EFFECT OF GOLD MODIFICATION ON THE PROPERTIES AND PHOTOACTIVITY OF Fe₃O₄/SiO₂/TiO₂ IN THE DEGRADATION OF NITROBENZENE

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ABSTRACT

Efficient gold-modified-Fe₃O₄/SiO₂/TiO₂ photocatalysts have been synthesized and employed for nitrobenzene degradation under UV-visible illumination. The results revealed that the prepared Fe₃O₄/SiO₂/TiO₂-Au photocatalysts displayed magnetic properties. In addition, the modification of Au reduced the energy of the band gap of the photocatalyst, increased the responsiveness of TiO₂ to visible light, and enhanced the photoactivity for nitrobenzene degradation. The optimum photocatalytic activity was obtained when 4% of Au was added to Fe₃O₄/SiO₂/TiO₂. The photodegradation percentages of 20 mg/L of nitrobenzene using Fe₃O₄/SiO₂/TiO₂-Au 4%, at pH 7 for 75 min under UV and visible light were 94.2% and 93.16%, respectively.

Keywords: Gold, Fe₃O₄/SiO₂/TiO₂, Photodegradation, Nitrobenzene, Visible Light.

INTRODUCTION

Water pollution still becomes a global problem where industrial wastewater becomes the main source of it. In this context, nitrobenzene is classified as a dangerous water pollutant due to its high toxicity and carcinogenicity which may pose significant threats to the environment. Structurally, the presence of nitro group on nitrobenzene may decrease the electron density of the aromatic ring, making this compound very stable and difficult to degrade. Therefore, the treatment of wastewater containing nitrobenzene should be developed. Several methods to remove nitrobenzene from wastewater have been applied, generally through the adsorption and biodegradation processes. Despite the effectiveness of this method, they still suffer from several limitations such as high processing costs. Photocatalysis has emerged as a simple and efficient process that offers high activity and selectivity in the degradation of water pollutants. Titanium dioxide (TiO₂) is the photocatalyst that is widely employed for the remediation of air and water pollutants. Because of its large bandgap energy, TiO₂ absorbs about 5% of the sunlight energy and thus limits its application as a photocatalyst. One of the effective methods to enhance the photoactivity of TiO₂ is to increase its surface area through doping with metals or non-metals. The efficiency of TiO₂ as a photocatalyst under visible light might be increased by doping TiO₂ with noble metals. The metals may trap the electrons and encourage interfacial charge transfer. In the previous studies, the increase of photoactivity of TiO₂ in visible radiation was perceived after doping TiO₂ with Au nanoparticles due to the electronic transitions between intrinsic bands in Au as well as the incidence of local surface Plasmon resonance (SPR). Within the wastewater treatment, the effective separation of photocatalysts after the degradation is required since it may significantly reduce the cost of the process. Since TiO₂ creates a fine particulate resulting in the difficult separation from suspension, the magnetization of TiO₂ may simplify the processing, separation, and recycling of photocatalysts by simply applying an external magnetic field. Magnetization using magnetite (Fe₃O₄) has gained great consideration owing to its magnetic-field capability, high coercivity, and high separation efficiency. However, the direct contact between TiO₂ and Fe₃O₄ can sometimes cause photodissolution resulting in the decrease of TiO₂ photoactivity. Coating with silica (SiO₂) has been reported to successfully prevent the charge transfer between TiO₂ and Fe₃O₄, ensuring the heterojunctions do not form and the photo-dissolution does not occur. The ability of SiO₂ to inhibit the electronic interaction
between TiO$_2$ and Fe$_3$O$_4$ also prevents the existence of recombination centers of electron–hole that leads to the decrease of the photoactivity of TiO$_2$. Based on the previous explanation, we report herein the preparation of TiO$_2$ photocatalysts modified with magnetite, silica, and gold (Au) with visible light-responsive and magnetic properties. The effect of Au on the photoactivity of the photocatalyst was assessed for the nitrobenzene degradation in UV-visible exposure.

**EXPERIMENTAL**

**Materials**

Materials (with pro analysis quality) used in the experiments were iron(III) chloride hexahydrate, iron(II) sulfate heptahydrate, titanium (IV) tetraisopropoxide (TTIP), tetraethyl orthosilicate (TEOS), sodium borohydride (NaBH$_4$), nitrobenzene, ammonium hydroxide 25 %, sodium hydroxide, hydrochloric acid, sodium citrate, ammonium sulfate, methanol, and ethanol. Some other chemicals (with technical quality) included gold, distilled water, and N$_2$ gas.

**Preparation of Fe$_3$O$_4$**

Iron(III) chloride hexahydrate (5.40 g) and iron(II) sulfate heptahydrate (2.70 g) were immersed in 0.10 L of distilled water under a nitrogen atmosphere. Into the solution, the concentrated ammonium hydroxide solution was introduced until pH 10. The mixture was sonicated for 1 h in an ultrasonic bath until a black precipitate was generated. The external magnet was utilized to separate the solid. Next, the mixture of the solid and 100 mL of 0.5 M of sodium citrate solution was sonicated for 10 min. The solid was then washed and dried.

**Preparation of Fe$_3$O$_4$/SiO$_2$**

Fe$_3$O$_4$ (3.00 g) was soaked into 30 mL of ethyl alcohol and was stirred by sonication for 10 min. Then, 2.60 mL of TEOS, the concentrated ammonium hydroxide solution (8 mL), and distilled water (1 mL) were respectively introduced into the mixture, followed by further sonication for another 3 h. Fe$_3$O$_4$/SiO$_2$ was obtained after drying the solid at 80°C.

**Preparation of Fe$_3$O$_4$/SiO$_2$/TiO$_2$**

Fe$_3$O$_4$/SiO$_2$/TiO$_2$ material was made by soaking the previously prepared Fe$_3$O$_4$/SiO$_2$ (0.10 g) in ethanol (20 mL). Having sonicated the mixture for 10 min, 1 mL of TTIP, 20 mg of (NH$_4$)$_2$SO$_4$, and 1 mL of water were introduced. Further sonication for 3 h of the mixture was conducted. The external magnet was used to the separation of the solid and the generated solid was then calcined at 500 °C for 3 h.

**Preparation of Fe$_3$O$_4$/SiO$_2$/TiO$_2$-Au**

Fe$_3$O$_4$/SiO$_2$/TiO$_2$-Au was synthesized based on the previous report$^{23}$ with slight modifications. The Fe$_3$O$_4$/SiO$_2$/TiO$_2$ (0.10 g) was mixed with 20 mL of ethanol. Into the mixture, 4 mL of HAuCl$_4$ with various concentrations of 2, 4, and 8 mM was put in and was sonicated for 10+30 minutes. The solution of NaBH$_4$ 0.1 M was put in to the prepared mixture until color change to purple was observed. The solid of Fe$_3$O$_4$/SiO$_2$/TiO$_2$-Au was washed and dried at 80 °C.

**Photo Degradation of Nitrobenzene**

Fe$_3$O$_4$/SiO$_2$/TiO$_2$-Au photo catalysts (20 mg) with various concentrations of Au were added into 15 mL of 20 ppm nitrobenzene at pH 7. The mixture was agitated for 75 min at (a) dark as well as under (b) visible and (c) UV light illumination in the reactor of photo catalysis. After the photo degradation process, the external magnet was employed to recover the photo catalyst. The photo activity of the photo catalyst was studied by determining the concentration of the remaining nitrobenzene solution using UV-Vis spectrophotometer.

**RESULTS AND DISCUSSION**

Fe$_3$O$_4$/SiO$_2$/TiO$_2$-Au photo catalysts were prepared in three steps including (1) preparation of magnetite (Fe$_3$O$_4$), (2) coating of magnetite with SiO$_2$ and TiO$_2$ as well as (3) modification of the synthesized Fe$_3$O$_4$/SiO$_2$/TiO$_2$ using gold nanoparticle using chemical reduction method. In this study, concentration of gold was varied. The effect of gold (Au) modification on the photocatalyst photo activity was assessed for nitrobenzene solution degradation.
Preparation and Characterization of Photocatalysts

All the prepared materials were analyzed using X-ray diffraction. Figure-1 shows the diffraction pattern of Fe\textsubscript{3}O\textsubscript{4} with characteristic diffraction peaks at 2 thetas of 30.61°, 36.03°, 43.83°, 54.51°, 57.75°, and 63.31°. These results are in accordance with the magnetite diffraction pattern in powder diffraction file (PDF) No. 19-0629, which has the Miller indices of (220), (311), (400), (422), (511), and (440), respectively. Based on these results, it can be indicated that the prepared magnetite has a cubic crystal system structure.

The diffraction of Fe\textsubscript{3}O\textsubscript{4}/SiO\textsubscript{2} (Fig.-1) shows new diffraction peaks at 2θ of 16° to 28°, indicating the characteristics of the amorphous silica. The presence of these peaks confirms that Fe\textsubscript{3}O\textsubscript{4}/SiO\textsubscript{2} has been successfully generated. Based on the diffraction of the Fe\textsubscript{3}O\textsubscript{4}/SiO\textsubscript{2}/TiO\textsubscript{2} material (Fig.-1), the presence of new diffraction peaks at 2θ of 25.37°, 38.01°, 44.24°, 55.10°, 68.85°, 70.58°, and 75.41° can be observed. These peaks are in accordance with the diffraction pattern of anatase TiO\textsubscript{2} which appears in PDF No. 21-1272. The diffraction of Fe\textsubscript{3}O\textsubscript{4}/SiO\textsubscript{2}/TiO\textsubscript{2}-Au (Fig.-1) shows new diffraction peaks at 2θ of 38.00°, 44.54°, 64.78°, 77.74°, and 82.93°, indicating the presence of Au atoms. These peaks, according to PDF No. 04-0784, are Au diffraction with the Miller indices of (220), (311), (222), (111), and (200). The diffraction pattern peaks at 2θ of 38.00°, 44.54°, 64.78°, 77.74°, and 82.93° shown in Fig.-1 are observed to be higher, indicating the higher concentration of Au in the prepared material. The diffraction peak at 2θ of 38.00° is the combined peak of TiO\textsubscript{2} and Au anatase.

It can be perceived in Fig.-1 that Fe\textsubscript{3}O\textsubscript{4}/SiO\textsubscript{2}/TiO\textsubscript{2}-Au (2%) gives larger 2θ at around 25° than that of Fe\textsubscript{3}O\textsubscript{4}/SiO\textsubscript{2}/TiO\textsubscript{2}. During the reduction process of Au\textsuperscript{3+} to Au\textsuperscript{0}, there are some Au\textsuperscript{+} and Au\textsuperscript{0} that are in interstitial positions in the TiO\textsubscript{2} crystal lattice, causing the distance between the planes in the crystal lattice of Fe\textsubscript{3}O\textsubscript{4}/SiO\textsubscript{2}/TiO\textsubscript{2}-Au (2%) to be smaller than that of Fe\textsubscript{3}O\textsubscript{4}/SiO\textsubscript{2}/TiO\textsubscript{2}. Increasing concentration of Au in the material leads to the shift of diffraction peak around 25° to a smaller 2θ (Table-1). This might occur due to the influence of the size of Au\textsuperscript{+} ion that may replace Ti\textsuperscript{4+} ion. The Au\textsuperscript{+} ion has larger ionic radii than that of Ti\textsuperscript{4+} in the TiO\textsubscript{2} crystal lattice, leading to an increase the value of the lattice parameters and the distance between the planes.

Figure-2 displays the transmission electron microscopy (TEM) image of the prepared Fe\textsubscript{3}O\textsubscript{4}/SiO\textsubscript{2}/TiO\textsubscript{2} material. The image shows that the Fe\textsubscript{3}O\textsubscript{4}/SiO\textsubscript{2}/TiO\textsubscript{2} is composed of black particles covered by a gray layer. While the darker area indicates Fe\textsubscript{3}O\textsubscript{4}, the lighter areas are the SiO\textsubscript{2} and TiO\textsubscript{2} layers. The Fe\textsubscript{3}O\textsubscript{4} appears...
darker than SiO₂ and TiO₂ due to the higher density of Fe₃O₄. It can also be seen that the material has a homogeneous spherical shape. Based on Fig.-2, the size of Fe₃O₄/SiO₂/TiO₂ is about 18 nm.

| Materials       | 2θ (°) | d (Å)  |
|-----------------|--------|--------|
| Fe₃O₄/SiO₂/TiO₂ | 25.380 | 3.5056 |
| Fe₃O₄/SiO₂/TiO₂-Au 2% | 25.483 | 3.4930 |
| Fe₃O₄/SiO₂/TiO₂-Au 4% | 25.404 | 3.5033 |
| Fe₃O₄/SiO₂/TiO₂-Au 9% | 25.384 | 3.5060 |

Based on Fig.-3, the darker particles are covered by gray and lighter colors. Similarly, the darker color is Fe₃O₄ and the lighter color are SiO₂ and TiO₂ layers. The small black dots on the Fe₃O₄/SiO₂/TiO₂ surface indicate the presence of Au atoms. The Au atoms looks darker since they have higher density than Fe₃O₄, SiO₂, and TiO₂. Figure-3 showed that the size of Fe₃O₄/SiO₂/TiO₂-Au is about 20 nm.

The magnetic properties of the prepared materials are quantitatively studied using VSM to determine the magnitude of the magnetic strength of the materials. Figure-4 shows that there are differences in magnetic properties and decreases in magnetic strength from Fe₃O₄ (76.03 emu/g) to Fe₃O₄/SiO₂ (32.80 emu/g), Fe₃O₄/SiO₂/TiO₂ (13.15 emu/g), and Fe₃O₄/SiO₂/TiO₂-Au (6.81 emu/g). It can be observed that the value of magnetic moment decreases with the addition of coating materials to Fe₃O₄. The addition of coating material causes a decrease in the attractiveness of the magnetic field owing to the existence of barriers of silica, TiO₂, and Au materials. The decrease in the magnetic strength of the material is also due to the reduced mass of magnetite in the sample.

Characterization with SR UV-visible was employed to evaluate the absorption pattern of the material at 300-800 nm (Fig.-5). The prepared materials’ band gap energy is analyzed employing the absorption
wavelength of the edge of each material using Planck law. Based on Fig.-5, the edge absorption wavelength values for Fe$_3$O$_4$/SiO$_2$/TiO$_2$ with Au concentrations of 0, 2, 4, and 9% are 391, 402, 416, and 415 nm, respectively. Moreover, the absorption around 500 nm indicates the SPR absorption of gold particles.

![Magnetization Curve of Materials](image)

**Fig.-4: Magnetization Curve of Materials**

The Fe$_3$O$_4$/SiO$_2$/TiO$_2$ absorption edge wavelength is in the UV light region, revealing that the material is photoactive in ultraviolet exposure. The addition of Au atoms to the material causes the existence of SPR on the surface of gold nanoparticles. As a consequence, the absorption edge wavelength may be altered towards the visible light region. It may create a lower level of energy so that the excitation of electrons in TiO$_2$ can occur at lower energy than TiO$_2$ without dopants. Based on calculations using the Planck law equation, the energy of band gap ($E_g$) of Fe$_3$O$_4$/SiO$_2$/TiO$_2$ with Au concentrations of 0, 2, 4, and 9% are 3.16, 3.07, 2.97 and 2.98 eV, respectively. The band gap energy tends to decrease as the Au concentration increases (up to 4% Au concentration). For Fe$_3$O$_4$/SiO$_2$/TiO$_2$-Au 9%, the $E_g$ value is slightly higher than that of Fe$_3$O$_4$/SiO$_2$/TiO$_2$-Au 4%. This is probably due to the Burstein-Moss effect, stating that an increase in the $E_g$ occurred due to the absorption edge being pushed to higher energy because of the fullness of several states near the conduction band at higher dopant concentrations. The results showed that Fe$_3$O$_4$/SiO$_2$/TiO$_2$-Au 4% has the lowest $E_g$ value and has a better ability to absorb visible light than the other prepared materials. It can be noticed that the gold modification may expand the energy of absorption of Fe$_3$O$_4$/SiO$_2$/TiO$_2$ to the visible area.

**Photocatalytic Degradation of Nitrobenzene**

Having prepared Fe$_3$O$_4$/SiO$_2$/TiO$_2$-Au photocatalysts, we turned our attention to the application of our photocatalysts in the degradation of nitrobenzene. The photodegradation study was carried out under dark and UV as well as visible irradiation. Analysis of the degradation results was carried out through UV-Vis
s spectrophotometry. This evaluation of photoactivity was performed using 15 mL of nitrobenzene 20 mgL⁻¹ at pH 7 for 75 min of irradiation. The reusability of the photocatalysts was also investigated. According to Fig.-6, the photocatalyst seems capable to degrade nitrobenzene in dark conditions. In the absence of light, the photocatalyst is not photoactive. Therefore, the process takes place through the adsorption of nitrobenzene on the photocatalyst. The photocatalytic process starts with the adsorption of nitrobenzene to the photocatalyst surface. When the light energy is available, the produced hydroxyl radical (OH•) will react and degrade nitrobenzene. The occurrence of adsorption on the surface of TiO₂ is supported by the previous study, where the organic compounds are adsorbed when TiO₂ interacts with organic compounds. Additionally, the higher the Au concentration in the material, the lower the ability to adsorb nitrobenzene. This is because the higher the Au concentration, the more Au⁺ replaces Ti⁴⁺ and Au⁰ forms on the TiO₂ surface, thus decreasing the adsorbent ability of TiO₂.

Figure-6 shows that Fe₃O₄/SiO₂/TiO₂-Au exhibits high photoactivity for the nitrobenzene degradation under exposure to visible radiation, proving that the addition of Au to the photocatalyst can enhance the activity in visible radiation. The occurrence of Au atoms can give SPR effect, hence photoexcitation occurs, and the resulting electrons are introduced into O₂ which is adsorbed onto TiO₂. Thus, the formation of superoxide radicals and OH• can be accelerated in the presence of O₂. The degradation of nitrobenzene catalyzed by Fe₃O₄/SiO₂/TiO₂ under exposure to visible radiation showed the lowest degradation percentage, indicating Fe₃O₄/SiO₂/TiO₂ is not active in visible light. Meanwhile, Fe₃O₄/SiO₂/TiO₂-Au 2% and Fe₃O₄/SiO₂/TiO₂-Au 4% increased nitrobenzene degradation while Fe₃O₄/SiO₂/TiO₂-Au 9% decreased nitrobenzene degradation (Fig.-6). This shows that the Fe₃O₄/SiO₂/TiO₂-Au 4% material gives the optimum degradation, with a degradation percentage of 93.18%. Under exposure to UV light (Fig.-6), Fe₃O₄/SiO₂/TiO₂-Au 2% and Fe₃O₄/SiO₂/TiO₂-Au 4% give greater photoactivity than Fe₃O₄/SiO₂/TiO₂ without dopants. This is because when an electron is excited, the electron moves toward the surface of the Au metal, thus preventing the electron and hole recombination. The transfer of electrons from the interior of the photocatalyst to the noble metal surface will enhance the efficiency of the photo-quantum which is the reason for the good photocatalyst activity. Fe₃O₄/SiO₂/TiO₂-Au 4% has a higher photoactivity than Fe₃O₄/SiO₂/TiO₂-Au 2%. Increasing the number of Au nanoparticles can increase the electron transfer to the Au surface, where the electrons will be transported to the adsorbed oxygen. This will facilitate the formation of more O₂•⁻ and will eventually form the OH• responsible for degradation. Exposure to UV light also obtained the optimum degradation of Fe₃O₄/SiO₂/TiO₂-Au 4%, with a degradation yield of 94.20%. Fe₃O₄/SiO₂/TiO₂ photocatalyst with Au concentrations of 2% and 4% exhibited greater photoactivity under ultraviolet exposure than visible light since the reaction occurred faster under ultraviolet light. Absorption of UV light will cause a greater number of electrons to move from Au in the photocatalyst to molecular oxygen than during absorption of visible light. Therefore, photocatalyst activity in UV light is better than in visible light. The photocatalytic activities of Fe₃O₄/SiO₂/TiO₂-Au 9% in visible and UV light are lower than those in smaller concentrations of Au. Excess of Au covering the surface of TiO₂ can be a center for recombination of photoinduction of electron holes, by this means reducing the photoactivity. Moreover,
the photoactivity of Fe₃O₄/SiO₂/TiO₂-Au 9% in ultraviolet illumination is lower than that in visible radiation. This is because, in UV light, electrons in the larger number resulting from absorption of UV light will recombine more easily than in visible light. Modification of photocatalysts using magnetite is aimed to add the magnetic properties, allowing the easier separation and the possibility to reuse the photocatalysts. Evaluation of the reusability of photocatalysts may be conducted to determine the stability of the synthesized material. The reusability test for the degradation of nitrobenzene solution was performed under visible radiation exposure of Fe₃O₄/SiO₂/TiO₂-Au 4% photocatalyst (Fig.-7).

It is interesting to remark that the degradation percentage of the nitrobenzene solution was not considerably reduced until the five-time application of photocatalyst. The slight decrease in the degradation percentage occurred since the partially degraded nitrobenzene solution covered the surface of the photocatalyst. The structural stability of Fe₃O₄/SiO₂/TiO₂-Au 4% photocatalyst after the degradation of nitrobenzene was examined using the XRD. As depicted in Fig.-8, the photodegradation process does not significantly change the diffraction pattern of the photocatalyst, where the characteristic peaks of TiO₂, Fe₃O₄, and Au are still observed. After the photocatalytic process, the material has a slightly lower intensity due to the presence of impurities (presumably the degradation products) remaining in the photocatalyst. These impurities can be removed by repeated washing with the distilled water.

**CONCLUSION**

In summary, the addition of Au nanoparticles to Fe₃O₄/SiO₂/TiO₂ may lower the bandgap energy of TiO₂ to visible region (from 3.16 eV to 2.97 eV). It allowed us to perform the photocatalytic degradation of...
The excellent photoactivity of 93.16% and 94.20% were achieved when the photodegradation process was carried out in the existence of Fe₃O₄/SiO₂/TiO₂–Au 4% photocatalyst under visible and ultraviolet irradiation, respectively. The Fe₃O₄/SiO₂/TiO₂–Au may be employed in the photodegradation of nitrobenzene for several times without the erosion of the outstanding photocatalytic activities. Therefore, Fe₃O₄/SiO₂/TiO₂–Au photocatalysts have a great potential to be further developed in wastewater treatment.

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