

Article

Synthesis of Titanium Dioxide/Silicon Dioxide from Beach Sand as Photocatalyst for Cr and Pb Remediation

Diana Rakhmawaty Eddy ¹,*¹, Soraya Nur Ishmah ¹, Muhamad Diki Permana ¹, Muhamad Permana ¹

- ¹ Department of Chemistry, Faculty of Mathematics and Sciences, Universitas Padjadjaran, Jl. Raya Bandung-Sumedang km. 21 Jatinangor, Sumedang, Jawa Barat 45363, Indonesia; sorayanurishmah@gmail.com (S.N.I.); muh.dikip18@gmail.com (M.D.P.)
- ² Graduate School of Science Education, Bengkulu University, Jl. W.R. Supratman Kandang Limun, Bengkulu 38371, Indonesia; lutfi@unib.ac.id
- * Correspondence: diana.rahmawati@unpad.ac.id; Tel.: +62-8132-273-1173

Received: 30 September 2020; Accepted: 27 October 2020; Published: 29 October 2020



Abstract: Heavy metals are non-biodegradable and have a high toxicity effect on microorganisms which makes their presence in the environment extremely dangerous. The method of handling heavy metal waste by photocatalysis techniques using TiO_2/SiO_2 composite showed a good performance in reducing harmful pollutants. In this study, SiO₂ from Bengkulu beach sand, Indonesia, was used as a support material for TiO_2 photocatalyst to remove Cr(VI) and Pb(II). SiO₂ was obtained through leaching techniques using NaOH as a solvent. The TiO_2/SiO_2 composite photocatalyst was synthesized using a solvothermal method at 130 °C and then characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and a particle size analyzer (PSA). Based on the XRD diffractogram, the synthesized TiO_2 showed the anatase structure while the SiO₂ showed the amorphous structure. The Ti-O-Si bond is defined in the infrared (IR) spectra, which indicates that the relationship between TiO_2 and SiO_2 is a chemical interaction. The results of SEM and PSA characterizations show agglomerated spherical (round) particles with a mean particle size of 616.9 nm. The TiO_2/SiO_2 composite of 7:1 ratio showed the highest photocatalytic activity after 180 min of ultraviolet (UV) irradiation, with a concentration-decrease percentage of 93.77% and 93.55% for Cr(VI) and Pb(II), respectively.

Keywords: photocatalyst; TiO₂/SiO₂ composite; solvothermal; silica sand

1. Introduction

The rapid growth of technology and manufacturing results in an increase in waste pollution to the environment. Heavy metals from industrial waste are one of contributors to water pollution [1]. These toxic metals cannot be broken down by microorganisms, and when accumulated in the body cause severe illness and even death [2]. Chromium or Cr is a metal that is commonly found in the environment because it is widely used in large industries such as metal coating, petrochemicals, mining, fertilizer, tanning leather, batteries, pesticides and the paper industry [2]. Chromium commonly comes in two forms, trivalent chromium Cr(III) and hexavalent chromium Cr(VI). Chromium in hexavalent form is 500 times more carcinogenic and very toxic compared to its trivalent form because it penetrates cell membranes and causes harmful effects. The maximum acceptable environmental threshold values for Cr(III) and Cr(VI) are 5 mg/L and 0.05 mg/L, respectively [1].

Besides chromium, water pollution due to the presence of lead is another global concern. Lead or Pb(II) is among the dangerous contaminants found in industrial waste. This compound causes



mutations and is carcinogenic. Besides human activities that produce Pb, it is also naturally present in water. Pb undergoes crystallization in the air and is subsequently dissolved in rainwater that enters water bodies such as rivers and lakes [3]. Indonesian government regulations stipulate that the maximum acceptable of Pb level for conventional drinking water treatment is $\leq 0.1 \text{ mg/L}$ [4].

Several methods for removing heavy metals from the environment have been actively investigated through various techniques such as adsorption, cross-flow microfiltration, precipitation and reverse osmosis [1,2]. However, these methods are relatively expensive and often inefficient when working at low concentrations. The method of photocatalysis using semiconductor material has the potential to reduce harmful pollutants and is also effective when working at low concentrations of Cr [5] and Pb [6].

Titanium dioxide (TiO₂) is a semiconductor material widely used as a photocatalyst in the purifying wastewater process because it has many advantages such as high photocatalytic activity, high chemical stability when exposed to acidic and basic compounds, high oxidizing power, and low toxicity and it is easy to obtain [7]. Anatase is a form of photocatalyst claimed to be the best for photocatalytic activity, but its transformation into rutile is a weakness that limits its photocatalytic activity. Several studies have been conducted to overcome this problem by modifying the surface of TiO₂ and synthesizing composite catalysts such as TiO₂/SiO₂, TiO₂/ZrO₂, TiO₂/Al₂O₃/SiO₂, and TiO₂/ZrO₂/Al₂O₃ [8]. Furthermore, the modification of TiO₂ using SiO₂ material to improve photocatalytic activity shows a high thermal stability and mechanical strength, and increases the active side of the photocatalyst surface. Another advantage of TiO₂/SiO₂ mixed oxides is that it inhibits agglomeration of TiO₂ and transformation from anatase to rutile [7].

Silica is obtained from both organic and inorganic natural materials, by synthesis and extraction. Based on the types of natural materials that are non-biological, silica is obtained from sand and coal waste such as flying ash sludge. Beach sand is one of sources of natural silica which is very abundant. Eddy et al. [9] extracted silica successfully from Palangkaraya beach sand, Indonesia with a benefit of 91.19% and Munasir et al. [10] extracted silica successfully from Tuban beach sand, Indonesia, reaching 98.9% gain. In addition, Ishmah et al. [11] and Firdaus et al. [12] have succeeded in extracting silica from Bengkulu beach sand, Indonesia, by 97.3% and 99.5%, respectively. In this research, we evaluated the extraction of silicon dioxide (SiO₂) from beach sand precursors and subsequently composite with titanium dioxide (TiO₂) as a photocatalyst for decreasing the concentrations of Cr(VI) and Pb(II).

2. Results and Discussion

2.1. Characterization of Catalyst

The solvothermal method is widely used for the manufacture of oxides and is usually performed at temperatures below 400 °C. The basic principle of this method is the growth of crystals based on material solubility in solvents under high-pressure conditions. Medium temperature conditions are generally used to increase chemical diffusion while high pressure results in lesser energy consumption compared to temperature. Calcination temperature in the synthesis process has a significant impact on the TiO₂ crystallinity phase, as it also affects the band gap energy value, which has a significant effect on photocatalytic performance. The anatase TiO₂ phase is the best TiO₂ crystal phase to be used in the photocatalytic process with 3.23 eV band gap energy. Based on research by [13], structures with optimal anatase phases are formed at temperatures of 400–600 °C. At temperatures above 600 °C, i.e., at 700 °C, the anatase structure phase begins to be transformed into rutile, the surface area decreases, and the photocatalyst activity is drastically weakened [14].

X-ray diffraction (XRD) analysis of TiO₂/SiO₂ composites was carried out to determine the characteristics of the TiO₂ formed. The resulting diffractogram showed conformity to Inorganic Crystal Structure Database (ICSD) 98-015-5245 for amorphous SiO₂ structures (tetragonal, space group P41/212), ICSD 98-017-2916 for TiO₂ anatase structures (tetragonal, space group I41/amd) and ICSD 98-016-7961 for TiO₂ rutile structures (tetragonal, space group P42/mnm). The TiO₂ P25 Degussa crystal showed a peak pattern with the peaks at $2\theta = 25.3^{\circ}$, 37.8° , 48.0° , 53.9° , 55.0° , 62.7° , 68.8° , 70.3° , and 75.1° that

might belong to (011), (004), (020), (015), (121), (024), (116), (220), and (125) crystal planes of anatase phase respectively. Moreover, the peaks at 27.4° and 36.1° were ascribed to the (110) and (011) planes of rutile phase. For TiO_2/SiO_2 composites there was an additional peak at 24.1° that was ascribed to the (011) planes of amorphous SiO₂ phase. Figure 1 shows that the composition of $TiO_2:SiO_2$ affects the peak intensity and the sharpness of the peak produced, while the higher the content of TiO_2 causes the sharpness of the peak intensity.



Figure 1. X-ray diffraction (XRD) pattern of (**a**) TiO_2 P25; (**b**) TiO_2/SiO_2 (1:1) composite; (**c**) TiO_2/SiO_2 (3:1) composite and; (**d**) TiO_2/SiO_2 (7:1) composite.

Using the High Score Plus software (PANalytical 3.0.5), a Rietveld refinement of the photocatalysts was performed. Table 1 shows that composite has a different anatase/rutile phase ratio. This shows that the SiO₂ plays a role in the formation of the anatase and rutile phase of TiO₂. At the same calcination temperature (500 °C), TiO₂:SiO₂ (7:1) shows the highest anatase/rutile phase ratio, this indicates that little amount of SiO₂ can effectively inhibit the transformation phase of anatase to rutile. However, excess SiO₂ added is also ineffective for inhibiting this transformation.

Table 1. Percentage of anatase, rutile and amorphous SiO₂ phase in photocatalysts.

Photocatalysts	Phase (%)			
	Anatase	Rutile	Amorphous SiO ₂	
TiO ₂ P25	85.7	14.3	-	
TiO ₂ :SiO ₂ (1:1)	49.0	6.5	44.4	
TiO ₂ :SiO ₂ (3:1)	69.0	8.3	22.6	
TiO ₂ :SiO ₂ (7:1)	97.9	0.9	1.2	

Crystallite size was determined using the Scherrer Equation [9]:

$$B = \frac{K\lambda}{D\cos\theta}$$
(1)

where D is the crystallite size, K is the Scherrer constant (0.9), λ is the wavelength of the X-ray radiation, B is the value of the peak FWHM (full width at half maximum), and θ is the diffraction angle.

The crystallite size is obtained in Table 2. The values of B and θ are taken for crystal plane (011). The peaks corresponding to (011) plane of the TiO₂:SiO₂ composite shift slightly to higher values of 2 θ and have wide peaks. The shift in the peak position to a higher angle (lower D value) may have resulted from the presence of SiO₂. Lower D value implies compressive strain, which may emanate from the presence of the Si–O–Ti bonding characteristics. For TiO₂:SiO₂ (7:1) composite, the percentage of rutile and amorphous SiO₂ phase were too low, making it inaccurate when calculating the crystallite size.

Dhata satalasta	Crystallite Size (nm)			
Photocatalysts -	Anatase	Rutile	Amorphous SiO ₂	
TiO ₂ P25	32.84	22.59	-	
TiO ₂ :SiO ₂ (1:1)	8.79	9.01	2.57	
TiO ₂ :SiO ₂ (3:1)	11.79	7.16	2.59	
TiO ₂ :SiO ₂ (7:1)	11.58	-	-	

Table 2. The crystallite size of photocatalysts.

Fourier transform infrared spectroscopy (FTIR) analysis was carried out to classify functional groups in the photocatalysts. The FTIR spectrum in the range 400–4000 cm⁻¹ of photocatalysts is shown in Figure 2. The strong and dominant absorption peak found in wave number 1090–1110 cm⁻¹ is the asymmetrical extension of the Si–O–Si (siloxane) bond. The peak presence at wave 798 cm⁻¹ indicates the vibrational strain of the Si–OH bond (silanol) in the amorphous SiO₂ structure. The absorption peak at wave number 475 cm⁻¹ is caused by O–Si–O (siloxy) bonding vibrations [11]. The peaks observed at 667–711 cm⁻¹ are ascribed to the Ti–O and O–Ti–O absorption bands [15]. The infrared (IR) absorption band characteristics at wave numbers 3411–3467 cm⁻¹ are the O–H stretching vibrations while at 1631–1638 cm⁻¹ they are a typical absorption for O–H bending vibrations [16] due to the surface hydroxyl group. The content of hydroxyl ions are very important for photocatalytic activity. The holes resulting from photogeneration on the surface of the catalyst react with hydroxyl ions to produce hydroxyl radicals, which are strong oxidants [15].



Figure 2. Fourier transform infrared (FTIR) spectrum of (**a**) SiO_2 ; (**b**) TiO_2 P25; (**c**) TiO_2/SiO_2 (1:1) composite; (**d**) TiO_2/SiO_2 (3:1) composite and; (**e**) TiO_2/SiO_2 (7:1) composite.

A typical characteristic band of SiO_2 and TiO_2 P25 was present in all composites, indicating the composite process was successful. The O–H stretching and bending vibrations observed in all

photocatalysts. The intensity of the O–H absorption peak increases with the addition of SiO₂. This can be understood by the fact that the characteristic of pure SiO₂ has properties of good adsorption of water from its surface [17]. In addition, the difference in O–H intensity between SiO₂ and TiO₂ P25 indicates that SiO₂ has an active O–H side which is good for surface reaction processes. TiO₂/SiO₂ composite formation is characterized by Ti–O–Si bond appearance in the IR spectrum at 940–960 cm⁻¹ wavelengths [17]. Table 3 shows the types of bonds present in SiO₂, TiO₂ and TiO₂/SiO₂ composite. The Ti–O–Si vibrational peak presence indicates that the interaction between TiO₂ and SiO₂ is a chemical reaction process (chemical bonding occurs) rather than a simple physical mixing process.

Bond Type	SiO ₂	TiO ₂ P25	TiO ₂ :SiO ₂ (1:1)	TiO ₂ :SiO ₂ (3:1)	TiO ₂ :SiO ₂ (7:1)
O–H streching	3467 cm^{-1}	3411 cm^{-1}	3429 cm^{-1}	3411 cm^{-1}	3429 cm^{-1}
O–H bending	1638 cm^{-1}	1635 cm^{-1}	1634 cm^{-1}	1631 cm^{-1}	1636 cm^{-1}
Si-O-Si	1091 cm^{-1}	-	1100 cm^{-1}	1105 cm^{-1}	1102 cm^{-1}
Ti-O-Ti	-	667 cm^{-1}	711 cm^{-1}	671 cm^{-1}	667 cm^{-1}
Ti-O-Si	-	-	942 cm^{-1}	958 cm^{-1}	942 cm^{-1}

Table 3. Wavenumber of SiO₂, TiO₂ P25 and TiO₂/SiO₂ composite for FTIR characterization.

Scanning electron microscopy (SEM) analysis is carried out to determine the morphology of TiO_2/SiO_2 composites. Based on the 7000-fold magnification SEM analysis shown in Figure 3, it is known that the TiO_2/SiO_2 composite particles are spherical (round) and agglomeration occurs.



Figure 3. The TiO_2/SiO_2 composite morphology by scanning electron microscopy (SEM).

The Energy Dispersive X-ray Spectroscopy (EDS) qualitative analysis is performed to determine the composition of TiO_2/SiO_2 composites. This analysis is based on the X-ray radiation emitted by the atoms in the sample. Figure 4 indicates that the EDS analysis of TiO_2/SiO_2 composites with ratio 3:1, as shown in the sample, elements of titanium (Ti), silicon (Si) and oxygen (O) with atomic percent, are 17.94%, 3.43% and 78.62%, respectively.

Particle size analysis (PSA) research on TiO_2/SiO_2 composites was carried out to determine the average size and size distribution of the particles. Table 4 shows the particle sizes of the TiO_2/SiO_2 composite. It is understood that the more SiO_2 that is added to the composite, the smaller the average particle size of TiO_2 formed. Z-average values of each composite ratio 1:1; 3:1; and 7:1 respectively were 557.4 nm, 616.9 nm and 683.9 nm. The increased number of SiO_2 causes a decrease in agglomeration and therefore reduces the particle size.



Figure 4. EDS of TiO₂/SiO₂ composite.

Table 4.	TiO ₂ /SiO ₂	composite	particle size	analysis	(PSA)	characterization
----------	------------------------------------	-----------	---------------	----------	-------	------------------

	TiO ₂ /SiO ₂ Ratio				
Particle Size	1:1	3:1	7:1		
Median (nm)	797.7	628.9	719.0		
Mode (nm)	698.5	620.1	696.4		
Z-Average (nm)	557.4	616.9	683.9		

Decreasing the size of the TiO₂ particle shortens the photoelectron time and the formation of a hole during photocatalytic reactions on the sample surface. It effectively reduces the photoelectron and hole recombination as well as increasing the photoelectron rate and the hole reduction or oxidation, which also increases the catalytic photocatalytic performance [8]. The composition of TiO₂ with SiO₂ produces a more uniform size-distribution of TiO₂ and a relatively small particle size; therefore, the surface area of TiO₂ gets larger and will increase its photocatalytic activity [17]. SiO₂ substrate is an adsorbent that provides an adsorption side that supports TiO₂ through the adsorption process so that more pollutants can be degraded as a remediation procedure [18].

2.2. Photocatalytic Activity

The photocatalyst activity of TiO_2/SiO_2 was tested for decreased concentration of Cr(VI) and Pb(II) metal ions in order to determine the synthesized photocatalyst performance compared to the Degussa TiO_2 P25. Chromium and lead were chosen as objects because they are examples of heavy metals often found in industrial waste streams. This test was performed using a simulation sample, namely Cr(VI) and Pb(II) ion solution.

Adsorption and photocatalytic test results of Cr(VI) ions are shown in Figure 5a,b. In the same time span, the efficiency of the decreased concentration of Cr(VI) ions in Figure 5a, the ultraviolet (UV) irradiation sample is greater than the decreased efficiency in Figure 5b without irradiation. This shows that composite powder plays a role as a photocatalytic agent for the reduction of Cr(VI). Adsorption and photocatalytic test results for Pb(II) ion are shown in Figure 6a,b. At the same time, the effect of decreasing the concentration of Pb(II) ions in Figure 6a, with the sample under UV irradiation being greater than the decreasing efficiency in Figure 6b without irradiation, shows that the composite powder plays a role as photocatalytic reducing agent in Pb(II).



Figure 5. (a) Adsorption activity and; (b) Photocatalytic activity of catalyst on Cr(VI). The experiment was conducted using 100 mL Cr(VI) ion solution 3 mg/L and 100 mg catalyst with 180 min treatment.



Figure 6. (a) Adsorption activity and; (b) photocatalytic activity of catalyst on Pb(II). The experiment was conducted using 100 mL Pb(II) ion solution 40 mg/L and 100 mg catalyst with 180 min treatment.

The Langumir–Hinshelwood first order kinetic model was applied to evaluate the reaction kinetics of photocatalysis. The first-order kinetics are calculated by [19]:

$$r_0 = -\frac{\mathrm{dC}}{\mathrm{dt}} = \mathrm{kC} \tag{2}$$

where r_0 is the initial photocatalytic reduction efficiency (mg/L·min), k is the rate constant of a pseudo-first order reaction. In the beginning of the reaction, t = 0, C_t = C_i, the equation can be obtained after integration:

$$\ln\left(\frac{C_t}{C_i}\right) = -kt \tag{3}$$

where C_i is the initial concentration (mg/L) of Cr(VI) or Pb(II), C_t is the concentration (mg/L) of Cr(VI) or Pb(II) in the solution at t min, and k (min⁻¹) is the rate constant.

Table 5 shows the kinetic study of the photocatalytic reduction of Cr(VI) and Pb(II). The addition of SiO₂ has an effect on the reaction kinetic constant. It can be seen that the presence of SiO₂ causes and increase in the rate constant, indicating that SiO₂ environment promotes the photocatalytic reduction processes. In addition, k presents a trend that gradually rises from 0.0084 min⁻¹ for TiO₂:SiO₂ (1:1) composite and then continuously increases to 0.0162 min⁻¹ for TiO₂:SiO₂ (7:1) composite in reduction of Cr(VI). Furthermore, the results show that Cr(VI) reduction efficiency by TiO₂:SiO₂ (7:1) composite was 1.9 times compared to TiO₂ P25. In the reduction of Pb(II), k also show a trend that gradually rises from 0.0105 min⁻¹ for TiO₂:SiO₂ (1:1) composite and then continuously increases to 0.0143 min⁻¹ for TiO₂:SiO₂ (7:1) composite. The reduction efficiency by TiO₂:SiO₂ (7:1) composite was 1.4 times that of TiO₂ P25. This indicates that suitable SiO₂ on TiO₂ promoted its photocatalytic ability significantly.

		/ / ~ • `	
Photocatalysts	k (min ⁻¹)	$r_0 (mg/L \cdot min)$	R ²
Photocatalysis of Cr(VI):			
TiO ₂ P25	0.0060	0.0180	0.9301
$TiO_2:SiO_2$ (1:1)	0.0084	0.0252	0.9462
TiO ₂ :SiO ₂ (3:1)	0.0101	0.0303	0.9645
TiO ₂ :SiO ₂ (7:1)	0.0162	0.0486	0.9559
Photocatalysis of Pb(II):			
TiO ₂ P25	0.0085	0.3400	0.9626
$TiO_2:SiO_2$ (1:1)	0.0105	0.4200	0.9224
TiO ₂ :SiO ₂ (3:1)	0.0135	0.5400	0.9060
TiO ₂ :SiO ₂ (7:1)	0.0143	0.5720	0.9443

Table 5. The kinetic study of photocatalysts.

The performance of photocatalyst exposed to UV irradiation has a better reduction on heavy metals' concentration compared to those not exposed to UV irradiation. This indicates that photons from a UV lamp determine the performance of the photocatalyst in Cr(VI) and Pb(II) ions. In a photocatalyst exposed to UV irradiation, the photoreduction process begins when photons with more energy than the photocatalyst band gap are absorbed by the TiO₂/SiO₂ photocatalyst. Therefore, the electron jumps from the valence band to the conduction band and forms a hole in the conduction band (h_{vb}). The electrons in the valence band (e_{cb}) and conduction band (h_{vb}) will react with oxygen (O₂) and water (H₂O) which are absorbed by the photocatalyst. It will then form •OH radicals that react with metals after the process of reduction occurs [20]. In the photocatalyst that was not exposed to UV irradiation (dark conditions), there are no photons that activate the performance of the photocatalyst. Therefore, there was no photoreduction under these conditions. The decrease of Cr(VI) and Pb(II) concentration occurred because of the adsorption process. Since silica has a high adsorption capacity [17], we concluded that the adsorption process increases due to the high content of silica in the photocatalyst.

The effectiveness of chromium and lead concentrations reduction is shown in Figure 7a,b. Photocatalytic activity tests with UV irradiation for Cr(VI) ions using a TiO₂ P25 photocatalyst only was 71.03%, while those using TiO₂/SiO₂ composites with ratios of 1:1; 3:1; and 7:1 were 79.59%, 82.81% and 93.77%, respectively. The efficiency of concentration reduction after UV irradiation for Pb(II) ions using TiO₂ photocatalyst only was 80.91% and for TiO₂/SiO₂ composites at 1:1; 3:1; and 7:1 ratio were 86.52%, 92.22% and 93.55%, respectively. Although the 1:1 composite has a lower average particle size than the others, the particle size of this composite ratio is very heterogeneous (it can be seen from the maximum width of the wider PSA histogram) causing faster agglomeration and, therefore, interferes with the photocatalysis performance of the reduced metal concentrations. For TiO₂/SiO₂ (7:1), composites have the highest anatase phase ratio make it the best photo actively. This is because the anatase valence band edge at higher energy level relative to redox potentials of absorbed molecules enhances the redox capability [21]. In addition, the TiO₂/SiO₂ (7:1) composites also have the highest O–H bond making them good for surface photocatalytic reactions.



Figure 7. (a) Efficiency of decreasing Cr(VI) concentrations and; (b) Pb(II) concentrations after ultraviolet (UV) irradiation for 180 min. The experiment was conducted using 100 mg catalyst.

3. Materials and Methods

3.1. Materials

The beach sand used in this study was from the Bengkulu province, Indonesia. Distilled water was used throughout the experiments. Highest-purity available chemicals used in this study were hydrochloric acid (HCl 37%, Merck, Kenilworth, NJ, United States), ethanol (C_2H_5OH 99.5%, Merck, Kenilworth, NJ, United States), potassium dichromate ($K_2Cr_2O_7$ 99%, Merck, Kenilworth, NJ, United States), sodium hydroxide (NaOH 98%, Merck, Kenilworth, NJ, United States), lead(II) nitrate (Pb(NO_3)_2 99.9%, Merck, Kenilworth, NJ, United States), titanium dioxide (TiO_2, P25 Degussa, Merck, Kenilworth, NJ, United States), and titanium tetraisopropoxide (TTIP, Ti(OC_3H_7)_4, 97%, Sigma-Aldrich, St. Louis, MO, United States).

3.2. Extraction of Silica

Initially, the beach sand was crushed using a ring mill and then sieved with a 325-mesh sieve. In addition, the sand that escaped the sieve was soaked for 12 h in HCl 2 M and filtered. The resulting residue was then washed with distilled water until no yellowish color was present and then dried at 110 °C. After that, the sandstone was reacted with NaOH 3 M at 95 °C while stirring for 4 h, and then filtered. The filtrate (sodium silicate) was then stirred and poured drop by drop to form a gel (pH 7) with HCl 6 M addition. The gel formed was stored for 18 h, and then filtered and rinsed with distilled water and dried at 110 °C. The dried gel was crushed to obtain silica powder.

3.3. The Synthesis of TiO₂/SiO₂ Composite

The TiO₂/SiO₂ composites were synthesized with mole ratio of 1:1; 3:1 [22]; and 7:1 (TiO₂:SiO₂). Titanium tetraisopropoxide (TTIP, 520 μ L) was prepared and then added to 40 mL of ethanol while stirring to prepare TiO₂/SiO₂ composites with a mole ratio of 3:1. Furthermore, the SiO₂ suspension was prepared from 0.036 g of the SiO₂ powder and sonicated in 20 mL of ethanol for 30 min. The SiO₂ suspension was then mixed with the TTIP solution, transferred to an autoclave of 100 mL, and heated in an oven at 130 °C for 15 h. After cooling until room temperature was achieved, the solution was centrifuged at 6000 rpm for 10 min, and then the pH solution was adjusted to 7.0. The TiO₂/SiO₂ composites formed were then dried at 110 °C for 2 h and calcinated at 500 °C for 5 h. A similar procedure was also applied to TiO₂/SiO₂ composites with 1:1 and 7:1 mole ratio variation.

3.4. Characterization of Catalysis

The XRD diffractogram was carried out using the XRD MiniFlex600 (Rigaku, Tokyo, Japan). Measurements were carried out at room temperature using Cu K α radiation (λ = 1.5406 Å) with scan range from 10° to 80° (2 θ). The Fourier transform infrared spectra were acquired by a FTIR (PerkinElmer, Spectrum100, Waltham, MA, United States) and a scan range from 400–4000 cm⁻¹. Particle size of the composites was measured by a particle size analyzer (PSA, Horiba SZ-100, Kyoto, Japan). Scanning electron microscopy (SEM) was performed by a SEM-EDX (Hitachi SU3500, Tokyo, Japan).

3.5. Photocatalytic Activity Test

The Cr(VI) ion solution 100 mL (3 mg/L) was added to a beaker glass and then added to 100 mg of TiO₂/SiO₂ composite. The mixture was then placed on a artificial homemade photoreactor and irradiated with an Hg lamp (HPL-N 125W, Philips, Shanghai, China, equal UV A with wavelength 315–400 nm) on a magnetic stirrer (IKA C-MAG MS 4, Staufen, Germany) with an irradiated area of 26 cm² for 180 min at room temperature. We then took 10 mL of Cr(VI) solution every 30 min using a syringe membrane. The concentration of metal ion was again measured using atomic absorption spectroscopy (AAS, Shimadzu AA7000, Kyoto, Japan). The same treatment (100 mg) was applied to TiO₂/SiO₂ composite with 3:1 and 7:1 ratio, and to TiO₂ without SiO₂ as a control. This photocatalytic activity test was also conducted without irradiation at the same time interval for each sample. The same photocatalytic activity test procedure was also applied to Pb(II) solution (40 mg/L).

4. Conclusions

The composite of SiO_2/TiO_2 increased the photocatalytic activity in decreasing Cr(VI) and Pb(II) concentrations. By using the optimal condition, the percentages of heavy metals concentration reduction were 93.77% and 93.55% for Cr(VI) and Pb(II) ions, respectively. The high effectiveness of this method for reducing the concentration of heavy metals can be used as an alternative remediation method on Cr and Pb waste.

Author Contributions: Conceptualization, D.R.E. and M.L.F.; methodology, S.N.I.; software, S.N.I. and M.D.P.; validation, D.R.E. and M.L.F.; formal analysis, S.N.I.; investigation, S.N.I. and M.D.P.; resources, S.N.I.; data curation, S.N.I.; writing—original draft preparation, S.N.I.; writing—review and editing, D.R.E. and M.D.P.; visualization, M.D.P.; supervision, D.R.E. and M.L.F.; project administration, D.R.E.; funding acquisition, D.R.E. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Research Grant from Kemenristek-BRIN 2020 with Student Thesis Research Grant Number 1827/UN6.3.1/LT/2020, 12 May 2020.

Acknowledgments: The author thanks Putri Rizka Lestari and Nobuhiro Kumada from the Center for Crystal Science and Technology, University of Yamanashi, for characterization analysis.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Sane, P.; Chaudhari, S.; Nemade, P.; Sontakke, S. Photocatalytic reduction of chromium(VI) using combustion synthesized TiO₂. *J. Environ. Chem. Eng.* **2018**, *6*, 68–73. [CrossRef]
- Ojemaye, M.O.; Okoh, O.O.; Okoh, A.I. Performance of NiFe₂O₄-SiO₂-TiO₂ Magnetic Photocatalyst for the Effective Photocatalytic Reduction of Cr(VI) in Aqueous Solutions. *J. Nanomater.* 2017, 2017, 5264910. [CrossRef]
- 3. Kotz, J.C.; Treichel, P.M.; Townsend, J.R. *Chemistry and Chemical Reactivity*, 7th ed.; Thomson Brooks/Cole: Pacific Grove, CA, USA, 2009.
- 4. Said, N.I. Pengolahan Air Limbah Domestik di DKI Jakarta "Tinjauan Permasalahan, Strategi dan Teknologi Pengolahan", 1st ed.; Badan Pengkajian dan Penerapan Teknologi: Jakarta, Indonesia, 2008; 606p.
- Eddy, D.R.; Rahayu, I.; Hartati, Y.W.; Firdaus, M.L.; Bakti, H.H. Photocatalytic activity of gadolinium doped TiO₂ particles for decreasing heavy metal chromium concentration. *J. Phys. Conf. Ser.* 2018, 1080, 012013. [CrossRef]

- 6. Bi, J.; Wang, J.; Huang, X.; Tao, Q.; Chen, M.; Wang, T.; Hao, H. Enhanced removal of Pb (II) and organics by titanate in a designed simultaneous process. *Sep. Purif. Technol.* **2020**, 251, 117339. [CrossRef]
- Besançon, M.; Michelin, L.; Josien, L.; Vidal, L.; Assaker, K.; Bonne, M.; Lebeau, B.; Blin, J.L. Influence of the porous texture of SBA-15 mesoporous silica on the anatase formation in TiO₂-SiO₂ nanocomposites. *New J. Chem.* 2016, 40, 4386–4397. [CrossRef]
- Cheng, Y.; Luo, F.; Jiang, Y.; Li, F.; Wei, C. The effect of calcination temperature on the structure and activity of TiO₂/SiO₂ composite catalysts derived from titanium sulfate and fly ash acid sludge. *Colloids Surf. A Physicochem. Eng. Asp.* **2018**, 554, 81–85. [CrossRef]
- 9. Eddy, D.R.; Puri, F.N.; Noviyanti, A.R. Synthesis and Photocatalytic Activity of Silica-based Sand Quartz as the Supporting TiO₂ Photocatalyst. *Procedia Chem.* **2015**, *17*, 55–58. [CrossRef]
- 10. Munasir; Sulton, A.; Triwikantoro; Zainuri, M.; Darminto. Synthesis of silica nanopowder produced from Indonesian natural sand via alkalifussion route. *AIP Conf. Proc.* **2013**, 1555, 28–31.
- 11. Ishmah, S.N.; Permana, M.D.; Firdaus, M.L.; Eddy, D.R. Extraction of Silica from Bengkulu Beach Sand using Alkali Fusion Method. *PENDIPA J. Sci. Edu.* **2020**, *4*, 1–5. [CrossRef]
- Firdaus, M.L.; Madina, F.E.; Yulia, F.S.; Elvia, R.; Soraya, N.I.; Eddy, D.R.; Cid-Andres, A.P. Silica Extraction from Beach Sand for Dyes Removal: Isotherms, Kinetics and Thermodynamics. *Rasayan J. Chem.* 2020, 13, 249–254. [CrossRef]
- Zhang, Y.; Weidenkaff, A.; Reller, A. Mesoporous Structure and Phase Transition of Nanosrystalline TiO₂. *Mater. Lett.* 2002, 54, 375–381. [CrossRef]
- Sikong, L.; Damchan, J.; Kooptarnond, K.; Niyomwas, S. Effect of doped SiO₂ and calcinations temperature on phase transformation of TiO₂ photocatalyst prepared by sol-gel method. *Songklanakarin J. Sci. Technol.* 2008, 30, 385–391.
- Devi, L.G.; Rajashekhar, K.E. A kinetic model based on non-linear regression analysis is proposed for the degradation of phenol under UV/solar light using nitrogen doped TiO₂. *J. Mol Catal. A Chem.* 2011, 334, 65–76. [CrossRef]
- 16. Lin, L.; Zheng, R.Y.; Xie, J.L.; Zhu, Y.X.; Xie, Y.C. Synthesis and characterization of phosphor and nitrogen co-doped titania. *Appl. Catal. B Environ.* **2007**, *76*, 196–202. [CrossRef]
- Sirimahachai, U.; Ndiege, N.; Chandrasekharan, R.; Wongnawa, S.; Shannon, M.A. Nanosized TiO₂ particles decorated on SiO₂ spheres: Synthesis and photocatalytic activities. *J. Sol-Gel Sci. Technol.* 2010, 56, 3–6. [CrossRef]
- Sellapan, R. Mechanisms of Enhanced Activity of Model TiO2/Carbon and TiO2/Metal Nanocomposite Photocatalysts; Department of Applied Physics Chalmers University: Gotebrog, Sweden, 2013.
- Pu, S.; Hou, Y.; Chen, H.; Deng, D.; Yang, Z.; Xue, S.; Zhu, R.; Diao, Z.; Chu, W. An efficient photocatalyst for fast reduction of Cr(VI) by ultra-trace silver enhanced titania in aqueous solution. *Catalysts* 2018, *8*, 251. [CrossRef]
- Zaccariello, G.; Moretti, E.; Storaro, L.; Riello, P.; Canton, P.; Gombac, V.; Montini, T.; Rodríguez-Castellón, E.; Benedetti, A. TiO₂-mesoporous silica nanocomposites: Cooperative effect in the photocatalytic degradation of dyes and drugs. *RSC Adv.* 2014, *4*, 37826–37837. [CrossRef]
- 21. Gao, M.; Zhu, L.; Ong, W.L.; Wang, J.; Ho, G.W. Structural design of TiO₂-based photocatalyst for H₂ production and degradation applications. *Catal. Sci. Technol.* **2015**, *5*, 4703–4726. [CrossRef]
- 22. Pal, A.; Jana, T.K.; Chatterjee, K. Silica supported TiO₂ nanostructures for highly efficient photocatalytic application under visible light irradiation. *Mat. Res. Bull.* **2016**, *76*, 353–357. [CrossRef]

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).