

## Research Article

# The Influence of Lead Concentration on Photocatalytic Reduction of Pb(II) Ions Assisted by Cu-TiO<sub>2</sub> Nanotubes

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Cu<sup>2+</sup> ions were successfully loaded into TiO<sub>2</sub> nanotubes using wet impregnation technique in 0.6 M Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O solution. The effect of reaction temperatures on the nanotube's morphology, crystal structure, and their photocatalytic reduction of Pb(II) ions were investigated. The high reaction temperature could improve the crystallinity of anatase phase. However, irregular and corrugated nanotubular surface covered with Cu precipitates was observed. In the present study, incorporation of an optimum content of Cu element (1.3 at%) into TiO<sub>2</sub> nanotubes at room temperature has an important function in enhancing the photocatalytic reduction of Pb(II) ions in alkaline condition (pH 11) due to the higher synergistic effects of photocatalytic reaction under UV illumination. The optimum concentration of Pb(II) ions for effective Pb(II) ions removal performance was found in between 20 and 60 ppm.

## 1. Introduction

Nowadays, toxic heavy metals are the major contaminants of electronic waste. It is a well-known fact that those heavy metals are elements having high atomic weights between 63.5 and 200.6 and a specific gravity greater than 5.0 [1]. Heavy metal contaminations in the aquatic environment including arsenic (As), cadmium (Cd), lead (Pb), chromium (Cr), copper (Cu), nickel (Ni), zinc (Zn), and mercury (Hg) pose an ecotoxicological effect to living creatures [2–4]. Some of these heavy metal contaminations come from fertilizer and sewage, but the biggest source is the effluent industrial discharged from various industries such as electronic industry, mining, electroplating, and battery manufacturing [5]. Since heavy metal contaminations cause serious health effect, wastewater regulations were established to minimize human and environmental exposure to hazardous chemical. The summary of various heavy metals and their permitted concentration is shown in Table 1.

Among various heavy metal contaminations shown in Table 1, Pb is our special concern due to persistency and recalcitrant of Pb in the environment. According to World Environmental Protection (WEP), Pb accounts for 98% of the total disposal or other releases of persistent, bioaccumulative, and toxic (PBT) chemicals. In addition, US Environmental Protection Agency (EPA) has reported that the disposal or other releases of PBT chemicals increased by 50%, mainly due to increases in Pb and Pb compounds [6]. The total disposal or other releases of Pb and Pb compounds were increased about 51% in 2010. Thus, Pb contaminants need urgent attention in order to save the environment and to overcome the adverse health risk of mankind [7, 8].

In this manner, various remediation methods such as precipitation-filtration, ion-exchange, reverse osmosis, oxidation reduction, electrochemical recovery, and membrane separation are commonly used to treat those heavy metal contaminations [5, 8, 9]. However, among all of the available methods, photocatalytic emerged as a promising advance

TABLE 1: The maximum contaminant level (MCL) standard for the most hazardous heavy metal [4].

Heavy metal	Toxicities	MCL (ppm)
As	Skin manifestations, visceral cancers, vascular disease	0.050
Cd	Kidney damage, renal disorder, human carcinogen	0.01
Cr	Headache, diarrhea, nausea, vomiting, carcinogenic	0.05
Cu	Liver damage, Wilson disease, insomnia	0.25
Ni	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.20
Zn	Depression, lethargy, neurological signs, and increased thirst	0.80
Pb	Damage the fetal brain, diseases of kidney, circulatory system, and nervous system	0.005
Hg	Rheumatoid arthritis and diseases of kidneys, circulatory and nervous system.	0.00003

technique because it is able to destroy and transform variety of pollutants by oxidative or reductive mechanism and converting them into nontoxic wastes [10–12]. Removal of lead from solutions by photocatalysis using irradiated platinumized TiO<sub>2</sub> was carried out by Kabra et al. Lead was found reduced to PbO on the platinum islands and also oxidized to PbO<sub>2</sub> by a valence band process as well as by oxygen radical species. Thus, the advance photocatalytic reduction technique was believed to be capable of removing heavy metal contaminants to low concentration of less than 20 ppm [8]. In this case, titanium dioxide (TiO<sub>2</sub>) is regarded as one of the most efficient and environmentally benign photocatalysts for reducing the heavy metal contaminants [13–16]. However, it still exhibit several intrinsic drawbacks, which limit its widespread technological applications [13, 17, 18]. Titanium dioxide photocatalysis has been demonstrated to be a promising method for the pollutant treatment mainly due to its capability of removing metal ions and complete mineralization or at least partly destroying a variety of organic pollutants.

Basically, TiO<sub>2</sub> is widely used in many applications such as water purification, to remove volatile organic compound, water electrolysis, painting, and many more. The major advantages of this TiO<sub>2</sub> photocatalysis are as follows.

- (i) Photocatalysis offers a good substitute for the energy-intensive conventional treatment methods with the capacity for using renewable and pollution-free solar energy.
- (ii) Unlike conventional treatment measures which transfer pollutants from one medium to another, photocatalysis leads to the formation of innocuous products.
- (iii) This process can be used to destroy a variety of hazardous compounds in different wastewater streams.

- (iv) It can be applied to aqueous and gaseous-phase treatments, as well as solid-soil phase treatments to some extent.

However, the use of pure TiO<sub>2</sub> has several drawbacks, such as poor visible light absorption and high recombination losses of the photo-induced electron-hole pairs [13, 17–20]. Many studies have highlighted that the coupling mechanism between the Cu<sup>2+</sup> ions and TiO<sub>2</sub> could facilitate better charge carrier separation in improving the photocatalytic performance [21–23]. However, most of these studies involved incorporation of Cu<sup>2+</sup> ions into TiO<sub>2</sub> photocatalysts in the form of particles/spheres or thin films, which do not possess high enough surface area for photon absorption [24, 25]. Moreover, most scholars mainly focused on the photo degradation of organic pollutants rather than the inorganic pollutants. The detail studies regarding Pb(II) ions removal at low concentration using photocatalytic activity are still lacking. Thus, a comprehensive study is essential to be explored by optimizing the reaction temperature of wet impregnation to obtain the preferred Cu-TiO<sub>2</sub> nanotubes, resulting in the best performance of Pb(II) removal. Detail studies regarding the synergistic relationship of Cu<sup>2+</sup> ions incorporated into TiO<sub>2</sub> nanotubes and its application on Pb(II) ions removal have been established in this work.

## 2. Experimental Procedure

High purity of titanium (Ti) foils (99.6% purity, STREM Chemicals) with thickness of 0.127 mm was used in the present study. The Ti foils (50 mm × 10 mm) were degreased by using sonication in ethanol for 30 min prior to electrochemical anodization process. Then, the Ti foil was placed in 100 mL ethylene glycol electrolyte (99% purity, Merck) composed of 5 wt % ammonium fluoride (NH<sub>4</sub>F) (98% purity, Merck) and 1 vol% of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) (30% H<sub>2</sub>O<sub>2</sub> and 70% H<sub>2</sub>O; J.T. Baker) at 60 V for 1 h. The electrolyte composition was fixed because it favors the formation of highly ordered TiO<sub>2</sub> nanotubes [26, 27]. Two electrodes configuration bath with Ti foil as anode and a platinum rod as cathode was prepared to conduct the electrochemical anodization. The as-anodized Ti foil was washed using distilled water and then dried in a nitrogen stream for 15 min. Next, the as-anodized Ti foil was annealed at 400°C in an argon atmosphere for 4 h. In the present study, the incorporation of copper (Cu<sup>2+</sup>) ions was conducted by immersing the annealed Ti foil in an optimized 0.6 M copper(II) nitrate trihydrate [Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O] solution (Merck) for 1 h at different reaction temperatures (room temperature, 27°C, 60°C, and 80°C). Subsequently, the resultant sample conducted heat treatment process at 400°C for 4 h under argon gas atmosphere. The main purpose of heat treatment process was obtained high crystalline phases of Cu-TiO<sub>2</sub>. The removal rate of Pb(II) ions (Merck at 1000 mg/L of concentration) was determined by using Atomic Absorption Spectrometer (AAS) Analyst 700. The measurement of Pb(II) ions absorption was measured after exposing to the UV light (120 W germicidal light) for 5 hours. The changes of the initial and final concentration after photocatalytic

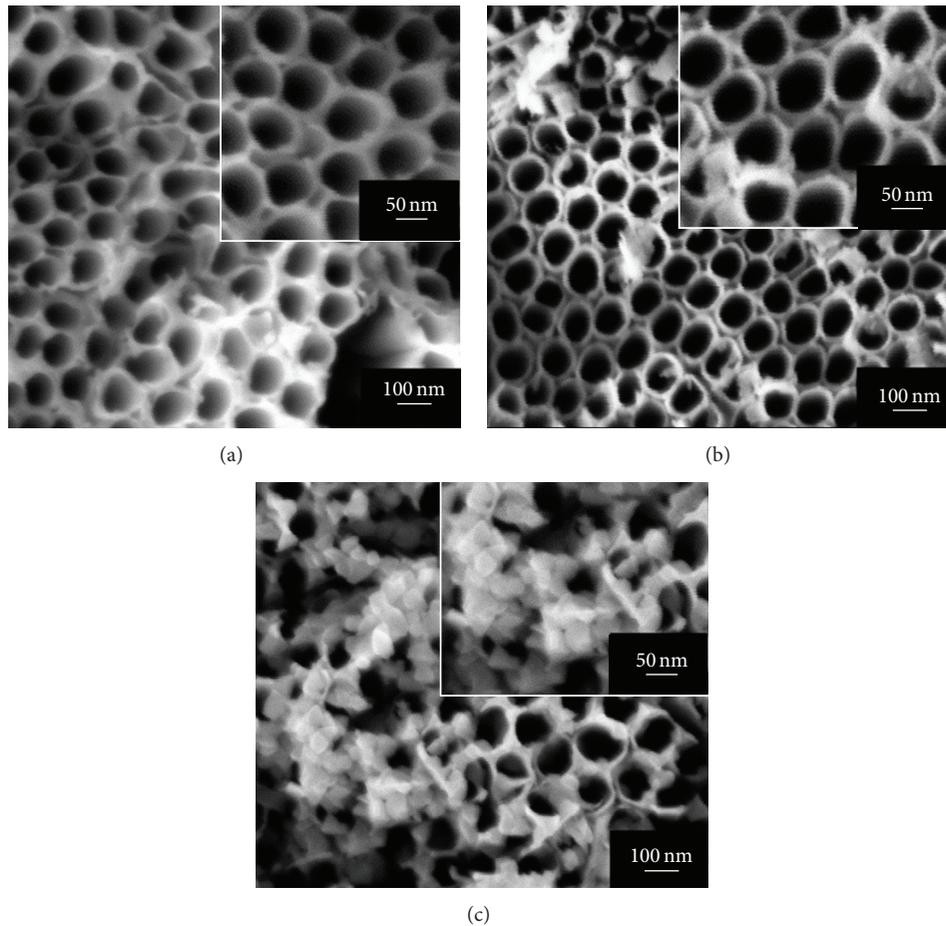


FIGURE 1: FESEM morphology of Cu-TiO<sub>2</sub> nanotubes prepared at (a) room temperature, (b) 60°C, and (c) 80°C in an optimize 0.6 M copper(II) nitrate trihydrate [Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O] solution for 1 h.

activity were observed and measured. The morphologies of the nanotubes were observed by field emission scanning electron microscopy (FESEM) using a Zeiss SUPRA 35VP at a working distance of 1 mm. The element analysis of Cu<sup>2+</sup> ions incorporated into TiO<sub>2</sub> was determined with Energy Dispersive X-ray (EDX) which is equipped in the FESEM. X-ray diffraction (XRD) was used to attain information about the structure and percentage of crystallinity of the anodized Ti foils and also sample that undergone annealing process. The phase identification of TiO<sub>2</sub> was done by using Philip model PW 1729, which was operated at 40 kV and 40 mV.

### 3. Results and Discussions

In this part of the experimental study, the effect of reaction temperatures on the Cu<sup>2+</sup> ions loaded on pristine TiO<sub>2</sub> nanotubes is discussed. It is a well-known fact that reaction temperatures during the wet impregnation have profound effect on various chemical processes. The reaction temperature affects the adsorption rate by altering the molecular interactions and the solubility of the adsorbate [28]. Figures 1(a) to 1(c) show the morphology of Cu-TiO<sub>2</sub> nanotubes prepared at room temperature, 60°C, and 80°C,

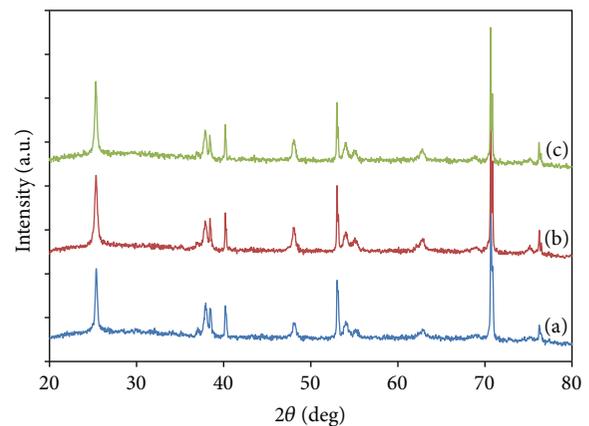


FIGURE 2: XRD patterns for postannealed Cu-TiO<sub>2</sub> nanotubes prepared at (a) room temperature, (b) 60°C, and (c) 80°C in an optimize 0.6 M copper(II) nitrate trihydrate [Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O] solution for 1 h.

respectively. As shown in the FESEM images, the pore opening of TiO<sub>2</sub> nanotubes synthesized at 60°C showed the almost similar appearance to the sample synthesized at

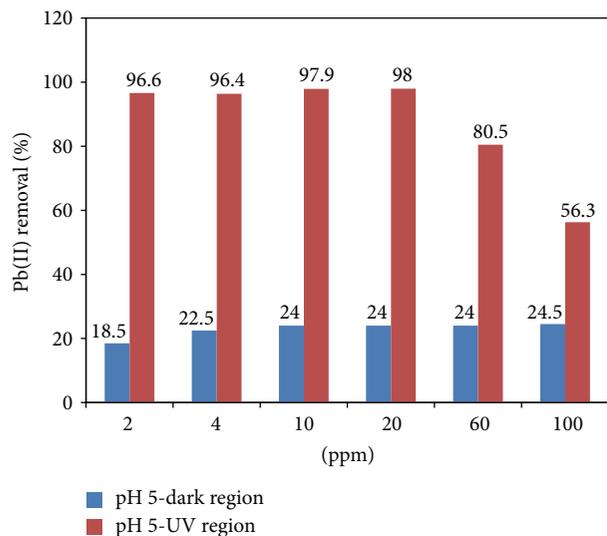


FIGURE 3: Percentage (%) of Pb(II) removal by Cu-TiO<sub>2</sub> nanotubes at pH 5 with different concentration of Pb(II).

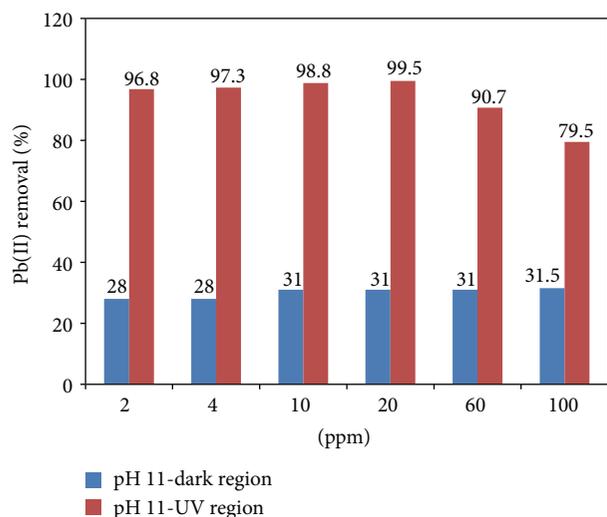


FIGURE 4: Percentage (%) of Pb(II) removal by Cu-TiO<sub>2</sub> nanotubes at pH 11 with different concentration of Pb(II).

room temperature. The average diameter of the open pores is about 80 nm. Interestingly, it could be observed that an irregular and corrugated nanotubular surface covered with Cu precipitates after synthesizing at reaction temperature at 80°C. Some of the nanotubular pore entrances was completely blocked with Cu precipitates. The reason might be attributed to the capability of Cu<sup>2+</sup> ions to diffuse into the lattice of TiO<sub>2</sub> nanotubes was drastically accelerated and when it exceeds its saturation limits, the Cu<sup>2+</sup> ions started to precipitate on the nanotubes surface. The incorporation of Cu<sup>2+</sup> ions on pristine TiO<sub>2</sub> nanotubes was further demonstrated by the EDX analysis, which exhibited the presence of Cu element of about 1.30 at% for the sample prepared at room temperature. In addition, other elements such as Ti, C, and O were traced in the EDX spectrum. At% of the Cu element within the

sample prepared at 60°C and 80°C was increased to 2.0 at% and 2.9 at%, respectively (not shown). Based on the results obtained, it could be deduced that as the reaction temperature was increased, at% of Cu element loaded in TiO<sub>2</sub> nanotubes was increased significantly. By incorporating Cu into titania matrix, new active sites will be introduced and enhance visible light absorption capacity. Both Cu<sup>2+</sup> and Cu<sup>+</sup> can act as effective electron scavenger which resulted in better separation between electron and hole and more free holes are available for oxidation process. Cu<sup>2+</sup> can act as electron trapper since its reduction potential is more positive than the conduction band of band edge of TiO<sub>2</sub>. The trapping of electrons by Cu<sup>2+</sup> and the trapping of holes by its reduced form were proposed to explain the decrease of the electron hole recombination rate and a higher production of HO• radicals [29]. In the present study, the influence of reaction temperature on the crystal structure of Cu-TiO<sub>2</sub> nanotubes was investigated via XRD measurement. The resultant XRD patterns of TiO<sub>2</sub> nanotubes prepared at different temperature after photocatalysis are shown in Figure 2. As demonstrated in the XRD patterns, peaks of anatase phase TiO<sub>2</sub> were at 2θ of 25.37°, 38.67°, 48.21°, and 54.10°, which corresponded to (101), (112), (200), and (105) crystal planes, respectively [30]. However, no obvious Cu phases could be detected from the XRD patterns although the percentage of Cu has exceeded 2 at%. This result manifested that Cu dopants existed in amorphous form. Besides, it could be noticed that the intensity of the (101) peak at 25.3° was increased by increasing the reaction temperature environment, indicating an increase in crystallinity of anatase phase for Cu-TiO<sub>2</sub> nanotubes. The possible improvement in the crystallization anatase structure at 60°C and 80°C could be explained with solid-state mechanism [10, 11]. The adsorption of OH<sup>-</sup> ions from water molecule on the surface of nanotubes was accelerated at high temperature. The adsorbed-OH<sup>-</sup> ions subsequently reacted with the titanium (Ti<sup>3+</sup>) ions in amorphous TiO<sub>2</sub> nanotubes. Ti<sup>3+</sup> was obtained during irradiation whereby, the electrons are captured by titanium ions (Ti<sup>4+</sup> + e<sup>-</sup>), leading to the formation of paramagnetic Ti<sup>3+</sup> ions [31]. This forms bridges between surface OH groups of different octahedral of TiO<sub>6</sub> within the lattice that shared common vertex. The dehydration consequently occurred and the structure of two octahedral sharing with one edge was formed in order to form anatase phase. Based on the aforementioned results, increasing the reaction temperatures benefits the crystallization of nanotubes but never benefits the incorporation of Cu<sup>2+</sup> dopants evenly to the nanotubes. Thus, the Cu-TiO<sub>2</sub> nanotubes prepared at room temperature were duplicated for the photocatalytic oxidation of Pb(II) ions study [32, 33].

pH at acidic and alkaline condition was selected and evaluated. The performance of Pb(II) ions removal using Cu-TiO<sub>2</sub> nanotubes at pH 5 and pH 11 was further investigated. Results also showed that the rates of the photocatalytic reduction of lead increased with pH. This effect was due to both reduction process and hydroxide precipitation. The initial concentration of Pb(II) solution was varied from 2 ppm, 4 ppm, 10 ppm, 20 ppm, 60 ppm, and 100 ppm. It is noteworthy to mention that the removal of Pb(II) ions is

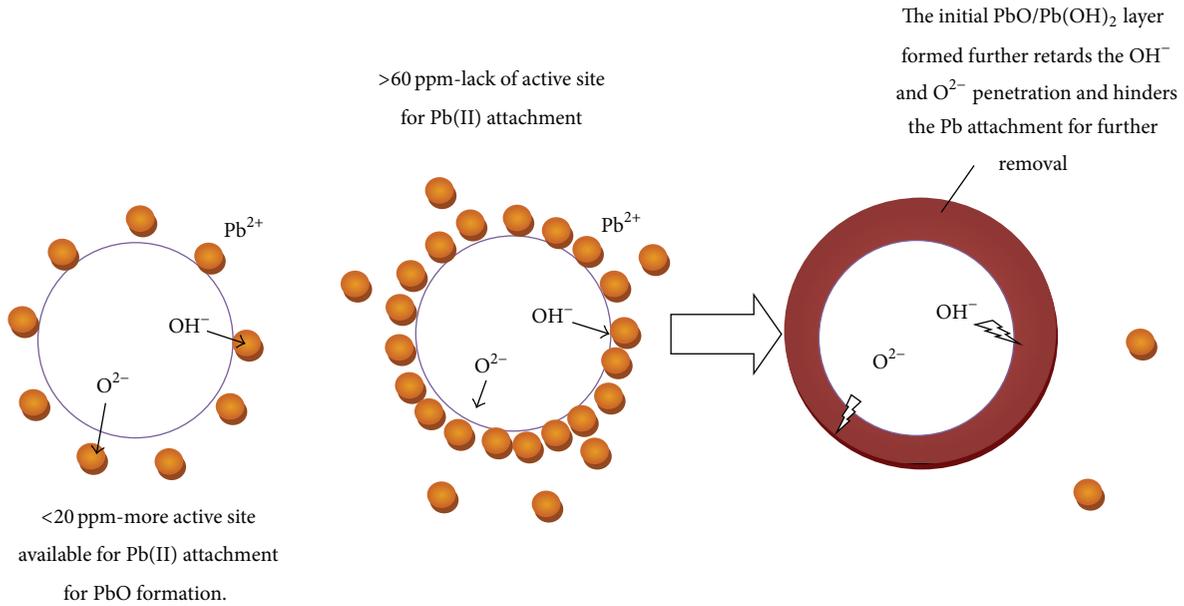


FIGURE 5: Schematic diagram illustrating that the formation of PbO/PbOH layer on TiO<sub>2</sub> retards the photocatalytic reaction for more Pb(II) removal.

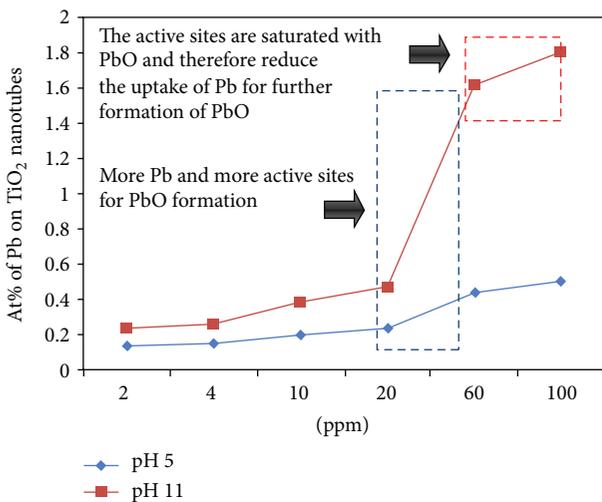


FIGURE 6: Atomic percentage (at%) of Pb on TiO<sub>2</sub> nanotubes at different concentration of Pb(II).

high with UV illumination as compared to dark environment regardless to pH 5 (Figure 3) or pH 11 (Figure 4). This clearly indicates that resultant Cu-TiO<sub>2</sub> nanotubes as active photocatalyst could be regarded as an applicable process for Pb(II) ions treatment. However, it was found that the Pb(II) ions removal in dark environment was greater at pH 11 as compared to pH 5. It is relevant to note that at pH value above 6, direct reaction within the OH<sup>-</sup> in base condition with free Pb(II) ions would be enhanced. As a result, Pb hydroxide complexes such as Pb(OH)<sup>+</sup>, Pb(OH)<sub>2</sub>, and Pb(OH)<sub>3</sub> could also be formed, which then precipitate from solution. This would reduce the remnant Pb(II) in the solution of pH 11 to greater extent as compared to pH 5. The similar trend could be observed when UV illumination was applied in the

Pb(II) ions treatment. The Pb(II) ions removal was much better for pH 11 as compared to pH 5. So the synergistic effects of photocatalytic reaction under UV illumination with formation of precipitates at pH 11 would reduce the total remnant Pb(II) ions in the solution to greater extent than pH 5 (which only subjected to photocatalytic reaction) [34]. This explains the results obtained at 100 ppm, whereby the percentage of removal of Pb at pH 11 is 79.5%, while at pH 5 was 56.3%. Other than that, the removal of Pb(II) ions under UV illumination was found high up to 20 ppm and slowly reduced after 60 ppm. This could be due to active surface of photocatalyst available on the surface of the TiO<sub>2</sub> nanotubes to attract Pb(II) ions for photocatalytic reaction is sufficient to remove 20 ppm of Pb(II) ions. However, at 60 ppm the removal of Pb(II) ions dropped to 80.5 and at 100 ppm to 56.3%. The reason might be attributed to the lack of active surface for Pb(II) ions attachment for photocatalytic reaction at high concentration and thick initial layer of PbO after photocatalytic reaction that hindered further diffusion of OH<sup>-</sup> and O<sup>2-</sup> ions for reduction of Pb(II). This is schematically illustrated in Figure 5 and was further affirmed with EDX analysis plotted in Figure 6. The results demonstrated that Pb content at the surface of the nanotubes was changing abruptly within 20 ppm to 60 ppm and then slowed down after 60 ppm onwards. This explains the results obtained at 100 ppm, which showed low percentage of Pb(II) ions removal. So the optimum concentration of Pb(II) that is suitable for photocatalytic reaction would be within 20–60 ppm. Additionally, these Cu-TiO<sub>2</sub> nanotubes can be reused and need further investigation.

#### 4. Conclusion

In summary, Cu-TiO<sub>2</sub> nanotubes were successfully prepared using electrochemical anodization and wet impregnation

techniques. The reaction temperature environment during wet impregnation played an important role in the morphological control and content of  $\text{Cu}^{2+}$  dopants diffused into the  $\text{TiO}_2$  nanotubes. It was found that at% of  $\text{Cu}^{2+}$  ions loaded into  $\text{TiO}_2$  nanotubes was increased significantly with increasing reaction temperatures. An irregular and corrugated nanotubular surface covered with Cu precipitates was observed under high reaction temperature of  $80^\circ\text{C}$ . In the present study, Cu- $\text{TiO}_2$  nanotubes were prepared at room temperature for the photocatalytic oxidation of Pb(II) ions removal. It was noticed that the Pb(II) ions removal performance was greater at pH 11 as compared to pH 5 under UV illumination and assisted by Cu- $\text{TiO}_2$  nanotubes due to the more direct reactions within the  $\text{OH}^-$  in base condition with free Pb(II) ions. In addition, our results show that the Pb content at the surface of the nanotubes was changing abruptly within 20 ppm to 60 ppm and then slowed down after 60 ppm onwards. Thus, the optimum concentration of Pb(II) ions for effective Pb(II) ions removal performance was 20–60 ppm.

### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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