Determination and characterization of titanium in environmental waters and sludges

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Abstract. By increasing the development of nanotechnology in recent times, there have been many commercial products contain nanomaterials. Type of nanomaterials that most widely used is Titanium dioxide (TiO2). These nanomaterials have been applied in various types of products, such as paints, cosmetics, etc. Unlike organic and inorganic pollutants, study and characterization of metal nanoparticle (NP) contaminants, such as TiO2 NP, have never been done in any part of Indonesia. Therefore, given the greater source of NP contaminants plus their long-term negative effects, it is deemed necessary to identify and characterize them in Indonesia. For the first case, Identification and characterization of TiO2 NP were performed in sludge and wastewater of paint and cosmetic company in the area of West Bandung district. Furthermore, the sludge and surface water of Saguling Reservoir and Cipeusing River were also analysed. Morphological and size analysis using scanning electron microscopy (SEM) and particle size analyser (PSA) revealed that most samples have NPs with a sphere shape; however, Energy Dispersive Spectroscopy (EDS) was only able to confirm the presence of titanium (Ti) element in sludge samples. Quantification of Ti (all ascribed to TiO2 NPs) in wastewater and sludge was done by graphite furnace-atomic absorption spectroscopy (GF-AAS) with high precision and accuracy. The results implied that Ti was accumulated higher in the sludge than in the water samples at the same sampling location.

Keywords: Titanium; TiO2 nanoparticles; wastewater; sludge

1. Introduction
Titanium (Ti) is an abundant element that has become an important industrial commodity since the past 10 decades. Generally, the source of Ti in nature are Ilmenite (FeTiO3) and rutile (which is the most common form of TiO2). Pure titanium metal was first isolated in 1910, but the metal was not commercially available until the development of the Kroll process by William Kroll in 1938 [1].

Currently, TiO2 NPs have been applied in various commercial products, for example in pigment paints, toothpaste, plastics, paper, ceramics, cosmetics and additives in food. This NP used widely and produced abundantly due to its thermodynamic stability, anticorrosion and photocatalytic properties [2,3]. TiO2 NPs applied as a pigment in paint and in sunscreen due to its excellent light-scattering properties and its ability to absorbs UV light, respectively [4,5].

TiO2 as one of the NPs is used on a large scale with various major particle sizes and crystal structures, such as anatase, rutile, and brookite [6]. Some literatures revealed that nanosize TiO2 could induce the production of reactive oxygen species (ROS), cause metabolic stress in the intracellular
environment, and raise the possible carcinogenic [7]. Furthermore, the results of the study have shown that TiO\(_2\) NP can induce intracellular oxidative stress, histopathological changes, and damage to the immune system which will cause various diseases such as asthma, neurological disorders, aging, and cancer [3,8].

Based on the regulation of Indonesian Ministry of Environment and Forestry (KEP-51/MENLH/10/1995), the limit concentration of Ti in liquid waste for paint industry is 0.5 mg.L\(^{-1}\) [9]. Whereas, Ti level has not been regulated for water quality standards by Indonesian government (government regulation No. 82 at 2001) [10].

By increasing of nanotechnology applications and the risk potency of engineered metal NP both to human and environment as mentioned above, assessing the fate of metal NPs in the environment is become urgent [11]. In addition, unlike organic and inorganic pollutants, the assessment of metal NPs contaminants in Indonesian waters has never been done. Therefore, identifying and characterizing engineered metal NPs coming from commercial products such as TiO\(_2\) NPs in Indonesian waters is imperative. In this work, we identified and characterized TiO\(_2\) NPs in the sludge and wastewater samples from the outlet of paint and cosmetic industry in West Bandung area district, which is allegedly one source of TiO\(_2\) NPs contaminant. Besides that, we analysed as well the sludge and surface water at some points along the path to Citarum River from West Bandung district (i.e. Cipeusing River and Saguling reservoir).

2. Materials and Methods

2.1. Materials

A series of the calibration curve was prepared by diluting 1000 mg.L\(^{-1}\) of titanium standard solution (SCP Science, Canada). De-ionized water with resistivity < 0.05 Mohm.cm\(^{-1}\) obtained from MQ reverse osmosis system was used in all experiment. Acid solutions used for sample digestion were Nitric Acid (HNO\(_3\)) 65 % Suprapur, Hydrofluoric Acid (HF) 40 %, and Boric Acid (BH\(_3\)O\(_3\)) that purchased from Merck, Germany. The sludge and water samples were collected from five places of upstream Citarum River in the area of Bandung Barat district, i.e. the water outlet of two paint companies and cosmetic company, Cipeusing River, and Saguling reservoir, as shown in Figure 1 with the GPS coordinate exhibited in Table 1.

![Figure 1. The map of water and sludge sampling location (Bandung Barat District area)](image-url)
Table 1. The GPS coordinate of water and sludge sampling location (Bandung Barat District)

| Location                  | Coordinate          |
|---------------------------|---------------------|
| Paint Company 1 (PC 1)    | S 06°53'44.6"; E 107°30'12.1" |
| Paint Company 1 (PC 2)    | S 06°50'53.5"; E 107°28'53.5"  |
| Cosmetic Company (CC)     | S 06°51'55.5"; E 107°30'21.9" |
| Cipeusing River (CR)      | S 06°53'22.2"; E 107°29'23.1"  |
| Saguling Reservoir (SR)   | S 06°54'14.4"; E 107°26'73.2"  |

2.2. Characterization of TiO\(_2\) NPs in waste water and sludge sample

2.2.1. Scanning Electron Microscopy (SEM) measurement
Prior to analysing using SEM, the water samples were centrifuged (Hitachi microcentrifuge type S150NX) at 120,000 rpm for 10 min. A quantity of precipitate or sample powder was placed onto a sample holder covered by carbon tape and then sputter-coated with thin layer of gold for getting high resolution images. The surface morphology and elemental analysis were examined using SEM (JEOL Type IT300, Japan) and Energy Dispersive X-ray Spectroscopy (EDS) instrument, respectively, at an acceleration voltage of 30 kV and magnification of 1,000-30,000x.

2.2.2. Particle Size Analyzer (PSA) analysis
Dynamic Light Scattering (DLS) instrument (Zetasizer Nano-ZS Malvern, UK) was used for analysing particle size distribution. Before conducting measurement, the sample suspension in deionized water was sonicated first to break up the agglomerates and subsequently tested at 25 °C with measurement position of 4.65 mm, and count rate of 97.7 kcps.

2.3. Quantification of Ti total (\(Ti_{\text{tot}}\)) in wastewater and sludge

2.3.1. Wastewater sample (wet acid digestion)
Sample preparation was done according to the standard method of American Public Health Association (APHA) 3030E (Nitric acid digestion). A quantity of 50 mL sample was mixed and boiled with 5 mL of HNO\(_3\) until digestion was complete indicated by a light-colored clear solution. After that, the sample was dissolved in 50 mL of 0.05 M HNO\(_3\) in volumetric flask and filtered by Whatmann paper number 40. This clear digestion solution was then tested for Ti total content by GF-AAS.

2.3.2. Sludge sample (microwave acid digestion)
The procedure of digestion for sludge sample followed the recommendation of microwave instrument guideline (Milestone-Italy). First, each sample was accurately weighed about 0.1 g in a vessel and mixed by vortex with 1 ml of de-ionized water. After that, 0.6 g of BH\(_3\)O\(_3\), 8 mL of HNO\(_3\), and 2 mL of HF were added into the vessel and let the solution at room temperature for 10-15 min. The mixed solution was then digested in Microwave Digestion System (Ethos Easy Milestone SK-15, Italy) at 200 °C (temperature condition presented in Figure 2) and 1200 watt. After digesting, the solution was cooled down to room temperature, dissolved in 100 mL of 0.05 M HNO\(_3\), and filtered by Whatmann filter paper number 40.
The clear digested solution of wastewater and sludge sample were analysed for Ti total content by GF-AAS (Agilent, United State) with the operational condition as presented in Table 2. Limit of detection (LOD) and limit of quantitation (LOQ) value for verification was achieved by digesting the blank using the same acid and parameter conditions as mentioned above. The performance of GF-AAS was validated by using titanium standard solution.

3. Results and Discussions

3.1. Physicochemical properties of TiO$_2$ NP in wastewater and sludge Samples

Using SEM instrument, the morphology characteristic of particles contained in the wastewater samples can be seen and analysed. As presented in Figure 3, the representative SEM images revealed that the wastewater samples consist of various forms of particles, e.g. sphere (3b.i), rod (3d.1), flakes (3f.i), and undefined shape (3a.i, 3c.i, 3e.i) with the high degree of agglomeration. Elemental analysis at the same spot of SEM picture disclosed that the wastewater particles generally contain the component of organic molecules, such as Carbon (C), Oxygen (O), Nitrogen (N), Chloride (Cl) and Sulphur (S), and some common inorganic elements in environmental water (i.e. Magnesium (Mg), Calcium (Ca), Silicon (Si), Aluminium (Al), Potassium (K), Sodium (Na), and Iron (Fe)). In this EDS experiment, the presence of Ti was no observed. It might be due to the very low concentration of Ti,
so it cannot be detected by EDS instrument or this metal truly does not exist in the samples. In order to confirm this, the detection of Ti using GF-AAS instrument was conducted and will be discussed in the subchapter 3.2.

![Figure 3. Surface morphology (i) and elemental analysis (ii) of (a) wastewater outlet PC1, (b) wastewater outlet PC2, (c) wastewater Outfall PC2, (d) wastewater outlet CC, (e) surface water of SR, and (f) surface water of CR.](image)

![Figure 4. Surface morphology (i) and elemental analysis (ii) of sample sludges coming from the outlet of PC1 (a), PC2 (b), and CC (c) industries, as well as the river CR (d).](image)

Similar to the wastewater samples, the particles of sludge samples from severe agglomeration as can be seen in Figure 4.i, thus cause the difficulty in particle’s size and shape determination. EDS results which are depicted in Figure 4.ii showed that most studied sludge samples contained Ti besides other organic and inorganic elements found in the wastewater samples. This finding is in agreement with the literature which found that the main reservoir of TiO$_2$ NPs in the environment was in the sediment compartment rather than water [12]. This happened because the high tendency of TiO$_2$ NPs to interact with the suspended particulate matter.
Size and distribution of particles in both wastewater and sludge samples was evaluated by using PSA. According to Figure 5a, particle size in wastewater samples was around 200-500 nm, whereas that of in river (CR) and reservoir (SR) water are about 700 and 600 nm, respectively. Interestingly, there was a decrease in particle size for sludge compare to wastewater sample at the same location, except for sample at the wastewater outlet of CC industry (Figure 5b). These results contradictory with the previous literature which mentioned that the larger size particles resulted from the aggregation will accumulate at the sludge compartment [12].

3.2. Quantification of Ti in wastewater and sludge samples by GF-AAS
We utilized a GF-AAS for Ti quantification in wastewater and sludge samples. For calibration purpose, standard solutions of titanium ranging from 0 - 500 μg.L⁻¹ were used. The calibration graph was linear over its concentration range and the coefficient of determination (R²) was >0.997 in both samples. Table 3 displays analytical parameters of Ti analysis in wastewater and sludge samples. According to data in Table 4, repeatability method (n=6) for wastewater and sludge samples was 4.42 % and 13.70 %, respectively. In addition, LoD and LoQ for wastewater were lower (13.74 μg.L⁻¹ and 21.56 μg.L⁻¹) than that of in sludge sample (29.65 μg.g⁻¹ and 49.80 μg.g⁻¹).

Accuracy of the methodology was examined by adding Ti standard solution into the sample matrix. Recovery percentage value was obtained by comparing the analyte (Ti standard) concentration before and after spiked into the sample matrix. The accuracy is good if % recovery value is in the range of 60-125 %. As we can see in table 4, the % recovery value is 119 % and 89 % for sludge and wastewater sample, respectively. It means the method for determination of titanium both in sludge and wastewater is accurate.

Table 5 and Table 6 showed the quantitative data of Ti concentration for sludge and wastewater samples, respectively. According to those tables, all studied samples contained Ti metal; however, sludge samples contain Ti about 100 times higher than wastewater samples. The range of Ti concentration in sludge was 0.1 – 1.65 %, while that of in wastewater was only about 0.001-0.009 %. The highest amount of Ti in sludge samples was owned by sludge coming from wastewater outlet of paint industry PC1 (Ti concentration: 16250.43 μg/g) and the lowest was sludge acquired from the river CR (Ti concentration: 1115.6 μg/g). Different from sludge samples, water sample collected from river CR had the highest content of Ti (Ti concentration: 97.9 μg/L) compared to the wastewater from the outlet of paint (PC) and cosmetic (CC) industries (Table 6). This occurs might be due to the accumulation of wastewater disposal from several factories around Bandung Barat.
### Table 3. Analytical parameters of Ti analysis in wastewater and sludge samples.

| Parameter                        | Wastewater       | Sludge         |
|----------------------------------|------------------|----------------|
| Repeatability, (%rsd)\(^a\)     | 4.42             | 13.70          |
| Limit of Detection (LoD),        | 13.74 (µg.L\(^{-1}\))\(^b\) | 29.65 (µg.g\(^{-1}\)) |
| Limit of Quantification (LoQ)    | 21.56 (µg.L\(^{-1}\))\(^c\) | 49.80 (µg.g\(^{-1}\)) |
| Instrument Detection Limit (µg.L\(^{-1}\))\(^b\) | 2.49             | 2.49           |

\(^a\)Repeatability : n=6
\(^b\)LoD : n=6 (3sd)
\(^c\)LoQ : n=6 (10sd)

### Table 4. Experimental recovery of sludge and wastewater sample solution obtained by GF-AAS.

| Samples   | Concentration of Ti (µg.L\(^{-1}\)) | % Recovery |
|-----------|-------------------------------------|------------|
| Sludge\(^a\) | 39.79\(^c\)                        | 119        |
| Wastewater\(^b\) | 114.63\(^c\)                     | 89         |

\(^a\)spiked with 30 µg.L\(^{-1}\) Ti standard solution
\(^b\)spiked with 100 µg.L\(^{-1}\) Ti standard solution
\(^c\)Repeatability : n=3

### Table 5. Concentration of total titanium (Ti\(_{tot}\)) in sludge sample.

| Sample | Ti Concentration (µg/g) | (%) |
|--------|-------------------------|-----|
| PC 1   | 16250.43 ± 260.67       | 1.65|
| PC 2   | 5733.39 ± 49.45         | 0.56|
| CC     | 4252.76 ± 39.30         | 0.44|
| CR     | 1115.61 ± 125.00        | 0.10|

n = 3 replicates

### Table 6. Concentration of total titanium (Ti\(_{tot}\)) in wastewater sample.

| Sample         | Ti Concentration (µg/L) | (%)  |
|----------------|-------------------------|------|
| Outlet PC1     | 27.67 ± 12.73           | 0.003|
| Outlet PC2     | 25.03 ± 0.62            | 0.002|
| Outfall PC3    | 62.82 ± 2.92            | 0.006|
| Outlet CC      | 33.87 ± 4.03            | 0.003|
| Water SR       | 16.40 ± 2.43            | 0.001|
| Water CR       | 97.90 ± 1.67            | 0.009|

n = 3 replicates
4. Conclusion
In summary, we have demonstrated the successful of PSA, SEM-EDS and GF-AAS analysis combination to characterize and quantify Ti in wastewater and sludge samples. Quantification of Ti in wastewater and sludge matrix can be done by GF-AAS with high precision and accuracy. Based on the EDS and AAS results, Ti was accumulated much higher in the sludge than in the wastewater sample at the same sampling location.

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Author contribution
Agustina Ircha Winda Pratiwi, Fahmi Idzni, and Indah Primadona contributed equally as the main contributor of this work. All authors read and approved the final paper.

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