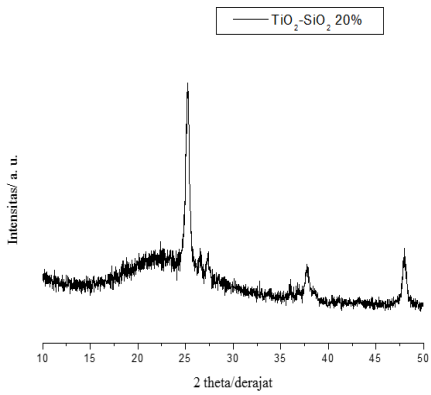


Fig. 2. XRD pattern of 20% TiO_2-SiO_2 photocatalyst

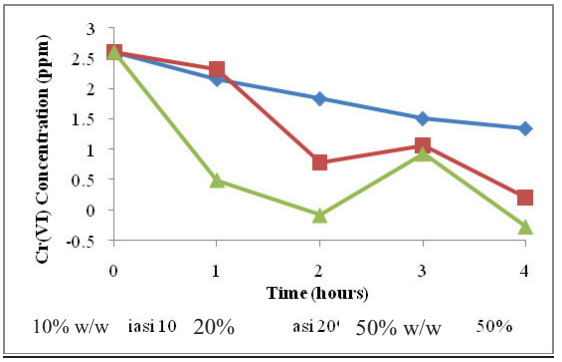


Fig. 3 The decline in the concentration of Cr (VI) using the TiO_2 - SiO_2 photocatalyst

Photocatalytic degradation of inorganic material, that is, metal ions Cr (VI) in aqueous solution as a model of industrial waste sample, was performed. The measurment results for TiO_2-SiO_2 in 50 mL of metal ion Cr (VI) in the designed reactor is shown in Figure 3. In the Figure 3, shows that 20% w/w TiO_2-SiO_2 photocatalyst gave the best performance in decreasing chromium (VI) concentration. When 20% w/w TiO_2-SiO_2 photocatalyst used in the photocatalytic process for 4 h, it can reduce 92.24% of the chromium (VI) content. The role of reduction of TiO_2-SiO_2 was comparable to its oxidation ability, by increasing the duration of the photocatalytic processes until 4 h, the Cr (VI) concentration in solution decreased. Joshi and Shrivastava. (2011)[6] eliminated the toxic hexavalent form of Cr (VI) from wastewater, using TiO_2, ZnO, and CdS. They concluded that photocatalysis is a promising technique for removing heavy metals from industrial effluents. In addition, Qiu et al. (2012)[9] proved that Cr (VI) and phenol could be degraded simultaneously by using TiO_2 induced with visible light.

The result was not comparable by Destiarti et al. (2015)[10] observed that by increasing the duration of the photocatalytic processes, the Cr (VI) concentrations in solution remained constant for 8 h. Therefore, TiO_2-SiO_2 cannot reduce Cr (VI). That result might be caused by specific properties of the catalyst in metal reduction. Additional research on TiO_2-SiO_2 in decreasing other metals is required.

Conclusions

Low temperature extraction method was successfully increased the SiO_2 content from quartz sand up to 91.19%. XRD data of the TiO_2-SiO_2 photocatalyst indicate that TiO_2 was immobilized on SiO_2. Titanium dioxide immobilized on silica can be used in a photocatalytic process to dangerous waste. Photocatalytic test of the synthesised photocatalyst indicate that 20% w/w TiO_2-SiO_2 was the best composition to reduce chromium (VI) concentration by reducing 92.24% of the metal ion in the sampel solution, while TiO_2 as control only reduce 75.40% chromium (VI) in the solution.

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