POLYANILINE (PANI)-SENSITIZED Fe$_3$O$_4$/SiO$_2$/TiO$_2$ NANOCOMPOSITES AS PHOTOCATALYST FOR THE REDUCTION OF Au(III) IONS

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ABSTRACT
Polyaniline (PANI)-sensitized Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanoparticles were synthesized and the material then applied as a photocatalyst to reduce Au(III). The Fe$_3$O$_4$ was synthesized through the sono-coprecipitation method using NH$_4$OH as a precipitating agent. The coating of SiO$_2$ and TiO$_2$ onto the Fe$_3$O$_4$ was then performed via a hydrolysis reaction and sol-gel process using ammonium peroxydisulfate as the initiator of the aniline polymerization. The parameters investigated in this work are the effect of medium acidity, equilibrium state and material responsiveness on visible light. The TEM images show that the photocatalyst had nanosized particles with an approximate size of 20.7 nm. The observed data from the activity test show the optimum pH and contact time of the photoreduction process were 5 and 180 minutes respectively. The effect of light exposure indicated that the polyaniline-sensitized Fe$_3$O$_4$/SiO$_2$/TiO$_2$ was effective for Au(III) reduction in visible light up to 92% of the initial concentration. The effect of the material revealed that polyaniline-sensitized Fe$_3$O$_4$/SiO$_2$/TiO$_2$ had better photocatalytic activity than that of TiO$_2$ and Fe$_3$O$_4$/SiO$_2$/TiO$_2$ in visible, UV and dark conditions.

Keywords: Polyaniline, Fe$_3$O$_4$, SiO$_2$, TiO$_2$, Au(III), Photoreduction

INTRODUCTION
A Gold(Au) is widely used as a component of PCBs. Leaching alloy on the PCB board with aqua regia solution leaches the gold(III) ions into the tetra chloroauric(III) complex, while the other metal ions such as Cu$^{2+}$, Ni$^{2+}$, Zn$^{2+}$ and Pb$^{2+}$ remain in their cation form. The Au(III) complex is easily reduced to gold metal, which can be seen from the high value of its reduction potential ($E^\circ = 1.002$ V). Accordingly, various types of gold recovery methods have been studied including electrolysis, adsorptive-reduction, and bio-reduction and biorecovery.

The race to recover gold from primary and secondary resources has led researchers to find the most suitable materials for low-cost methods. Cyanide and mercury methods are ancient methods for gold recovery but should be avoided due to their high toxicity. Therefore, finding new materials and methods for gold recovery has been the subject of research in recent years. In recent developments, photon-based reactions known as photoreactions have been widely used for the photodegradation of organic matter and photoreduction of cationic metals. Various catalyst materials based on titanium have already been applied for environmental purposes. These include the utilization of bare TiO$_2$ to reduce Au(II) ions and Au(III) ions waste by UV-light; TiO$_2$/Fe$_3$O$_4$ for quinoline photo-degradation by UV light; and Fe$_3$O$_4$/SiO$_2$/TiO$_2$ to reduce silver ion and methylene blue photo-degradation by UV-light. Most previous studies have used anatase as the main material due to its bandgap energy, which is higher than the other two possibilities (rutile and brookite). Therefore, in recent years photoreaction-based TiO$_2$ materials have focused on anatase crystals. However, the limitation of TiO$_2$ utilization only in a UV range ($\lambda$<380 nm) has motivated this study to modify the TiO$_2$ material using PANI as the light sensitizer. Recently, polyaniline-modified TiO$_2$ has been informed to show significantly better photocatalytic activity and it is expected to have potential applications as a photocatalyst in the reduction of Au(III) ions.
activity than that of unmodified TiO₂ under visible light irradiation, because of the delocalized conjugated structures in electron-transfer processes of polyaniline.

In this study, polyaniline-sensitized Fe₃O₄/SiO₂/TiO₂ was synthesized and then applied as a photocatalyst for reducing of Au(III) ions. Compared to other photocatalyst materials for gold recovery, this type of photocatalyst has proven to be far more effective. The effect of light wavelength was also determined to evaluate performance in UV, visible light and dark conditions. The presence of Fe₃O₄ as supporting material is expected to make photocatalyst materials separable from the aqueous medium and reusable. This developed material is also expected to be an alternative gold recovery method for both primary and secondary resources.

EXPERIMENTAL

Materials and Method
Analytical grade FeCl₃•6H₂O, FeSO₄•7H₂O, NH₄OH, (NH₄)₂S₂O₈, TEOS 98%, TTIP 97%, ethanol 98%, C₆H₅NH₂ 99%, HCl 36%, Oleic Acid, distilled water, solution of [AuCl₄]⁻ and N₂ gas were used throughout the experiments. Instrumentals included an infra-red spectrophotometer (Shimadzu FT-IR Prestige 21), atomic absorption spectrophotometer (Perkin Elmer 3110), UV-Vis spectrophotometer, X-ray diffractometer (Shimadzu XRD-6000), Diffuse Reflectance UV-Visible Spectrophotometer (Shimadzu 2450), Vibrating Sample Magnetometer (OXFORD VSM 1.2H), and Transmission Electron Microscope (JEOL JEM-14000).

General Procedure
Synthesis of Fe₃O₄
FeSO₄•7H₂O and FeCl₃•6H₂O (1:2) were dissolved in distilled water under an N₂ atmosphere. A NH₄OH 25% and OAc were added to the Fe²⁺/Fe³⁺ solution mixture under sonication until a precipitate was formed. After aging for 1 hour, the solid was washed until pH 7 was obtained and then was dried at 80 °C to obtain Fe₃O₄ capped OAc.

Synthesis of Fe₃O₄/SiO₂
The solid of Fe₃O₄ was dispersed with ethanol 98% and sonicated for 20 minutes. A TEOS 98% was then added to the dispersion. A distilled water and NH₄OH were added to the dispersion, which was then ultrasonicated for 1 hour, washed until pH 7 was obtained. The solid was separated using an external magnetic bar and was dried at 80 °C to obtain Fe₃O₄/SiO₂.

Synthesis of Fe₃O₄/SiO₂/TiO₂
An ethanol 98%, TTIP 97%, and distilled water were mixed with the Fe₃O₄/SiO₂. The mixture was sonicated for 2 hours and then the solid in the dispersion was separated using an external magnetic bar. The solid was calcined at 500 °C for 3 hours to form anatase crystal of TiO₂ in Fe₃O₄/SiO₂/TiO₂.

Synthesis of Polyaniline-Sensitized Fe₃O₄/SiO₂/TiO₂
The Fe₃O₄/SiO₂/TiO₂ was mixed with 25 mL HCl 0.2 M and sonicated for 30 minutes. A 1 mL of (NH₄)₂S₂O₈ and C₆H₅NH₂ 99% was then added to the mixture and stirred for 10 hours. Subsequently, the solid was separated and dried at 80 °C to get polyaniline-sensitized Fe₃O₄/SiO₂/TiO₂.

Effect of the Medium Acidity
A solution of 100 mg L⁻¹ [AuCl₄]⁻ 25 mL was prepared, with acidity adjusted to pH 3, 4, 5, 6 and 7. Into every solution, 15 mg of the photocatalyst was poured into the photocatalysis reactor. The suspension was stirred with UV light exposure for 180 minutes. The remaining [AuCl₄]⁻ was analyzed using an atomic absorption spectrophotometer.

Effect of Contact Time
A solution of 100 mg L⁻¹ [AuCl₄]⁻ 25 mL was prepared, with acidity adjusted to the optimum pH. Into the solution, 15 mg of the photocatalyst was poured into the photocatalysis reactor. The suspension was...
stirred with UV light exposure for 0, 30, 60, 120, 180 and 210 minutes. The [AuCl₄]⁻ in solution was then analyzed using an atomic absorption spectrophotometer.

**RESULTS AND DISCUSSION**

Infra-Red Spectroscopic analysis (Fig.-1) shows the vibration of PANI-sensitized Fe₃O₄/SiO₂/TiO₂. The vibration band at 570 cm⁻¹ shows the Fe–O originated from Fe₃O₄ and those at 1700 and 1300 cm⁻¹ indicate C=O of free –COOH and –COO⁻, which interact with Fe.²⁶-²⁸ Asymmetry peak and asymmetry Si–O–Si are shown at 800 and 1080 cm⁻¹. The absorption band at 940-960 cm⁻¹ shows the binding of Ti by Si–O (Si–O–Ti), and that at 500-700 cm⁻¹ is the fingerprint of Ti–O–Ti.²³ The band at 1319 cm⁻¹ (PANI-sensitized Fe₃O₄/SiO₂/TiO₂) indicates the stretching C–N of polyaniline, followed by C=C benzene at 1481 cm⁻¹.²⁵,²⁹

![FTIR Spectra of the Synthesized Materials](image1)

The presence of each material and its crystallinity was determined by the X-ray diffraction method. The synthesis of Fe₃O₄ through the coprecipitation method obtained face-centered cubic (fcc) materials through with peaks at 2θ= 30; 35; 43.37; 57.2; and 62.8° (Fig.-2), which refer to basal spacings of (220), (311), (400), (511), and (440) respectively. The obtained basal spacings match the Miller Index of JCPDS 00-001-1111 referring to the fcc structure. Meanwhile, G in the Fe₃O₄ diffractogram refers to the indication of goethite, which is a common impurity of Fe₃O₄ synthesized through the coprecipitation method.

![XRD Patterns of the Synthesized Materials](image2)
The coating of SiO$_2$ onto the Fe$_3$O$_4$ has a similar diffractogram to the Fe$_3$O$_4$ material before coating. However, the crystallinity of Fe$_3$O$_4$ decreases slightly due to the presence of amorphous SiO$_2$ on the Fe$_3$O$_4$ surface. Meanwhile, the Fe$_3$O$_4$/SiO$_2$/TiO$_2$ have combined peaks between the Fe$_3$O$_4$ and TiO$_2$ anatase, followed by new peaks of basal spacing of (001), (112), (220), (105), (213) and (215), which refer to TiO$_2$ anatase. A slight shift of TiO$_2$ anatase compared to JCPDS 00-021-1272 TiO$_2$ indicates that TiO$_2$ has successfully interacted with SiO$_2$ on the surface of the Fe$_3$O$_4$. In addition, there is no difference between the 2θ of polyaniline-sensitized Fe$_3$O$_4$/SiO$_2$/TiO$_2$ and Fe$_3$O$_4$/SiO$_2$/TiO$_2$.

As semiconductor ability depends on its bandgap energy, in this study analysis based on diffusion-reflectance UV-visible was conducted to determine the bandgap energy of TiO$_2$ and polyaniline-sensitized Fe$_3$O$_4$/SiO$_2$/TiO$_2$. The DR-UV spectra, as shown in Fig.-3, indicate that the presence of PANI is confirmed by the appearance of a peak at the wavelength of more than 400 nm and shifts the absorbance to the visible light. The bandgap energy (E$_g$) obtained of bare TiO$_2$, Fe$_3$O$_4$/SiO$_2$/TiO$_2$ and polyaniline-sensitized Fe$_3$O$_4$/SiO$_2$/TiO$_2$ were 3.20, 3.15 and 3.00, respectively.

The morphology of the synthesized materials was revealed through TEM image (Fig.-4). The dark image shows the presence of Fe$_3$O$_4$ and TiO$_2$, with the grey color indicating the presence of SiO$_2$ and PANI. TEM image also revealed the typical size of synthesized Fe$_3$O$_4$, Fe$_3$O$_4$/SiO$_2$, Fe$_3$O$_4$/SiO$_2$/TiO$_2$ and polyaniline-sensitized Fe$_3$O$_4$/SiO$_2$/TiO$_2$ approximately 13.9 nm, 14.8 nm, 18.2 nm and 20.7 nm.
Magnetic properties were established through qualitative and quantitative analysis. Fig.-5-A shows that the composites were easily dispersed in water and were also attracted to the external magnetic field in less than 5 minutes. Further analysis was performed by VSM to determine the magnetism of the materials. The magnetic curves shown in Fig.-5-B indicate the magnetism of bare Fe$_3$O$_4$, Fe$_3$O$_4$/SiO$_2$/TiO$_2$ and PANI-sensitized Fe$_3$O$_4$/SiO$_2$/TiO$_2$ were 33.10, 4.38 and 2.51, respectively. It was also found that the magnetism of the composites significantly decreased after modification by SiO$_2$, TiO$_2$ and polyaniline. Nevertheless, the polyaniline-sensitized Fe$_3$O$_4$/SiO$_2$/TiO$_2$ is still easy to be recovered from the solution using the external magnetic bar.

**Activity Test**

Photoreduction depends on the speciation of Au(III) and the surface charge of the catalyst in the aquatic medium. Fig.-6 shows the optimum reduced Au(III) at pH 5, in which gold ions are dominated by [AuCl$_4$]$^-$, and the amines of PANI and the TiO$_2$ photocatalyst are positively charged, as –NH$_3^+$ and TiOH$_2^+$ respectively. The opposite charges lead to sorption through electrostatic bonding, then the adsorbed [AuCl$_4$]$^-$ is reduced to Au(0). At pH < 4, the high abundance of TiOH$_2^+$ decreases the presence of electrons. Meanwhile, at high pH, the similar charges between the photocatalyst and [AuCl$_4$]$^-$ result in ineffective sorption. In addition, the existence of hydroxide ion leads to the Au precipitation, leading to ineffective photoreduction. $^{30}$
lead to a higher number of such photons. The equilibrium of light exposure time at 180 minutes with the percentage of Au(III) reduction is 92%. After that time, no increase in the reduced Au(III) ions were detected.

Fig.-7: Effect of Visible Light Exposure on the Photoreduction of Au(III) Ions with a PANI-Sensitized \( \text{Fe}_7\text{O}_3\text{SiO}_2\text{TiO}_2 \) Catalyst in Visible Irradiation

In this study, three different materials have been tested for the reduction of Au(III). The effect of these is shown in Fig.-8.

Fig.-8: Reduced Au(III) with the Exposure of (A) Visible Light and (B) UV-Light

In all light regions, it was revealed that PANI-sensitized \( \text{Fe}_7\text{O}_3\text{SiO}_2\text{TiO}_2 \) had higher efficiency in reducing Au(III) than TiO\(_2\) and \( \text{Fe}_7\text{O}_3\text{SiO}_2\text{TiO}_2 \). It can be observed that PANI-sensitized \( \text{Fe}_7\text{O}_3\text{SiO}_2\text{TiO}_2 \) is the most effective photocatalyst in visible light due to the presence of PANI as a sensitizer (Fig.-8A). Fig.-9A shows that PANI as a sensitizer absorbed the photon energy induced at the \( \pi-\pi^* \) transition, leading to electron excitation on the \( \pi^* \) orbitals. As excitation occurs, the electrons move quickly to the conduction bands (CB) of the TiO\(_2\).\(^{25,29,30} \) The excited electrons are then used as a reducing agent for the Au(III) photoreduction process. The level of reduced Au(III) in visible light was found to be 92%. In UV light (Fig.-8B, Fig.-9B), both TiO\(_2\) and PANI absorb photon energy to form electron excitation and holes.\(^{25,30} \) Electron excitation from the valence band (VB) of TiO\(_2\) to the highest energy occupied molecular orbital (HOMO) of polyaniline increases the photocatalytic activity of the nanocomposites by around 89%.

Fig.-10A and 10B show the reduction process of Au without light exposure. In dark conditions, it is assumed that no electrons are excited. This means that without light exposure, the sorption is dominated by adsorption. As explained as the effect of medium acidity, the opposite charges of PANI-sensitized \( \text{Fe}_7\text{O}_3\text{SiO}_2\text{TiO}_2 \) (\( \text{NH}_4^+ \) and TiOH\(_2^-\) ) and \( \text{[AuCl}_4^-\) (at optimum pH) lead to sorption through electrostatic bonding; the adsorbed \( \text{[AuCl}_4^-\) is then reduced to Au(0). The remaining Au in the solution was around 72% because the functional group content of both materials was lower than the PANI-sensitized \( \text{Fe}_7\text{O}_3\text{SiO}_2\text{TiO}_2 \), which consists of two different functional groups.
**CONCLUSION**

Polyaniline (PANI)-sensitized Fe$_3$O$_4$/SiO$_2$/TiO$_2$ has been successfully synthesized through a combination of sono-coprecipitation, hydrolysis and the sol-gel method. The observed data from the activity test show the optimum pH and contact time of the photoreduction process to be 5 and 180 minutes respectively. The effect of light exposure indicates that PANI-sensitized Fe$_3$O$_4$/SiO$_2$/TiO$_2$ was effective in Au(III) reduction in visible light up to 92% of the initial concentration. The effect of the materials reveals that PANI-sensitized Fe$_3$O$_4$/SiO$_2$/TiO$_2$ has better photocatalytic activity than that of TiO$_2$ and Fe$_3$O$_4$/SiO$_2$/TiO$_2$ in visible, UV light, and in dark conditions.

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