

## Photocatalytic Reduction of $\text{AuCl}_4^-$ by $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$ Nanoparticles

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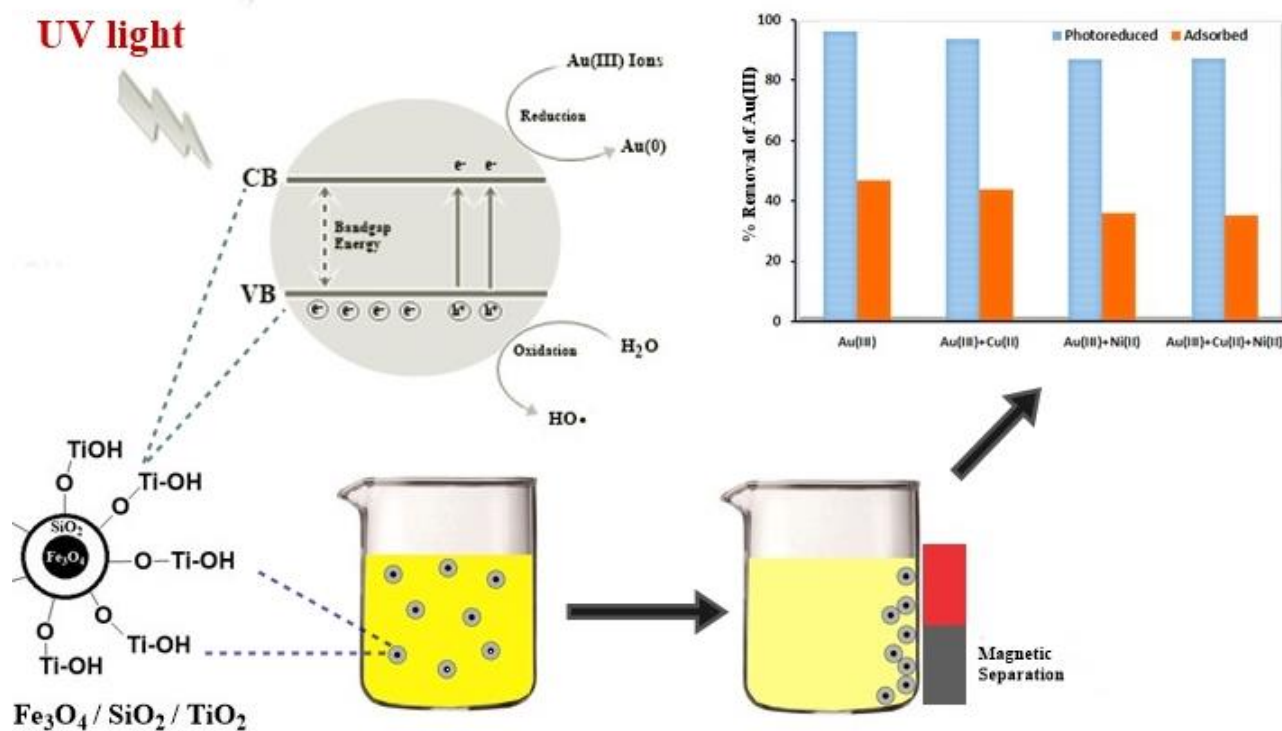
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### ABSTRACT

Metallurgy and recovery of gold in electronic waste sometimes involve the reduction of tetrachloroaurate ion ( $\text{AuCl}_4^-$ ) to elemental gold form. Currently, for the reduction of tetrachloroaurate ion, people use reducing agents such as hydroquinone and sodium borohydride. Photocatalysts of  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$  nanoparticles were prepared and tested for the reduction of tetrachloroaurate ion under UV light illumination. The magnetite ( $\text{Fe}_3\text{O}_4$ ) nanoparticle was first prepared by coprecipitation and sonication, followed by  $\text{SiO}_2$  and  $\text{TiO}_2$  coatings via the sol-gel process and calcination. The products were confirmed by XRD and TEM. The photocatalytic reduction of tetrachloroaurate ion was performed in a closed reactor equipped with a UV light source. The results indicated that  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$  nanoparticles were successfully prepared, which retained good magnetic and photocatalytic properties. The photocatalytic reaction is best performed at a pH of 5 under UV irradiation for 2 h, which is capable of reducing 96% of the tetrachloroaurate present in the mixture. The co-presence of  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions in the solution leads to a decrease in yield due to competitive reduction and adsorption. The photocatalyst is recoverable by the use of a magnetic bar and may find application for gold recovery and metallurgy.

**Keywords:** nanoparticle,  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$ , photoreduction, tetrachloroaurate



## Graphical Abstract

### 1. Introduction

Gold is one of the precious metals, well-known for its beauty, corrosion resistance, malleability, and ease to form alloys. It has been used to prepare coins and jewelry since ancient times. Along with technological advances, gold is now used in the production of electronic devices for its excellent electrical conductivity. The rapid technological progress and consumptive nature of society lead to the shortening of the use of electronic devices, which use gold in many of their components. It speeds up the discharge of electronic devices waste. Among other rare earth metal elements, the valuable component of the electronic device waste is gold.

Roughly, the waste of electronic devices contains 40% of metals, including heavy metals such as copper (20%), tin (4%), nickel (2%), lead (2%), silver (0.02%) and precious metals such as gold (0.1%) (Gramatyka *et al.*, 2007). Therefore, metal recovery of electronics waste is an important way,

not only from the management of hazardous waste point of view but also from the recovery process of the precious metals.

The process of gold recovery from electronic equipment waste requires several steps that are dissolution, separation, and purification (Cui and Zhang, 2008). In the purification step, the photocatalytic reduction method is usually applied by utilizing a semiconductor, which is relatively new and potentially useful as an alternative green method. More importantly, it does not produce harmful by-products (Kida et al., 2009; Barakat, 2010).

Titanium dioxide is often used as a photocatalyst because of its low toxicity, superior photocatalytic performance, and good chemical stability. Several studies on the application of titanium dioxide for gold recovery have been reported, such as by Grieken *et al.*, (2005) who have reviewed the gold recovery process from electroplating waste in the  $[\text{Au}(\text{CN})_2]^-$  complex using a titanium dioxide photocatalyst. Wojnicki *et al.* (2013) have conducted a study of gold photoreduction kinetics in the complex form  $\text{AuCl}_4^-$  using  $\text{TiO}_2$ . Wahyuni *et al.* (2015) have successfully examined the application of gold recovery by photocatalytic reduction of  $\text{AuCl}_4^-$  ion by utilizing  $\text{TiO}_2$  photocatalyst with the addition of other metal ions such as  $\text{Ag}(\text{I})$ ,  $\text{Cu}^{2+}$ , and  $\text{Fe}^{3+}$ .

The photocatalytic reaction commonly takes place in the suspension of a photocatalyst having a nanometer size, so that an efficient separation process is required to recover the catalyst from the aqueous medium. Several studies have been conducted regarding suspended  $\text{TiO}_2$  separation efforts in heterogeneous photocatalysis processes, e.g., flocculation, sedimentation and microfiltration (Xi and Geissen, 2001; Rottman, 2013). But such methods need additional costs for chemicals, takes a relatively long time, are relatively expensive and need control during the separation process.

Photocatalysts such as glass beads, silica gel, glass fibers in mesh form, and zeolites are coated with titanium to alleviate the problem (Szabo et al., 2013). Although this method can provide solutions to problems related to the difficulty of liquid-solid phase separation, slurry-type reactors are more advantageous than immobilized photocatalyst systems in terms of available surface area and better mass-transfer characteristics. The magnetization of the photocatalyst can facilitate the process of

photocatalyst recovery with the help of a magnetic bar. This modification is able to combine the characteristics of the surface to volume ratio and settling process commonly observed by larger particles (Beydoun et al, 2000).

The TiO<sub>2</sub> modification of the catalyst can be done by superimposing on the surface of the magnetic material. Beydoun *et al.* (2000) have reported work on the modification of magnetite by superimposing with titania to give photocatalyst nanocomposite. However, direct contact between the titania and iron oxide could lower photocatalytic activity and cause a photo dissolution event. To avoid this problem, in the later research Beydoun and Amal (2002) modified magnetite by coating with SiO<sub>2</sub> as an insulating layer for direct charge transfer between Fe<sub>3</sub>O<sub>4</sub> core and TiO<sub>2</sub> shell. The SiO<sub>2</sub> layer with porous structures enables the surface area to increase and to facilitate better access for target species to reach the active site of the material (Ullah *et al.*, 2015). Several studies on addition of SiO<sub>2</sub> layer to the Fe<sub>3</sub>O<sub>4</sub>/TiO<sub>2</sub> nanocomposite show a better performance in photooxidation of organic compounds such as sucrose (Beydoun and Amal, 2002), methyl orange (Gad-Allah *et al.*, 2007), acetaminophen, antipyretin, caffeine, metoprolol, bisphenol A (Álvarez *et al.*, 2010), methylene blue (Kunarti *et al.*, 2016) and photoreduction of silver(I) ions (Kunarti *et al.*, 2017). We have been working on the photocatalytic reduction of metallic ions (Kunarti *et al.*, 2017; Fajri, 2017). In this contribution, photocatalytic reduction of tetrachloroaurate ion by Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/TiO<sub>2</sub> nanoparticles is reported. This work is novel since the photoreduction of tetrachloroaurate ion using this type of photocatalyst has not been reported elsewhere. In addition, the photoreduction of tetrachloroaurate is usually done with TiO<sub>2</sub> photocatalyst. The introduction of magnetic material of magnetite to the TiO<sub>2</sub> photocatalyst allows us to separate and reuse the photocatalyst. Further, the effect of some operating conditions such as pH and time is evaluated. In addition, the co-presence of Cu<sup>2+</sup> and Ni<sup>2+</sup> that are commonly found along with AuCl<sub>4</sub><sup>-</sup> is also examined. These two metals are also present in the minerals containing gold.

## **2. Materials and methods**

### *2.1. Chemicals*

Iron(II) chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ), iron(III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), tetraethyl orthosilicate (TEOS, >99%), trisodium citrate dihydrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ ), ethanol, ammonia solution (25% v/v), tetrachloroauric acid ( $\text{HAuCl}_4$ ) were purchased from Merck. Titanium(IV) tetraisopropoxide (TTIP, >97%) was acquired from Aldrich. Deionized water was used as the main solvent throughout the experiments. The chemicals were used as received without further purification.

### 2.2 Preparation of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$ nanoparticles

Magnetite,  $\text{Fe}_3\text{O}_4$ , and  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  nanoparticles were prepared according to the previous work (Kunarti *et al.*, 2017) with slight modification. They were synthesized through a sol-gel method. Briefly,  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  was dispersed in 30 mL ethanol 98% followed by the addition of 0.20 mL deionized water and 1 mL TTIP. The mixture was ultrasonicated for 3 hours. The produced material was washed with ethanol several times. The solids were dried, and the product obtained was calcined at 500 °C for 3 h. The as prepared  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$  nanoparticles were characterized and then applied for the recovery of gold through photoreduction of tetrachloroauric ions

### Product characterization and analysis

X-ray diffraction patterns were recorded on Shimadzu XRD 6000, with  $\text{Cu-K}\alpha$  radiation. The XRD patterns were used to confirm the crystal structure of the synthesized materials. Transmission electron microscopy (TEM) images were obtained on JEOL JEM-1400 TEM with an acceleration voltage of 120 kV. The magnetic properties were quantified using a cryogen-free physical measurement vibrating sample magnetometer (Oxford VSM 1.2H). The tetrachloroaurate ions in the solution were determined by using atomic absorption spectrometry (AAS) (Perkin Elmer 3110).

### 2.3 Photocatalytic reduction of tetrachloroauric

The photoreduction of tetrachloroaurate ion was performed in a batch system in a closed vessel equipped with a UV-lamp (40 W, 220 V, wavelength 340-390 nm). A 25 mL  $\text{AuCl}_4^-$  solution of 50 mg/L, and the catalyst weighed 0.025 g were placed in the glass vessel. The nanoparticles were dispersed by stirring the suspension continuously using magnetic stirrer under UV-irradiation. After the reaction, the solution tetrachloroaurate ions were analyzed by AAS. In this study, the effect of pH

and time, and the addition of  $\text{Cu}^{2+}$ , and  $\text{Ni}^{2+}$  ions were also studied. The predetermined condition is presented in Table 1.

Variable	Preset
pH	1, 3, 5, 7, 9
Reaction time (h)	0.5, 1, 2, 3, 4
Mas of photocatalyst (mg)	25
Concentration of $\text{AuCl}_4^-$ (mg/L)	50
Concentration of $\text{Ni}^{2+}$ (mg/L)	50
Concentration of $\text{Cu}^{2+}$ (mg/L)	50

#### *Reduction of $\text{AuCl}_4^-$ ions in a mixture with $\text{Cu}^{2+}$ or $\text{Ni}^{2+}$*

A portion of 0.025 g of  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$  nanoparticles photocatalyst was incorporated into the mixture of  $[\text{AuCl}_4]^-$  and  $\text{Cu}^{2+}$  (or  $\text{Ni}^{2+}$ ) solution with a molar ratio of 1:1 at pH 5 in the photocatalyst reactor while stirred and irradiated with UV light for 2 h. After photoreaction, the tetrachloroaurate ion ions content was analyzed by AAS, and the photocatalyst material was separated from the solution using an external magnetic bar.

#### *Reduction of $\text{AuCl}_4^-$ ions in a mixture with both $\text{Cu}^{2+}$ and $\text{Ni}^{2+}$ ions*

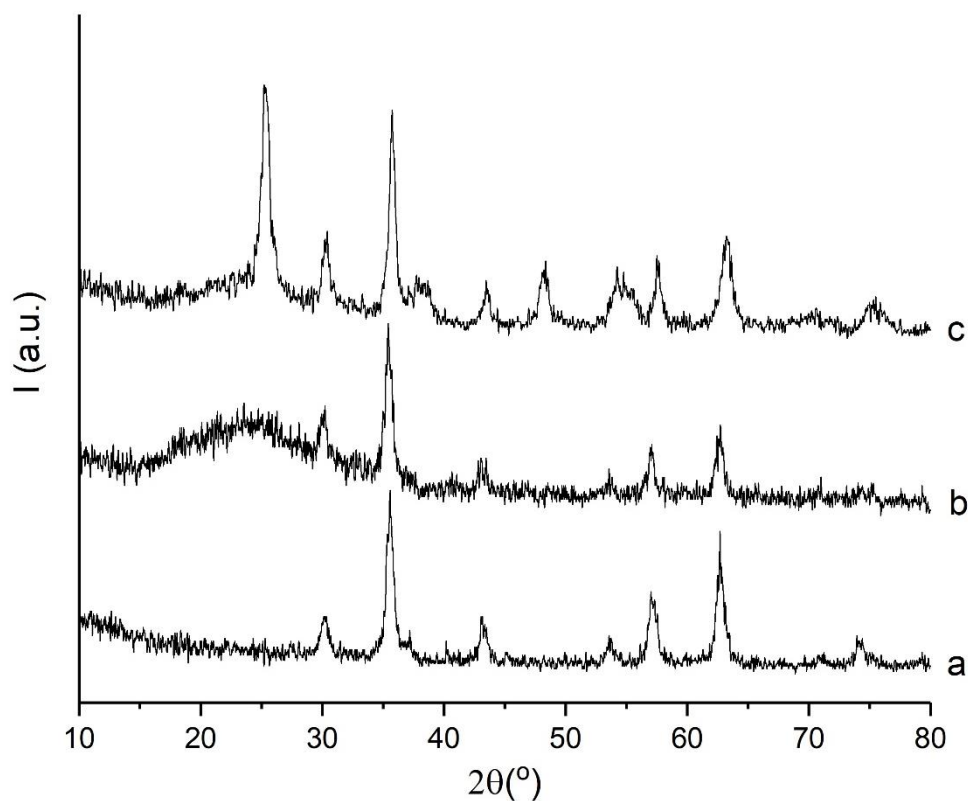
$\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$  nanoparticles photocatalyst weighed 0.025 g was dispersed into the mixture of  $\text{AuCl}_4^-$ ,  $\text{Ni}^{2+}$ , and  $\text{Cu}^{2+}$  solution with a molar ratio of 1:1:1 in a reactor while being stirred and irradiated with UV light. The solution pH was preset at 5. Irradiation was done for 2 h. After photoreaction, the solid material was separated from the solution using an external magnetic bar, and the metal content was sampled by AAS.

### **3. Results and Discussion**

#### *3.1. Characterisation of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$ nanoparticles*

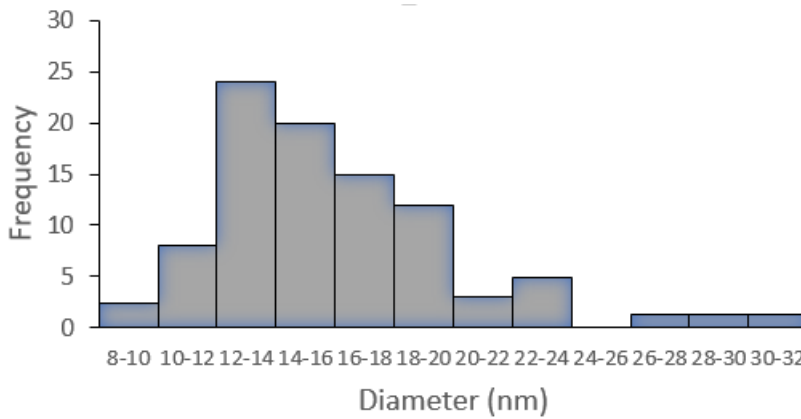
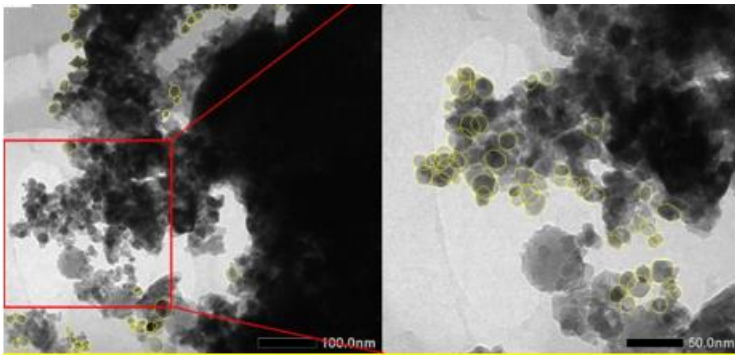
Figure 1 shows the diffraction patterns for  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4/\text{SiO}_2$ , and  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$ . The  $\text{Fe}_3\text{O}_4$  diffractogram agrees with the JCPDS No. 01-1111 as confirmed with the peaks at  $2\theta=30.22$ ,  $35.56$ ,  $43.14$ ,  $57.04$ , and  $62.66^\circ$  (Fig. 1a), which indicates face-centered cubic (*fcc*) crystal structure. A similar pattern was observed after coating with  $\text{SiO}_2$  with the addition of a wide peak at  $2\theta$  about 21-

26°. This peak is believed to be due to the amorphous SiO<sub>2</sub> phase. Peaks of the anatase phase of TiO<sub>2</sub> appear at 25.22°, 48.36, and 54.22 on the diffraction pattern of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/TiO<sub>2</sub>. A similar result was also reported by previous studies (Kunarti et al., 2016; Kunarti et al., 2017) and literatures (Schatz *et al.*, 2009; Xue *et al.*, 2013)



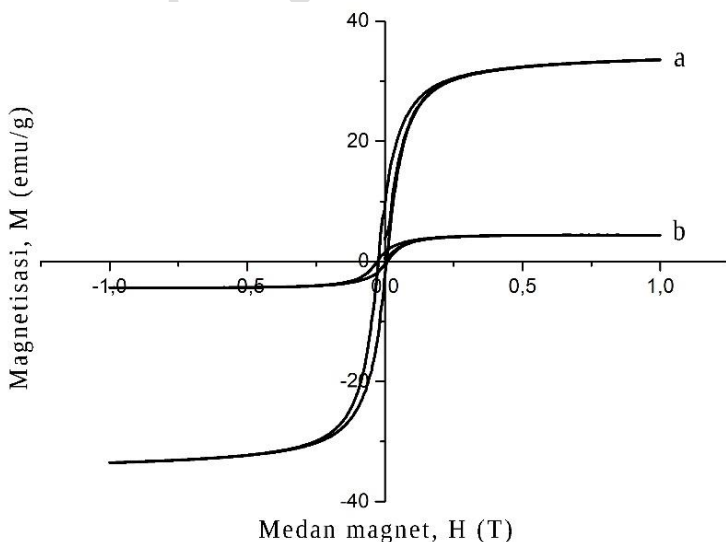
**Figure 1.** XRD patterns of (a) Fe<sub>3</sub>O<sub>4</sub>, (b) Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> and (c) Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/TiO<sub>2</sub> nanoparticles

The TEM images of the obtained nanoparticles are presented in Figure 2. It is observed that there are spherical dark images of Fe<sub>3</sub>O<sub>4</sub> core particles covered by a bright shell of SiO<sub>2</sub> and TiO<sub>2</sub> at the outer shell, which very similar brightness with the SiO<sub>2</sub> inner shell. It is believed that TiO<sub>2</sub> coats the outer shell of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> nanoparticles. The mean diameter of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/TiO<sub>2</sub> nanoparticles is estimated to be 14 nm.



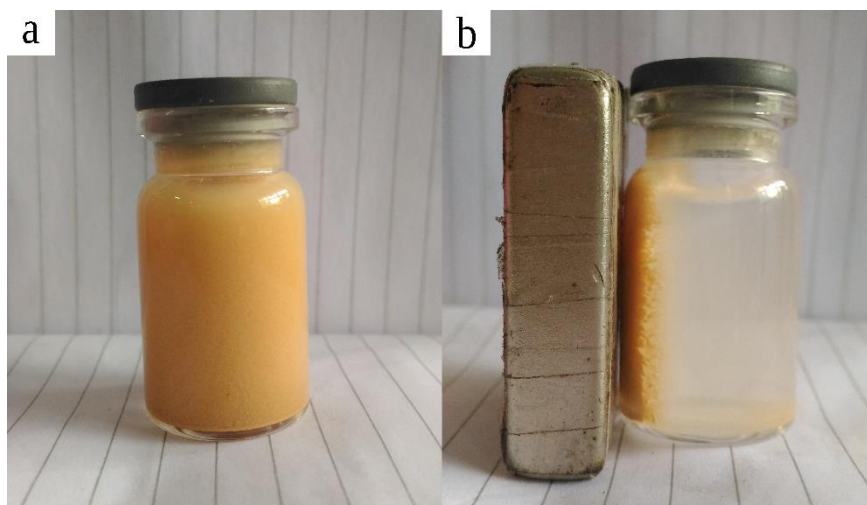
**Figure 2.** TEM images of Fe<sub>3</sub>O<sub>4</sub> nanoparticles after coating with SiO<sub>2</sub> and TiO<sub>2</sub>

The magnetic properties of the products were recorded quantitatively by use of a vibrating sample magnetometer (VSM) (Figure 3). The data suggest that there is a decrease in the magnetic properties of Fe<sub>3</sub>O<sub>4</sub> after coating with SiO<sub>2</sub> and/or TiO<sub>2</sub>. The magnetic hysteresis indicates the superparamagnetic nature of materials. Although there is an appreciable decrease, in general the magnetism of the product is still good (4.38 emu/g). This magnetic property still allows us to recover the solids by an external magnetic bar after application (Figure 4).





**Figure 3.** VSM curve of (a) Fe<sub>3</sub>O<sub>4</sub>, and (b) Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/TiO<sub>2</sub> nanoparticles

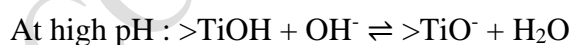


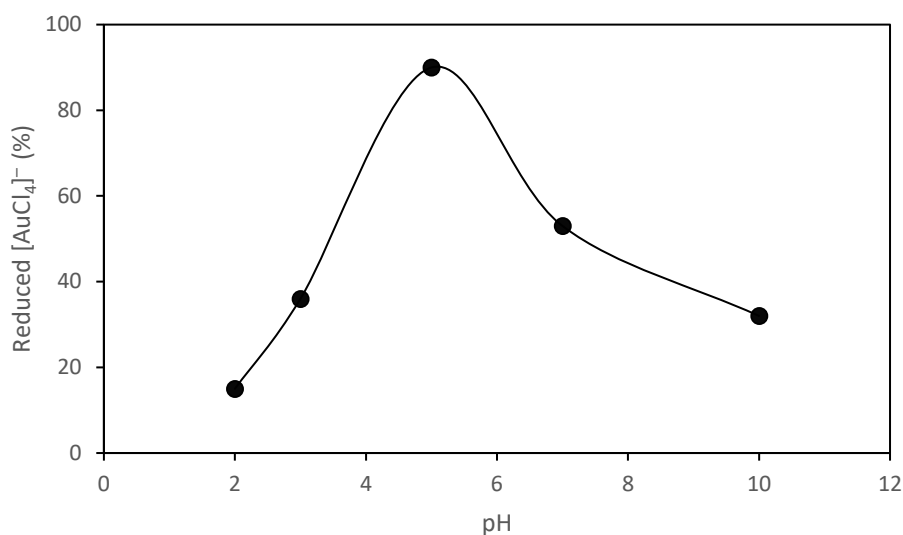
**Figure 4.** The picture of photocatalyst (a) before and (b) after interaction with a magnetic bar.

### 3.2 Photocatalytic reduction of tetrachloroauric

#### 3.2.1. The effect of reaction pH

The medium acidity is one of the critical parameters in the photocatalytic reduction process. The pH of the medium affects the charge of the TiO<sub>2</sub> and AuCl<sub>4</sub><sup>-</sup> species. Figure 5 shows the effect of pH on AuCl<sub>4</sub><sup>-</sup> ion reduction. The photocatalytic reduction increases along with increasing pH and reaches an optimum condition at pH 5. The ease of TiO<sub>2</sub> to give electrons and to form OH is strongly affected by surface speciation of TiO<sub>2</sub>. The specification of the surface of TiO<sub>2</sub> (>TiOH) in the aqueous solution is commonly written as follows (Hoffmann *et al.*, 1995)





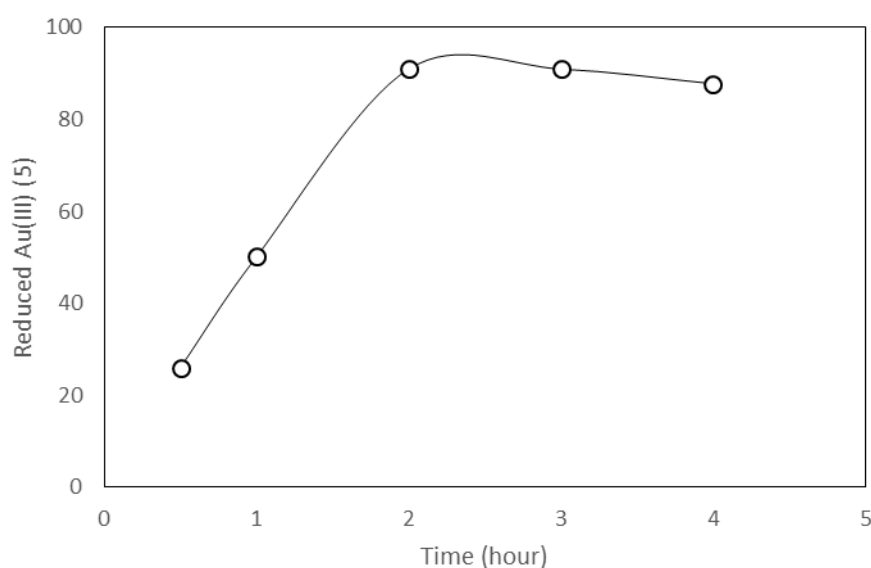
**Figure 5.** Effect of pH on the photocatalytic reduction of  $\text{AuCl}_4^-$

At pH less than 3,  $>\text{TiOH}$  is dominant to form  $>\text{TiOH}_2^+$ . The presence of  $>\text{TiOH}$  is abundant at pH 3 to 10. Meanwhile, at pH above 10, the  $>\text{TiOH}$  is dominant as  $>\text{TiO}^-$ , so at the pH of 5,  $\text{TiO}_2$  will be in the form of  $\text{TiOH}_2^+$  species and the lower the pH, the more  $\text{TiOH}_2^+$  species. At pH 5,  $\text{TiO}_2$  is present as  $\text{TiOH}_2^+$  species which will interact with anionic charged of  $[\text{AuCl}_4]^-$  solution. In the presence of UV rays, the photocatalyst will absorb energy from UV rays so that electrons will be transferred from the valence band to the conduction band of  $\text{TiOH}_2^+$ . The  $\text{AuCl}_4^-$  species will interact with the surface of the photocatalyst, so when  $\text{AuCl}_4^-$  is on the surface of the photocatalyst, there will be an  $\text{AuCl}_4^-$  reduction process to metallic gold. At the pH below 5, however, there is a decrease in the reduced  $\text{AuCl}_4^-$  concentration. This is because the number of  $\text{TiOH}_2^+$  species is very abundant, resulting in the number of electrons produced decreases. However, when the pH above 5 species of  $\text{TiO}_2$  will turn into  $\text{TiO}^-$  then the interaction between  $\text{TiO}^-$  and  $\text{AuCl}_4^-$  becomes difficult result in a lack of  $\text{AuCl}_4^-$  which can be reduced. In addition, the increase in pH in the solution also causes a species change from  $\text{AuCl}_4^-$  into precipitation that makes the reduction process ineffective.

### 3.2.2 The effect of reaction time

**Figure 6** shows the effect of the irradiation time on the reduction of  $\text{AuCl}_4^-$  ions. The longer the irradiation time the more  $\text{AuCl}_4^-$  to be reduced. A slight decrease in the reduction after 2 h was observed. The number of electrons formed for the occurrence of the reduction process is influenced

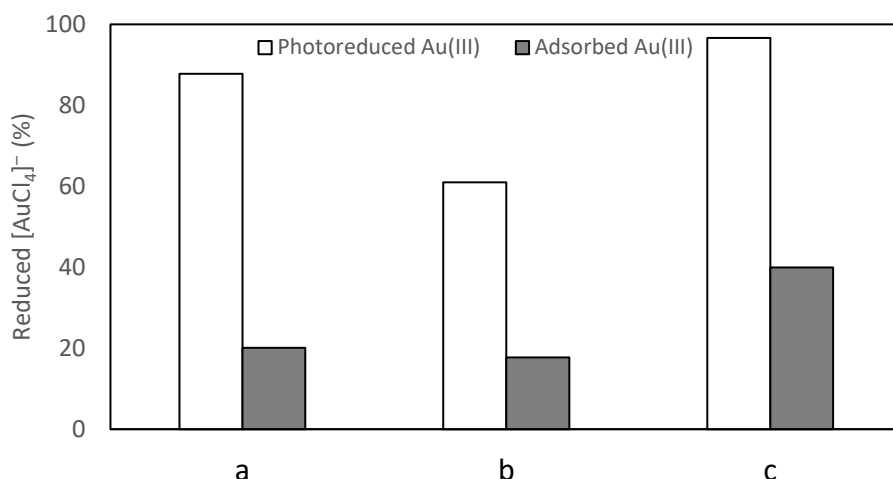
by the number of rays that affect the photocatalyst surface. Figure 6 shows that at the time of irradiation 0-2 h an increase in  $\text{AuCl}_4^-$  ion reduction. This is caused by the longtime of irradiation that impacts more photon energy on the photocatalyst. This results in more electrons being formed and the reduction of  $\text{AuCl}_4^-$  ions to  $\text{Au}^0$  will increase. Photoreduction for 2h is the optimum point of irradiation. In a longer reduction process, the surface of the photocatalyst has been covered by the Au-precipitate resulting from the reduction process thus blocking the interaction between the photocatalyst and the UV light, resulting in constant photocatalytic activity. However, in the results of this study, there is a decrease in the percentage of reduction, this may be due to desorption of the release of  $\text{AuCl}_4^-$  ions that have bound to  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$  nanoparticles.



**Figure 6.** Effect of irradiation time on the photocatalytic reduction of  $\text{AuCl}_4^-$  to  $\text{Au}^0$

### 3.2.3 The effect of $\text{SiO}_2$ on the catalytic reduction of $\text{AuCl}_4^-$

To evaluate the obtained photocatalysts in the reduction of  $\text{AuCl}_4^-$  ions, the photoreduction reaction was carried out with and without UV light exposure. Figure 7 shows the amount of  $\text{AuCl}_4^-$  ions both reduced and adsorbed using each of photocatalysts with and without UV light exposure.



**Figure 7.** Reduction of  $\text{AuCl}_4^-$  with photocatalyst of (a)  $\text{TiO}_2$ , (b)  $\text{Fe}_3\text{O}_4/\text{TiO}_2$  and (c)  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$

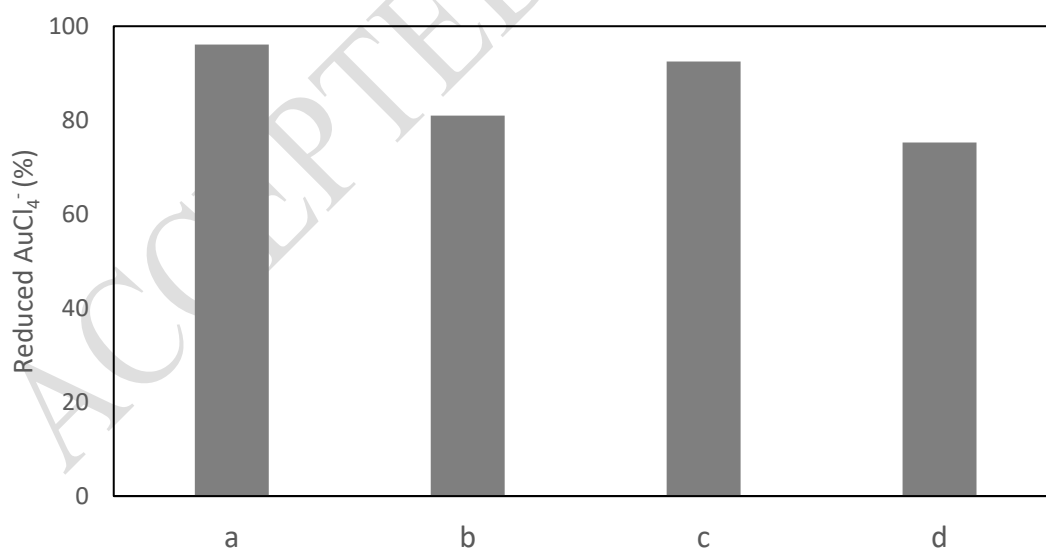
**Figure 7** appears that under UV-light irradiation, the  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$  nanoparticles have a better photocatalytic activity to reduce  $\text{AuCl}_4^-$  than that of  $\text{Fe}_3\text{O}_4/\text{TiO}_2$ , and  $\text{TiO}_2$ . The  $\text{Fe}_3\text{O}_4/\text{TiO}_2$  nanoparticles have the lowest  $\text{AuCl}_4^-$  photoreduction activity could be due to direct contact between the  $\text{TiO}_2$  and the  $\text{Fe}_3\text{O}_4$ , where the  $\text{Fe}_3\text{O}_4$  nanoparticles act a recombination center (Beydoun and Amal, 2002). This recombination causes a small number of  $\text{TiO}_2$  conduction electrons ( $e_{cb^-}$ ) to play a role in reducing  $\text{AuCl}_4^-$  ions hence the percentage of  $\text{AuCl}_4^-$  species is small. This phenomenon did not occur for  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$ , because of the presence of the  $\text{SiO}_2$  layer as a charge-transfer insulator was able to prevent electron-hole recombination. This causes the photoreduction activity of  $\text{AuCl}_4^-$  ions using  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$  better than that of  $\text{Fe}_3\text{O}_4/\text{TiO}_2$ . Meanwhile, the  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$  nanoparticle has a higher photoreduction activity than  $\text{TiO}_2$  due to the presence of the  $\text{SiO}_2$  layer (Liu *et al.*, 2011). The  $\text{SiO}_2$  layers which have a porous structure can increase the surface area for adsorption so that it facilitates the access of  $\text{AuCl}_4^-$  Au ions to the photocatalyst active site. In addition, the presence of silica is also capable of immobilizing  $\text{TiO}_2$  so that can minimize the agglomeration of  $\text{TiO}_2$  particles that may occur in  $\text{TiO}_2$  particles. This condition causes the photoreduction process of  $\text{AuCl}_4^-$  ions using  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$  to be more efficient.

It is known that the photocatalytic reduction process is initiated and/or accompanied by the adsorption of the species on the TiO<sub>2</sub> surface. Figure 7 shows the results of AuCl<sub>4</sub><sup>-</sup> ions adsorption by photocatalysts, in the absence of UV light irradiation. It appears that the Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/TiO<sub>2</sub> photocatalyst has the best adsorption ability. The presence of a SiO<sub>2</sub> layer which has a large surface area seems to have better characteristics of mass transfer. The AuCl<sub>4</sub><sup>-</sup> adsorption by Fe<sub>3</sub>O<sub>4</sub>/TiO<sub>2</sub> solid is smaller than that of TiO<sub>2</sub>, which is likely due to its lower surface area. It is in good agreement with the previous report (Banisharif *et al.*, 2013).

### 3.2.4 Photocatalytic reduction of AuCl<sub>4</sub><sup>-</sup> ions in the presence of Ni<sup>2+</sup> and Cu<sup>2+</sup>

Besides gold, nickel and copper are found in electronic waste (Gramatyka *et al.*, 2007). To recover gold from electronic waste, it is first soaked in a strong acid solution to produce AuCl<sub>4</sub><sup>-</sup>, Ni<sup>2+</sup>, and Cu<sup>2+</sup>. Ni<sup>2+</sup> and Cu<sup>2+</sup> ions can be photocatalytically reduced by TiO<sub>2</sub> (Joshi *et al.*, 2011). The presence of Ni<sup>2+</sup> and Cu<sup>2+</sup> ions might affect the photoreduction of AuCl<sub>4</sub><sup>-</sup> ions. In this study, AuCl<sub>4</sub><sup>-</sup> photoreduction reaction is also carried in the solution containing Ni<sup>2+</sup> and Cu<sup>2+</sup> ions. The reaction was performed using Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/TiO<sub>2</sub> photocatalyst under UV irradiation. The results are presented in

Figure 8.



**Figure 8.** Reduction of AuCl<sub>4</sub><sup>-</sup> catalyzed by Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/TiO<sub>2</sub> a) without Ni<sup>2+</sup> and Cu<sup>2+</sup>, b) with Ni<sup>2+</sup> in the mixture where AuCl<sub>4</sub><sup>-</sup> to Ni<sup>2+</sup> molar ratio 1: 1, c) with Cu<sup>2+</sup> in the mixture where AuCl<sub>4</sub><sup>-</sup> to Cu<sup>2+</sup> molar ratio of 1: 1, and d) with Ni<sup>2+</sup> and Cu<sup>2+</sup> in the mixture where AuCl<sub>4</sub><sup>-</sup> to Ni<sup>2+</sup> to Cu<sup>2+</sup> molar ratio of 1:1:1

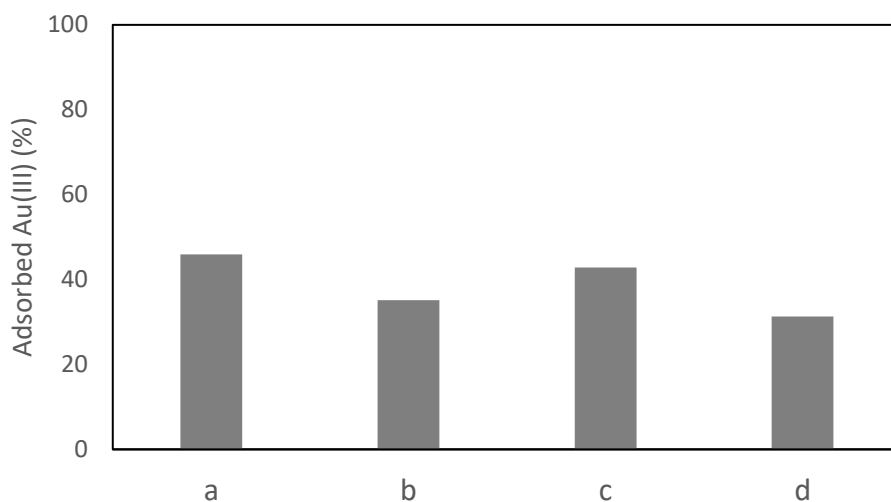
Figure 8 shows that the addition of  $\text{Ni}^{2+}$  ions causes a decrease in the number of  $\text{AuCl}_4^-$  ions reduced from 96.13% to 80.98%. In the absence of  $\text{Ni}^{2+}$  ions, all conduction band ( $e_{cb^-}$ ) electrons produced by  $\text{TiO}_2$  are used to reduce Au ions while in the presence of  $\text{Ni}^{2+}$  ions, both Au ions and  $\text{Ni}^{2+}$  ions capable of being reduced by  $\text{TiO}_2$  so that during the photoreduction reaction takes place, there is competition in the use of the conduction band electrons ( $e_{cb^-}$ ) produced by  $\text{TiO}_2$ . This causes some conduction band electrons ( $e_{cb^-}$ ) to be used to reduce  $\text{AuCl}_4^-$  ions and the other part is used to reduce  $\text{Ni}^{2+}$  ions. Decreasing the number of conduction band electrons ( $e_{cb^-}$ ) to reduce  $\text{AuCl}_4^-$  ions causes a decrease in reduced  $\text{AuCl}_4^-$  ions.

Evaluation of  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$  activity for  $\text{AuCl}_4^-$  ion reduction was also made by comparing the photocatalytic activity of  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$  in the presence of  $\text{Cu}^{2+}$  ions with the molar ratio of 1: 1 under UV illumination. The result is presented in Figure 8. It shows a slight decrease in the percentage reduction of Au ions in the mixture of  $\text{AuCl}_4^-$  and  $\text{Cu}^{2+}$  ions. It can be concluded that the presence of  $\text{Cu}^{2+}$  ions can decrease the percentage reduction of  $\text{AuCl}_4^-$  ions although relatively small and insignificant. This is because the  $\text{Cu}^{2+}$  ions in the solution can also be reduced to cause competition with  $\text{AuCl}_4^-$  ions in binding the electrons. However, since the reduction of  $\text{Cu}^{2+}$  ions is slower, which is indicated by a value of  $E^0$  ( $E^0 = 0.340$  eV) which is much lower than that of  $\text{AuCl}_4^-$  ions ( $E^0 = 1.002$  eV). The  $\text{Cu}^{2+}$  ions are more difficult to be reduced than  $\text{AuCl}_4^-$  ions so that the presence of  $\text{Cu}^{2+}$  ions does not significantly affect the  $\text{AuCl}_4^-$  ion reduction.

Reduction of  $\text{AuCl}_4^-$  was also performed in the presence of  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$ . Figure 8 reveals that the presence of  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  leads to a decrease in  $\text{AuCl}_4^-$  photoreduction. The addition of  $\text{Ni}^{2+}$  has a stronger effect than that of  $\text{Cu}^{2+}$ . Both  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  can be reduced, as suggested by their standard reduction potentials of -0.25 V and 0.34 V, to form  $\text{Ni}^0$  and  $\text{Cu}^0$  respectively, which competes with  $\text{AuCl}_4^-$  photoreduction. The standard reduction potentials of  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  are much lower than those of  $\text{AuCl}_4^-$ , which is much more difficult to reduce than  $\text{AuCl}_4^-$ . Based on their standard reduction potential,  $\text{Cu}^{2+}$  is easier to reduce than  $\text{Ni}^{2+}$ . However, the opposite result is observed.  $\text{AuCl}_4^-$  ions are reduced directly to  $\text{Au}^0$  ions while  $\text{Cu}^{2+}$  ions may be reduced to  $\text{Cu}^+$  and  $\text{Cu}^0$ . When  $\text{Cu}^+$  and  $\text{Cu}^0$

species escape from the surface of  $\text{TiO}_2$  and meet with  $\text{AuCl}_4^-$  ions, there will be redox reaction among  $\text{AuCl}_4^-$ ,  $\text{Cu}^+$  and  $\text{Cu}^0$  ions where  $\text{Cu}^+$  and  $\text{Cu}^0$  will oxidize back to  $\text{Cu}^{2+}$  ions. The  $\text{AuCl}_4^-$  has a higher reduction potential value so it is reduced, while  $\text{Cu}^+$  and  $\text{Cu}^0$  which have a smaller reduction potential value then they are oxidized. The cross-redox reaction interface probably happens, in which the  $\text{AuCl}_4^-$  reduction can occur because of the bridge of the previously reduced  $\text{Cu}^{2+}$  ions. So that the only small decreased of  $\text{AuCl}_4^-$  ion reduction process in the presence of  $\text{Cu}^{2+}$  ion in this study is probably affected by the reduction potential values of each metal ions as well as the crossing redox reaction interface effect. Meanwhile, this phenomenon does not happen for  $\text{Ni}^{2+}$  ion. Moreover, the decrease in the amount of reduced  $\text{AuCl}_4^-$  ions in the mixture of  $\text{AuCl}_4^-$ ,  $\text{Ni}^{2+}$ , and  $\text{Cu}^{2+}$  in [Figure 8](#) more likely due to the deposition of nickel and copper on the surface of the photocatalyst, so active site of the photocatalyst is covered by metal thereby reducing the amount of reduced  $\text{AuCl}_4^-$ . The presence of  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions in the mixture slightly hinder the reduction of  $\text{AuCl}_4^-$ .

The stronger effect is shown by the presence of  $\text{Ni}^{2+}$ . It is clearly not caused by competition in the photoreduction, but it prominently caused by adsorption of  $\text{Ni}^{2+}$  on the surface of  $\text{TiO}_2$ . As presented previously, the photocatalytic reduction process is always initiated and/or accompanied by adsorption on the surface of photocatalyst (Wahyuni *et al.*, 2015; Kunarti *et al.*, 2017). When  $\text{AuCl}_4^-$  in the solution is along with  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions, the adsorption of the three ions should be involved. The  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions having a smaller size than  $\text{AuCl}_4^-$ , can be adsorbed faster than Au (III). Consequently, the adsorption of  $\text{AuCl}_4^-$  is inhibited by  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$ , causing a decrease in the  $\text{AuCl}_4^-$  adsorption, and so the lower photoreduction. This result is in accordance with the previous study in the reduction of  $\text{AuCl}_4^-$  using  $\text{TiO}_2$  as the photocatalyst (Wahyuni *et al.*, 2015). The role of  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  in the lowering  $\text{AuCl}_4^-$  photoreduction caused by adsorption competition is supported by data obtained from a process without light exposure as illustrated by [Figure 9](#). It is seen in the figure that adsorption of  $\text{AuCl}_4^-$  decreased in the presence of  $\text{Ni}^{2+}$  but only slightly decreased when  $\text{Cu}^{2+}$  is present.



**Figure 9.** Adsorption of  $\text{AuCl}_4^-$  by  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$  a) without  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$ , b) with  $\text{Ni}^{2+}$  in the mixture where  $\text{AuCl}_4^-$  to  $\text{Ni}^{2+}$  molar ratio of 1: 1, c) with  $\text{Cu}^{2+}$  in the mixture where  $\text{AuCl}_4^-$  to  $\text{Cu}^{2+}$  molar ratio of 1: 1, and d) with  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  in the mixture where  $\text{AuCl}_4^-$  to  $\text{Ni}^{2+}$  to  $\text{Cu}^{2+}$  molar ratio of 1:1:1

As discussed earlier, at pH 5 the surface of  $\text{TiO}_2$  is dominated by  $\text{TiOH}_2^+$  and  $\text{TiOH}$  groups, hence the species  $\text{AuCl}_4^-$  and  $\text{AuCl}_3\text{OH}^-$  ions are adsorbed through the complex formation and electrostatic interactions. It has also been reported that at pH 5 or lower,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions are dominant. This makes an electrostatic interaction between the  $\text{Ni}^{2+}$  ion and the positively charged surface of  $\text{TiOH}_2^+$  is not possible to occur so that the adsorption of  $\text{Ni}^{2+}$  ions on the photocatalyst surface is likely to occur through electrostatic interactions between  $\text{Ni}^{2+}$  ions and  $\text{SiO}_2$ . This phenomenon also takes place for  $\text{Cu}^{2+}$  ions.

$\text{SiO}_2$  has a  $\text{pH}_{\text{pzc}}$  (potential zero charges) value of about 2.0, therefore at pH 5, the  $\text{SiO}_2$  has a negatively charged surface. The porous structure of  $\text{TiO}_2$  allows a silica layer to have contact with the solution. So that electrostatic interactions between  $\text{SiO}_2$  and  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  can occur. In addition, the adsorption process of  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions can also take place through the interaction between these ions and free electron pairs on oxygen atoms on the surface of  $>\text{TiOH}$ . The interaction between  $\text{TiO}_2$  and  $\text{Ag}^+$  ions has also been reported previously (Kunarti *et al.*, 2017). Adsorbed  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  can cover the surface of  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$  nanoparticles to prevent adsorption of either  $\text{AuCl}_4^-$  or



$\text{AuCl}_3\text{OH}^-$  and prevent further reduction. Therefore, the presence of  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions slow down the photoreduction of  $\text{AuCl}_4^-$  as indicated in Figure 9(d).

#### 4. Conclusions

The  $\text{AuCl}_4^-$  ions have been photocatalytically reduced to metallic gold using  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$  nanoparticles as photocatalyst. The  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$  nanoparticles were prepared by combined methods of co-precipitation, sonochemical and sol-gel synthesis, as well as calcination at  $500^\circ\text{C}$ . The products have magnetic moment of  $4.38\text{ emu/g}$ , which could be separated from the solution mixture by using an external magnetic bar. The materials photocatalytically reduced 96 % of  $\text{AuCl}_4^-$  ions in the solution, at  $0.025\text{ g}$  photocatalyst loading,  $50\text{ mgL}^{-1}$   $\text{AuCl}_4^-$  solution concentration under UV light illumination. The addition of  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions decreases the amount of the ions to be reduced due to the competition between reduction and adsorption processes. This prepared photocatalyst is expected to find application in the recovery of gold from electronic waste, which are abundant and complex.

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