



## Synthesis and Characterization of Photocatalytic Activity of Hematite/ Cobalt Oxide/ Graphite Nanocomposites

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### A B S T R A C T

In this study, at first step nanopowder particles of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (Hematite) and Co<sub>3</sub>O<sub>4</sub> were synthesized separately through simple chemical method from an aqueous solution of iron (III) nitrate nonahydrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) and cobalt (II) nitrate hexahydrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) as precursors. After that, three composites from synthesized nanopowders of Fe<sub>2</sub>O<sub>3</sub> with 8, 16 and 24 wt.% of Co<sub>3</sub>O<sub>4</sub> were prepared. Graphite nanopowder was added to one composition of samples in weight percentages of 1.17 and 2.35. The composition and morphology of the composites were investigated by XRD and FE-SEM, respectively. FE-SEM analysis showed that the morphology of the powders and composites were all spherical in nanoscale. The photocatalytic activity of the composites was examined by measuring the photo-degradation of the aqueous solution of methylene blue under simulated solar light. To determine the photo catalytic activity, the degradation of methylene blue (MB) in the absence of light (dark test) was taken as well. Results showed that addition of Co<sub>3</sub>O<sub>4</sub> to Fe<sub>2</sub>O<sub>3</sub> decrease the activity of photo-catalytic process while nano-graphite enhanced photo-catalytic process by upward of ~2 % with respect to the composite without graphite nanoparticles. Stoichiometric calculations showed that the amount of hydrogen produced by water by the composite of Fe<sub>2</sub>O<sub>3</sub>-16% Co<sub>3</sub>O<sub>4</sub>-2.35% Graphite nanoparticles was 27  $\mu$ mol H<sub>2</sub>/h.g under solar light irradiation.

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## 1. INTRODUCTION

Today's political, economic and economic crises, such as limiting the viability of fossil fuel reserves, environmental concerns, population congestion, economic growth, and consumption coefficient, are all world-wide issues that push researcher to finding new solutions [1]. In an age where we are all concerned about the side effects of fossil fuels, such as global warming, pollutants spreading, and the termination of these fuels, hydrogen can be taken into consideration[1-3]. There are four ways to produce hydrogen gas from different sources: hydrogen gas from natural gas, oil, coal and water electrolysis, sharing 48, 30, 18 and 4% of Hydrogen production respectively [4]. When hydrogen is produced from hydrocarbons such as fossil or bio-fuels, trapping CO<sub>2</sub> and isolating it are among the requirements of production program. Hydrogen produced from water,

on the other hand, does not pose a challenge of conversion point, whereas it does require energy from an external source[5]. If this energy comes from a renewable energy source such as solar energy, hydrogen could be potential option of green energy and supplying energy to any device from laptops to submarines [2, 3]. Photo catalytic of water is one of the inexpensive and clean methods for producing hydrogen gas [4]. Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) posses some of essential features such as an ideal band gap of 2.2 eV with broad visible light absorption up to 590 nm which enable it to absorb 40% of the wavelengths. It also has excellent stability under aqueous operating conditions and a valence band positioned sufficiently low for oxidizing that made hematite as one of the most attractive materials for photo-electrochemical (PEC) water splitting [6, 7]. However, relatively low efficiency (12.9%), low electron mobility, lower potential conduction band than needed for hydrogen

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reduction and high rate of recombination of electrons/holes are classified as major limitations [7, 8]. To overcome these disadvantages application of nanotechnology has provided improvement by producing nanoparticle catalysts and morphological modification in order to minimize the charge collection distance while maintaining good light absorption. For instance, H. Wender et al reported that synthesis hematite nano-rings altered the edge of the bandage in a way to increase hydrogen gas production from an aqueous solution [9]. Other ways are doping strategy and making composite with other semiconductor materials or metals that modify the function of the photo-catalyst. Ch. Liu et. al in 2017 reported that hematite/carbon composite improves photocatalytic performance of hematite [10]. They claimed that 120 mg photo-catalytic powder could produce 6.667  $\mu\text{mol H}_2/\text{hg}$ . Therefore, it is of great interest to study the photoelectric properties of  $\alpha\text{-Fe}_2\text{O}_3$  nanostructures in combination with other materials to make composite for their promising application in photo-catalysis or photoelectric conversion device. For instance, in of  $\text{TiO}_2/\text{BiVO}_4$  composite,  $\text{BiVO}_4$  nanoparticles promoted absorption and production of electrons,  $\text{TiO}_2$  is key role to convert electron to water [11]. In another endeavor using nanoparticles of Gold and  $\text{TiO}_2$  composite reduced the probability of electron-holes recombination [12]. A number of other n-type semiconductors, such as  $\text{TiO}_2$  [12, 13],  $\text{ZnO}$  [13] and  $\text{Co}_3\text{O}_4$  [14, 15] have been studied as photo anode materials for water splitting however, all requirements have not yet been accomplished by that compounds. These materials are good candidates for making composite by hematite. Perry et al. Reported that  $\text{Co}_3\text{O}_4$  nanoparticles produce 2000  $\mu\text{mol H}_2/\text{hg}$  from water: ethanol (1:20) solution under light radiation [16, 17].

In this study, we synthesize hematite and  $\text{Co}_3\text{O}_4$  nanoparticles in order to prepare composition of hematite/ $\text{Co}_3\text{O}_4$ . In order to promote electron transfer mechanism and improve the performance of photocatalytic properties Graphite is added to hematite. The photo activity performance of hematite in composition with cobalt oxide and graphite in form of  $\text{Co}_3\text{O}_4/\text{Fe}_2\text{O}_3$  nano-composite and  $\text{Co}_3\text{O}_4/\text{Fe}_2\text{O}_3$  /G (FCG) nano-composites are studied for the first time and result have been discussed.

## 2. MATERIALS AND METHODS

### 2.1. Material Synthesis

To prepare a  $\text{Fe}_2\text{O}_3\text{-Co}_3\text{O}_4$  nanocomposite at first step  $\alpha\text{-Fe}_2\text{O}_3$  (Hematite) and  $\text{Co}_3\text{O}_4$  nanopowders were separately synthesized by the chemical route. ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) (99.9%, Merck), ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) (99.9%, Merck),  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  (99.9 Merck) and ethanol  $\text{C}_2\text{H}_5\text{OH}$  (99.5 % Merck) were used as the starting materials. Distilled water was used as a solvent. For synthesis of  $\alpha\text{-Fe}_2\text{O}_3$  (Hematite),  $\text{Fe}$

$(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was dissolved in distilled water with stirring at room temperature. After a while, ethanol solution was added dropwise to the stirring mixture at room temperature. The pH value was defined according to the experimental conditions given in reference [18]. The resulting dark dispersion was continuously stirred for 1 h at room temperature and then temperature was raised to 80  $^\circ\text{C}$  and maintained until yielding a black powder. The black powder was calcined in a furnace at 500  $^\circ\text{C}$  for 3 h to obtain a complete crystalline nanopowder. The synthesis procedure of  $\text{Co}_3\text{O}_4$  included dissolving  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (99.9% of Merck) in 100 ml of distilled water and di-ammonium oxalate  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  (99.99 Merck) separately as well. Ammonium oxalate solution was immediately poured into the cobalt nitrate solution at room temperature that led to precipitation of pink cobalt oxalate with the chemical formula of  $\text{CoC}_2\text{O}_4$ . During the precipitation process, the solution is stirred continuously until completion. At this stage, cobalt oxalate is conformed completely, and stirrer is turned off to deplete the sedimentary sediment and the waste solution. After drying, the sediment was transferred into an electric furnace for calcination where it was kept at 500  $^\circ\text{C}$  for 3 hours resulting in  $\text{Co}_3\text{O}_4$  black powder [19].

### 2.2. Preparation of Composite Catalysts

Composite catalysts were prepared in different weight ratios of  $\text{Co}_3\text{O}_4/\text{Fe}_2\text{O}_3$ , thermal operation was performed for 1 hour at 700  $^\circ\text{C}$  and the products were labeled FCx (x= 8, 16, 24 wt. %) corresponding to the weight ratio of the  $\text{Co}_3\text{O}_4/\text{Fe}_2\text{O}_3$  nanocomposites. The  $\text{Co}_3\text{O}_4/\text{Fe}_2\text{O}_3$  /G (FCG) nano-composites were prepared by adding Graphite nanopowder to  $\text{Co}_3\text{O}_4/\text{Fe}_2\text{O}_3$  in weight values of 1.17 and 2.35% wt% of graphite to determine the effect of graphite addition on photoactivity. After adding graphite, the resulting composite was heated for one hour at 700  $^\circ\text{C}$  in an electric furnace.

### 2.3. Characterization

The prepared nanopowders and composites samples were characterized with X-ray powder diffractometer (XRD). The XRD used was Philips X-Ray Diffract meter with  $\text{Cu K}\alpha$  radiation source ( $\lambda = 1.54274$ ). The morphology of samples was characterized by Field emission scanning electron microscopy (FESEM) Vega Tescan. Synthesized powders were ultrasonically dispersed into ethanol and the suspensions were then spread on the surface of aluminum foil to prepare sample for FESEM. Gold coating was performed before observation for better conductivity.

The UV-Vis diffused reflectance spectra (DRS) were taken using a Perkin Elmer, Model Lambda 25.

### 2.3. Photocatalytic Activity Test

The prepared composites were used to degrade Methylene Blue (MB) under a 55 W xenon lamp, and its photocatalytic

performance was studied through comparison with P25. Photocatalytic samples of 10 mg were added to 100 mL of a  $10^{-5}$  Molar of MB solution and magnetically stirred for 0.5 h in the dark to obtain the adsorption–desorption balance, and the xenon lamp was then turned on. A 5 mL sample of the solution was taken out every 20 min and centrifuged at a high speed; then, it was tested using a UV-vis spectrophotometer in 664 nm, with distilled water as a contrast. The concentration of MB was calculated according to Lambert–Beer’s law. The concentration of MB can be determined from the intensity of the color peak (664 nm) of solution. A standard calibration curve was constructed in the working range of 1.8–3.1 ppm (Figure 1).

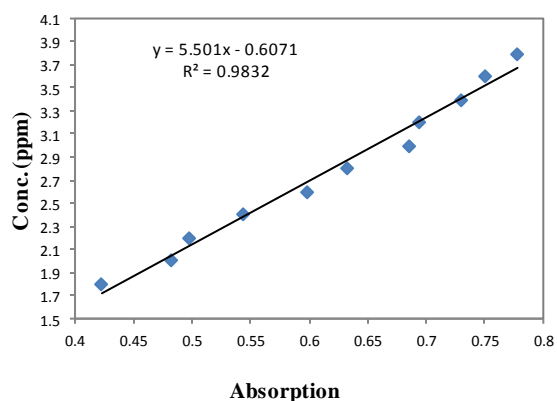
The measurements were carried out over the wavelength range of 400–1000 nm. The concentration of MB was calculated according to Lambert–Beer’s law by using Equation (1) that indicates relation between UV absorption and MB concentration:

$$C = 5.3968 A - 0.564 \quad (1)$$

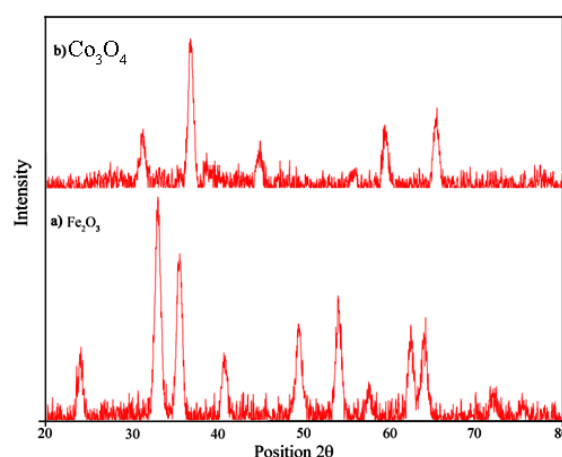
where C (ppm) is MB concentration and A is the absorption value obtained in UV-Vis measurements.

### 3. RESULTS AND DISCUSSION

The crystal structure of the synthesized catalysts  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles and Co<sub>3</sub>CO<sub>4</sub> nanoparticles were examined via XRD measurement and the data is shown in Figure 2. The observed pattern after heat treatment at 500 °C of the collected products exhibited all the expected peaks from the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> structure (a) and Co<sub>3</sub>CO<sub>4</sub> (b) without any detectable peaks from impurities and other phases. Powder X-ray diffraction (XRD) data can be indexed to the characteristic peaks of hematite (JCPDS 33-06 64) and Cobalt Oxide (JCPDS 01-076-1802).

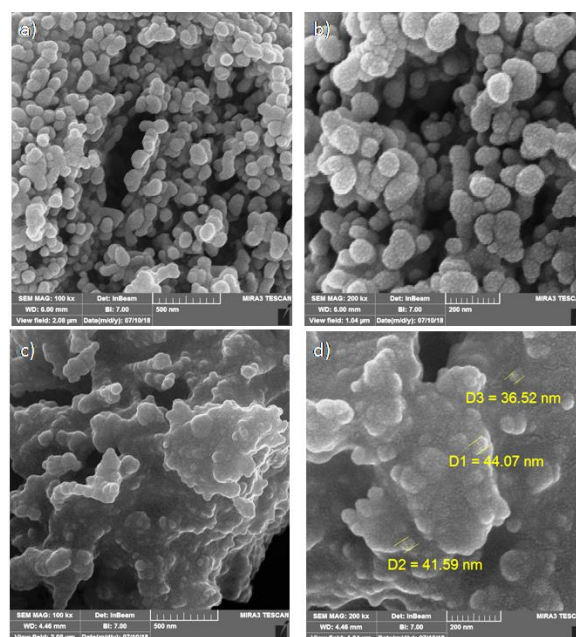


**Figure 1.** UV-Vis spectroscopy calibration curve for MB concentration



**Figure 2.** XRD patterns of the synthesized a) Hematite and b) Co<sub>3</sub>CO<sub>4</sub> powder after calcinations at 500 °C

Morphologies of the synthesized  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>CO<sub>4</sub> nanoparticles were characterized using scanning electron microscopy. The SEM images of the samples are shown in Figure 3. It can be seen that the synthesized Co<sub>3</sub>CO<sub>4</sub> nanopowder catalysts have very homogenous morphologies, regular dispersion and with nearly spherical shapes varying in size from approximately 30 to 50 nm. A closer look, specifically on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, allows to see that these particles consist of significantly smaller sphere-like grains with the size around 40–60 nm confirming that the synthesized nano-sized  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles have formed these soft agglomerations.



**Figure 3.** SEM images of the synthesized Co<sub>3</sub>CO<sub>4</sub> (a, b) and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (c, d) nanoparticles after calcinations at 500 °C

Composites of powder were prepared with heat treatment specified amounts of each of the powders after mechanically mixed together. All heat treatments were performed at a temperature of 700 °C. Figure 4 shows XRD pattern of Fe<sub>2</sub>O<sub>3</sub>/Co<sub>3</sub>O<sub>4</sub>/Graphite (FC3G2) composite (2.35 wt.% Graphite was added to FC3: 84 Fe<sub>2</sub>O<sub>3</sub>/16Co<sub>3</sub>O<sub>4</sub> (wt.%)). It shows that the composite comprises of all three compounds of Fe<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>, and Graphite.

The three different compounds of synthesized hematite nanopowder, 84 Fe<sub>2</sub>O<sub>3</sub>/16Co<sub>3</sub>O<sub>4</sub> (wt.%) composite and Fe<sub>2</sub>O<sub>3</sub>/Co<sub>3</sub>O<sub>4</sub>/Graphite (FC3G2) composite (2.35 wt.% Graphite added to FC3) were characterized by UV-visible absorption spectra to compare their optical absorption properties. Results are shown in Figure 5. The spectra show changes in the behavior of absorbance wavelengths when cobalt oxide and graphite were added to hematite powder and formed composites. Accordingly, it can be concluded that the absorbance of ultraviolet waves (wavelengths 190 to 200 nm) in FC3G2 composite is about 7.36% more than that of hematite; nevertheless, in visible ranges (between 400 and 700 nm) hematite absorbs about 30% more lights compared to FC3G2 composite. By adding cobalt oxide to hematite, the absorption peak is shifted to the left (indicated by green color in Figure 5), indicating an increase in the energy of band gap. With the addition of graphite to the two based composite of Fe<sub>2</sub>O<sub>3</sub>/Co<sub>3</sub>O<sub>4</sub>, the absorption edge has increased (blue curve), which means that graphite has no effect on the energy band gap and has only increased the absorption of ultraviolet waves.

The photocatalytic activity was examined by a colorant decomposition test using MB, which is very stable chemical dye under normal conditions. In general, absorption spectra can be used to measure the concentration changes of MB in extremely dilute

aqueous solution. The MB displays an absorption peak at the wavelength of about 664 nm. Time-dependent photo-degradation of MB is shown in Figure 6. In all curves in

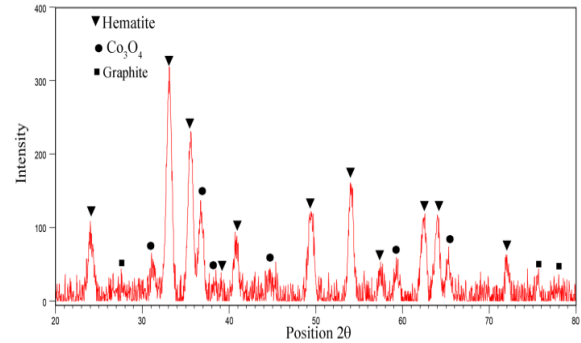


Figure 4. XRD patterns of the Fe<sub>2</sub>O<sub>3</sub>/Co<sub>3</sub>O<sub>4</sub>/Graphite (FC3G2) composite powder after heat treatment at 700 °C

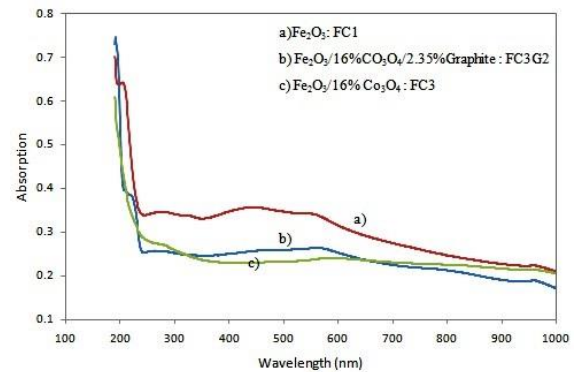


Figure 5. UV-visible absorbance spectrum

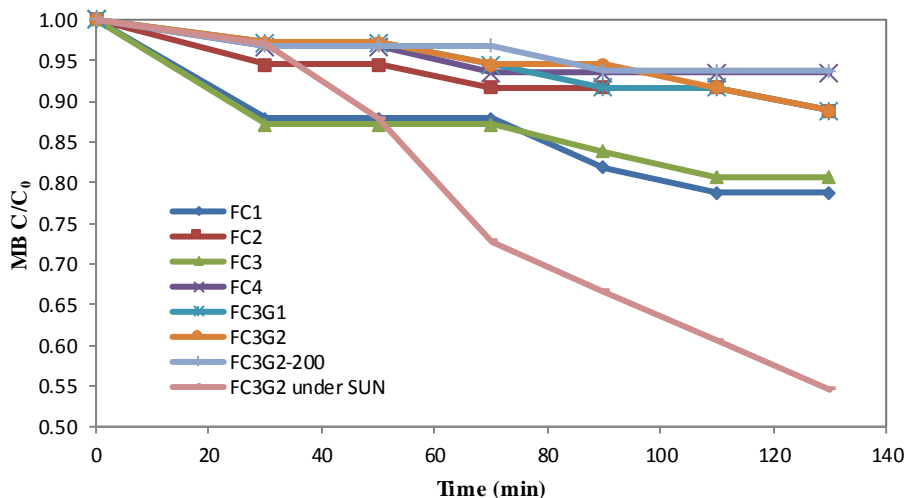


Figure 6. Changes in MB concentration photocatalytic degradation in the presence of different compounds of catalysts nanopowders: Pure Fe<sub>2</sub>O<sub>3</sub> (FC1), Composites of Fe<sub>2</sub>O<sub>3</sub>/Co<sub>3</sub>O<sub>4</sub> (FC2, FC3 and FC4), Composite Fe<sub>2</sub>O<sub>3</sub>/Co<sub>3</sub>O<sub>4</sub>/Graphite (FC3G2)

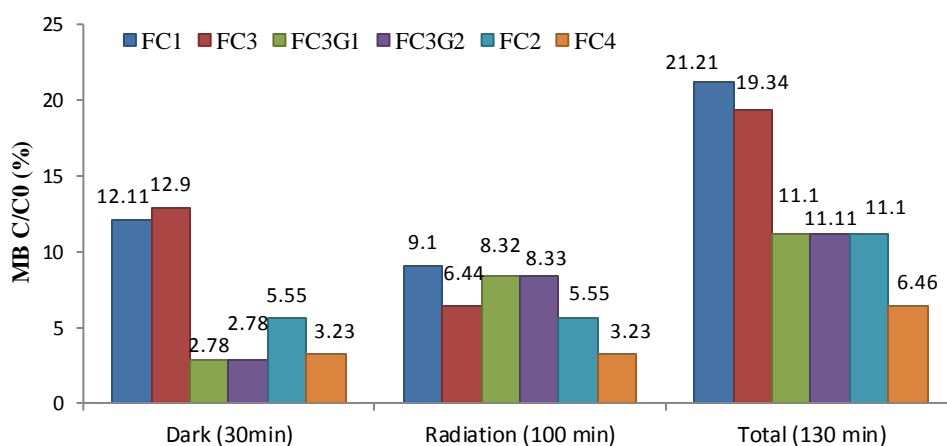
the first 30 minutes, decreasing in methylene blue concentration will be due to surface absorption of the powder since the test was performed in absolute darkness for 30 min. after which radiation was started up to 130 min that exhibited the photocatalytic activity of the catalysts powder. It is illustrated that MB decomposes in the presence of pure hematite and in composite samples of  $\text{Fe}_2\text{O}_3/\text{Co}_3\text{O}_4$  with 8, 16 and 24 wt.% of  $\text{Co}_3\text{O}_4$ . The results of the dark tests showed that increasing  $\text{Co}_3\text{O}_4$  did not follow a fixed pattern for surface adsorption of methylene blue molecules. Methylene blue is a cationic dye that is widely used in the textile industry [20]. The surface charge of hematite particles is negative [21], while the surface charge of  $\text{Co}_3\text{O}_4$  particles is positive +41[22]. Therefore, raising the amount of  $\text{Co}_3\text{O}_4$  leads to decrease of the absorption of methylene blue molecules on the surface of the composite powder. According to those results, the distribution of hematite and  $\text{Co}_3\text{O}_4$  particles is expected to be such that the hematite particles surrounded the cobalt oxide particles, in which case the effect of adding cobalt oxide to the absorption or excretion of methylene blue molecules is reduced because there are fewer interfaces between cobalt oxide particles and methylene blue molecules. For instance, in the FC3 composite containing 16% cobalt oxide,  $\text{Co}_3\text{O}_4$  particles are more surrounded by hematite than in the FC4 composite with 24 wt.% cobalt oxide. According to the results shown in Figure 6, the highest amount of adsorbent in dark belongs to FC3 and the lowest surface absorbance is for FC2 containing 8% cobalt. Moreover, according to Fabrizio Creazzo et al. [22], if the FCC network of  $\text{Co}_3\text{O}_4$  cuts from the side of (110), one side of the disconnected network will have a negative charge, while the other side will have a positive charge [22]. Based on this, it can be predicted that in the composition containing 16% cobalt oxide, the levels of sections with

negative charge of cobalt oxide had a higher level of common with methylene blue solution, which caused more absorption of methylene blue molecules and in the composition containing 8% cobalt oxide had a more positively cross-sectional area with the methylene blue solution.

The results reveal that the introduction of Graphite improves the photocatalytic activity by reducing the surface absorbance. This can conclude that Graphite as a conductive material reduces the recombination of electrons and holes that leads to improving photoactivity. It is seen from Figure 6 that in FC3G2 samples with 2.35 wt.% Graphite, the photo activity increased by 1.89% compared to FC3 sample without Graphite.

The photo activity of nano-composite FC3G2 in the two concentrations of 100 ppm and 200 of catalysts were compared and result is shown in Figure 6. The photo activity of nano-composite in concentration of 100 ppm showed better result. The decrease in photo activity by increasing the amount of photocatalytic powder is due to raising the population of particles that leads to more collision between particles, then decreasing the active surface for absorbing electromagnetic waves. The photocatalytic activity of catalysts reduces about 2% by increasing the amount of photocatalytic powder to 200 ppm.

Figure 7 shows an overview of the performance of all synthesized nano-composites. The highest rate of photo activity is related to hematite nanoparticles (FC1), and among the composites, the best photocatalytic performance belongs to the FC3G2 composite with 2.35 wt.% Graphite. On the other hand, the lowest amount of photo activity is related to FC4 composite, which contains the highest amount of cobalt oxide. Therefore, adding cobalt oxide to the composite has not yielded to desired results.



**Figure7.** Comparing photocatalytic activity in the presence of different compounds of catalysts nanopowders

The photo activity of nano-composite FC3G2 was examined under sunlight. The results of this experiment show that the photo activity of the nano-composite under irradiation of the solar light is about 4.5 times higher than that of the photo activity in the xenon 55 W lamp that caused degradation of about 55% of methylene blue. The higher removal efficiency of methylene blue over FC3G2 composite compared to all experiments done under radiation of xenon 55 W lamp is probably due to increase in dye adsorption on the photocatalyst surface under solar light which will react with active species in the photo catalysis process.

Calculations show that this photocatalytic nano-composit powder can produce 5.7  $\mu\text{mol H}_2$  per hour in a 1 liter of water under radiation of xenon 55 W. However, this same composite produced 27  $\mu\text{mol H}_2$  per hour under solar light irradiation. The results indicated that the removal efficiency of photo activity could be enhanced effectively in FC3G2 composite under solar light irradiation; that phenomenon has been reported by S Lub et al. [23].

#### 4. CONCLUSION

Nano-hematite and nano-cobalt oxide were successfully synthesized by simple chemical method without using a surfactant or templates. The synthesis process employs low-cost raw materials and yields a phase-pure, polycrystalline product. Compositing strategy in order to promote photocatalytic properties of hematite was studied. According to the UV-vis experiment graphite improves the photocatalytic activity of hematite. However, adding  $\text{Co}_3\text{O}_4$  to hematite transports the edge of the adsorbent to lower wavelengths, which means that the band gap has increased. The photocatalytic activities of the nano-hematite were determined by investigating the degradation of MB upon irradiation of UV lamp and solar light in the presence of the hematite and other composites. Of the various compounds synthesized, hematite nanoparticles were found to have the best photocatalytic performance during the degradation of MB, however among the composites, FC3G2 composite (containing 2.35% graphite and 16% cobalt oxide) had the best photocatalytic performance. Photocatalytic activity of FC3G2 composite under solar light was higher than that of UV irradiation. Photocatalytic activity of FC3G2 composite under solar light was higher than that of UV irradiation.

#### 5. REFERENCES

- Lee, J.S., "Photocatalytic water splitting under visible light with particulate semiconductor catalysts", *Catalysis Surveys from Asia*, Vol. 9, (2005), 217-227. DOI: 10.1007/s10563-005-9157-0.
- Maeda, K. and Domen, K., "New non-oxide photocatalysts designed for overall water splitting under visible light", *The Journal of Physical Chemistry C*, Vol. 111, No. 22, (2007), 7851-7861. DOI: 10.1021/jp070911w.
- Osterloh, F.E., "Inorganic materials as catalysts for photochemical splitting of water", *Chemistry of Materials*, Vol. 20, No. 1, (2008), 35-54. DOI: 10.1021/cm7024203.
- Mangold, K.-M., "Introduction to hydrogen technology. By roman j. Press, k. S. V. Santhanam, massoud j. Miri, alla v. Bailey, and gerald a. Takacs", *ChemSusChem*, Vol. 2, No. 8, (2009), 781-781. DOI: 10.1002/cssc.200900109.
- Dutta, S., "A review on production, storage of hydrogen and its utilization as an energy resource", *Journal of Industrial and Engineering Chemistry*, Vol. 20, (2014), 1148-1156. DOI: 10.1016/j.jiec.2013.07.037.
- Maeda, K., Xiong, A., Yoshinaga, T., Ikeda, T., Sakamoto, N., Hisatomi, T., Takashima, M., Lu, D., Kanehara, M., Setoyama, T., Teranishi, T. and Domen, K., "Photocatalytic overall water splitting promoted by two different cocatalysts for hydrogen and oxygen evolution under visible light", *Angewandte Chemie International Edition*, Vol. 49, No. 24, (2010), 4096-4099. DOI: 10.1002/anie.201001259.
- Liu, S., Kokot, S. and Will, G., "Photochemistry and chemometrics—an overview", *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, Vol. 10, No. 4, (2009), 159-172. <https://doi.org/10.1016/j.jphotochemrev.2010.01.001>.
- Chen, Y.H. and Lin, C.C., "Effect of nano-hematite morphology on photocatalytic activity", *Physics and Chemistry of Minerals*, Vol. 41, No. 10, (2014), 727-736. DOI: 10.1007/s00269-014-0686-9.
- Wender, H., Gonçalves, R.V., Dias, C.S.B., Zapata, M.J.M., Zagonel, L.F., Mendonça, E.C., Teixeira, S.R. and Garcia, F., "Photocatalytic hydrogen production of  $\text{CO}(\text{OH})_2$  nanoparticle-coated  $\alpha\text{-Fe}_2\text{O}_3$  nanorings", *Nanoscale*, Vol. 5, No. 19, (2013), 9310-9316. DOI: 10.1039/C3NR02195E.
- Liu, C.a., Fu, Y., Xia, Y., Zhu, C., Hu, L., Zhang, K., Wu, H., Huang, H., Liu, Y., Xie, T., Zhong, J. and Kang, Z., "Cascaded photo-potential in a carbon dot-hematite system driving overall water splitting under visible light", *Nanoscale*, Vol. 10, No. 5, (2018), 2454-2460. DOI: 10.1039/C7NR08000J.
- Zhu, Y., Wan, T., Wen, X., Chu, D. and Jiang, Y., "Tunable type i and ii heterojunction of coox nanoparticles confined in g-c3n4 nanotubes for photocatalytic hydrogen production", *Applied Catalysis B: Environmental*, Vol. 244, (2019), 814-822. <https://doi.org/10.1016/j.apcatb.2018.12.015>.
- Nahar, S., Zain, M., Kadhum, A., Abu Hasan, H. and Hasan, M.R., "Advances in photocatalytic  $\text{CO}_2$  reduction with water: A review", *Materials*, Vol. 10, (2017), 629. DOI: 10.3390/ma10060629.
- Miao, R., Luo, Z., Zhong, W., Chen, S.-Y., Jiang, T., Dutta, B., Nasr, Y., Zhang, Y. and Suib, S., "Mesoporous  $\text{TiO}_2$  modified with carbon quantum dots as a high-performance visible light photocatalyst", *Applied Catalysis B: Environmental*, Vol. 189, (2016), 26-38. DOI: 10.1016/j.apcatb.2016.01.070.
- Moro, F., Yu Tang, S.V., Tuna, F. and Lester, E., "Magnetic properties of cobalt oxide nanoparticles synthesised by a continuous hydrothermal method", *Journal of Magnetism and Magnetic Materials*, Vol. 348, (2013), 1-7. <https://doi.org/10.1016/j.jmmm.2013.07.064>.
- Mohamed, R.M., McKinney, D.L. and Sigmund, W.M., "Enhanced nanocatalysts", *Materials Science and Engineering: R: Reports*, Vol. 73, No. 1, (2012), 1-13. <https://doi.org/10.1016/j.mserr.2011.09.001>.

16. Mangrulkar, P.A., Joshi, M.M., Tijare, S.N., Polshettiwar, V., Labhsetwar, N.K. and Rayalu, S.S., "Nano cobalt oxides for photocatalytic hydrogen production", *International Journal of Hydrogen Energy*, Vol. 37, No. 13, (2012), 10462-10466. <https://doi.org/10.1016/j.ijhydene.2012.01.112>.
17. Moniz, S.J.A., Shevlin, S.A., Martin, D.J., Guo, Z.-X. and Tang, J., "Visible-light driven heterojunction photocatalysts for water splitting – a critical review", *Energy & Environmental Science*, Vol. 8, No. 3, (2015), 731-759. DOI: 10.1039/C4EE03271C.
18. Farahmandjou, M. and Soflaee, F., "Low temperature synthesis of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nano-rods using simple chemical route", *Journal of Nanostructures*, Vol. 2, (2015), 413. DOI: 10.7508/jns.2014.04.002.
19. Manteghi, F., Kazemi, S.H., Peyvandipour, M. and Asghari, A., "Preparation and application of cobalt oxide nanostructures as electrode materials for electrochemical supercapacitors", *RSC Advances*, Vol. 5, No. 93, (2015), 76458-76463. DOI: 10.1039/C5RA09060A.
20. Liu, L., Zhang, B., Zhang, Y., He, Y., Huang, L., Tan, S. and Cai, X., "Simultaneous removal of cationic and anionic dyes from environmental water using montmorillonite-pillared graphene oxide", *Journal of Chemical & Engineering Data*, Vol. 60, No. 5, (2015), 1270-1278. DOI: 10.1021/je5009312.
21. Mustafa, S., Tasleem, S. and Naeem, A., "Surface charge properties of Fe<sub>2</sub>O<sub>3</sub> in aqueous and alcoholic mixed solvents", *Journal of Colloid and Interface Science*, Vol. 275, No. 2, (2004), 523-529. <https://doi.org/10.1016/j.jcis.2004.02.089>.
22. Creazzo, F., Galimberti, D.R., Pezzotti, S. and Gageot, M.-P., "Dft-md of the (110)-CO<sub>3</sub>O<sub>4</sub> cobalt oxide semiconductor in contact with liquid water, preliminary chemical and physical insights into the electrochemical environment", *The Journal of Chemical Physics*, Vol. 150, No. 4, (2019), 041721. DOI: 10.1063/1.5053729.
23. Lubis, S., Sheilatina and Murisna, "Synthesis, characterization and photocatalytic activity of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/bentonite composite prepared by mechanical milling", *Journal of Physics: Conference Series*, Vol. 1116, (2018), 042016. DOI: 10.1088/1742-6596/1116/4/042016.

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### Persian Abstract

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#### چکیده

در این مطالعه، در مرحله‌ی اول ذرات نانوپودر  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (هماتیت) و Co<sub>3</sub>O<sub>4</sub> به طور جداگانه با استفاده از روش شیمیایی ساده محلول آبی از نیترات آهن و نیترات کبالت از پیش‌ماده‌های اولیه Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O و هگزاهیدرات (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) سنتز شدند. پس از آن، سه کامپوزیت از نانوپودرهای سنتز شده به ترتیب با افزودن ۸، ۱۶ و ۲۴ درصد وزنی Co<sub>3</sub>O<sub>4</sub> به Fe<sub>2</sub>O<sub>3</sub> تهیه شدند. نانوپودر گرافیت نیز به یک ترکیب از نمونه‌های ذکر شده به میزان ۱،۱۷ و ۲،۳۵ درصد وزنی اضافه شد. ترکیب فازی و ساختاری و مورفولوژی کامپوزیت‌ها به ترتیب توسط XRD و FE-SEM بررسی شدند. تحلیل FE-SEM نشان داد که مورفولوژی پودرها و کامپوزیت‌ها همه در مقیاس نانو و کروی شکل هستند. فعالیت فوتوکاتالیستی کامپوزیت‌ها با اندازه گیری تخریب محلول آبی متیلن بلو تحت تابش نور خورشید شبیه‌سازی شده بررسی شد. برای تعیین فعالیت فوتوکاتالیستی، تخریب آبی متیلن (MB) در غیاب نور (آزمایش تاریک) نیز گرفته شد. نتایج نشان داد که افزودن Co<sub>3</sub>O<sub>4</sub> به Fe<sub>2</sub>O<sub>3</sub> باعث کاهش فعالیت فرآیند فوتوکاتالیستی می‌شود، در حالی که نانو گرافیت فرآیند فوتوکاتالیستی را به میزان ~ ۲٪ نسبت به کامپوزیت بدون نانوذرات گرافیت افزایش می‌دهد. محاسبات استوکیومتری نشان داد که مقدار هیدروژن تولید شده توسط آب توسط نانوذرات کامپوزیت Fe<sub>2</sub>O<sub>3</sub>/Co<sub>3</sub>O<sub>4</sub>/Graphite در برابر تابش نور خورشید برابر با ۲۷ μmol H<sub>2</sub>/h.g است.

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