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Visible light-induced photocatalytic performance of green $MnFe_2O_4$ and $CoFe_2O_4$ nanoparticles

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ABSTRACT
Water photocatalytic treatment has found more attention in recent years. Photocatalytic process can degrade various organic pollutants in water using free solar energy. In this study, manganese ferrite ($MnFe_2O_4$) and cobalt ferrite ($CoFe_2O_4$) as magnetic photocatalysts were prepared through novel, green and simple co-precipitation route. So, marshmallow extract was applied as green capping agent for morphological engineering of products. The crystalline structure, shape, and particle size of prepared products were characterized via X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) techniques. The cubic phase of the products with sphere-like morphology were formed. The BET analysis revealed that the prepared $MnFe_2O_4$ (72.30 m^2 g^{-1}) and $CoFe_2O_4$ (65.85 m^2 g^{-1}) have sufficient surface area for photocatalytic application. The UV-vis diffuse reflectance spectroscopy (DRS) analysis was applied for assessment of the optical properties of these products. The optical band gap of as-obtained $MnFe_2O_4$ and $CoFe_2O_4$ were 2.42 and 2.71 eV, respectively. Finally, the results indicated that the $MnFe_2O_4$ can removed 78, 84, and 92% of methyl orange, methylene blue, and acid violet 7 from water, after 80 min UV irradiation respectively. It was found that the photocatalytic activity of $CoFe_2O_4$ is lower than $MnFe_2O_4$. Also, the further examination revealed that the photocatalytic efficiency has decreased under visible light irradiation. This study introduces $MnFe_2O_4$ and $CoFe_2O_4$ as excellent photocatalysts for degradation of organic pollutants.

Keywords: Magnetic nanomaterials, Optical properties, Photocatalyst, Surface area, Water pollutant.
Article type: Research Article.

INTRODUCTION
Photocatalysis is a technology that has gained significant attention in recent years due to its ability to transform light energy into chemical one (Sakka 2013; Subramaniam *et al.* 2019). It involves using a catalyst to facilitate the conversion of light into chemical energy (Toe *et al.* 2021). Using catalysts is essential in photocatalysis, since it can enhance the efficiency of the process (Dutta *et al.* 2021; Zhu *et al.* 2021; Falih *et al.* 2022; Khadhim & Al-gubury 2023; Al-Zaidi *et al.* 2023). $MnFe_2O_4$ and $CoFe_2O_4$ are two of the catalysts that have been proven to be highly effective in enhancing photocatalytic activity. Manganese ferrite and cobalt ferrite are two of the most commonly used catalysts in photocatalysis (Singh & Singhal 2019; Shakir *et al.* 2021; Chaudhari *et al.* 2022; Zimur *et al.* 2023). Manganese ferrite is a type of magnetic iron oxide that has a spinel structure. It has a high surface area, which makes it an excellent candidate for enhancing photocatalytic activity (Ferreira *et al.* 2022; Manohar *et al.* 2022). Cobalt ferrite is a type of ceramic material that has a spinel structure. It is a popular catalyst in photocatalysis due to its high stability and durability (Mmelesi *et al.* 2021; Annie Vinosha *et al.* 2021). Manganese ferrite and cobalt ferrite have different physical and chemical properties. $MnFe_2O_4$ has a higher surface area than cobalt ferrite, which makes it more effective in enhancing photocatalytic activity. Manganese ferrite is

also more stable than cobalt ferrite, which means that it can be reused multiple times without losing its activity. $CoFe_2O_4$, on the other hand, has a higher durability than manganese ferrite, which means that it can withstand harsh conditions without losing its activity (Elkholy *et al.* 2017; Miri *et al.* 2022). Manganese ferrite and cobalt ferrite have been shown to have a significant impact on photocatalytic activity. It has been found to enhance the efficiency of photocatalysis by increasing the rate of electron-hole recombination (Annie Vinosha *et al.* 2021; He & Ge 2022). This is because these ferrites have a high surface area, which provides a large number of active sites for the reaction to occur. The high surface area also allows for the adsorption of organic pollutants, which can then be degraded by the photocatalytic process (Bodaghi *et al.* 2020; Gautam *et al.* 2020). $MnFe_2O_4$ and $CoFe_2O_4$ have also been found to be highly effective in enhancing the degradation of dyes and other pollutants. This is due to its ability to absorb visible light, which is the most abundant source of light in the environment. The absorption of visible light by manganese ferrite results in the generation of electron-hole pairs, which can then be used to degrade the pollutants (Sharma *et al.* 2020; Shah *et al.* 2022). Manganese ferrite and cobalt ferrite have been compared with other catalysts in photocatalysis, such as titanium dioxide and zinc oxide. It has been found that manganese ferrite is more effective than these catalysts in enhancing photocatalytic activity. This is due to its high surface area and attractive magnetic behavior, which provides more active sites for the reaction to occur and facilitate to recovery and reuse (Mapossa *et al.* 2021; Annie Vinosha *et al.* 2021). Manganese ferrite is also more stable than these catalysts, which means that it can be reused multiple times without losing its activity. It is also believed that the absorption of visible light by manganese ferrite plays a significant role in enhancing photocatalytic activity. The absorption of visible light results in the generation of electron-hole pairs, which can then be used to degrade pollutants (Park *et al.* 2019; Wu & Song 2023; Mishra *et al.* 2023). The high stability of these ferrites also contributes to the enhanced photocatalytic activity, which as mentioned above, it allows for the catalyst to be reused multiple times without losing its activity (Imran Din *et al.* 2019; Kefeni & Mamba, 2020; Manohar *et al.* 2022; Ortiz-Quiñonez *et al.* 2022). The use of manganese ferrite and cobalt ferrite in photocatalysis have promising future prospects. However, there are several challenges that need to be addressed. One of the challenges is the cost of production, as manganese ferrite and cobalt ferrite are relatively expensive compared to other catalysts. Another challenge is the stability of these ferrites under harsh conditions, which needs to be improved for it to be used in industrial applications (Dutta *et al.* 2019; Ismael 2021; Bahadoran *et al.* 2022). In this work, $MnFe_2O_4$ and $CoFe_2O_4$ nanoparticles were synthesized through novel green chemical co-precipitation and hydrothermal routes. The structural and morphological properties of products were characterized via XRD, SEM, EDS and TEM analyses. In addition, the magnetic behavior of products was investigated via VSM analysis comprehensively. Finally, the photocatalytic activity of products were examined against different organic dyes under UV and visible light.

MATERIALS AND METHODS

Materials

Manganese (II) nitrate hexahydrate ($Mn(NO_3)_2.6H_2O$), iron (III) chloride hexahydrate ($Fe(NO_3)_3.6H_2O$), sodium hydroxide, ethanol and other applied chemical reagents were purchased from Merck Company.

Marshmallow extraction

Marshmallow extract was provided by adding 8 g fresh marshmallow to 200 mL deionized water and then stirring it under 60 ºC for 30 minutes. Finally, using a filter paper, the homogeneous solution was separated and the obtained extract was used as a capping agent for preparation of nanoparticles.

Green synthesis of $MnFe_2O_4$ and $CoFe_2O_4$ nanostructures

The manganese ferrite nanoparticles was prepared via dissolving 1:2 molar ratio of $Mn(NO_3)_2.6H_2O$ and $Fe(NO_3)_3.6H_2O$ in distilled water separately. Then, 10 mL fresh marshmallow extract was added to the Fe^{3+} solution and stirred at room temperature. Afterward, the Mn^{2+} solution was mixed with Fe^{3+} and extract solution. Then NaOH (2M) solution was slightly added to the mixture and stirred for one hour. Finally, the as-obtained solid was separated by centrifugation for 10 min at 12000 rpm. Final product was obtained after drying solid at 90 ºC for overnight. Finally, the dried product was heated at 900 ºC for 2 h. The same chemical process was applied for preparation of cobalt ferrite nanoparticles. $Co(NO_3)_2.6H_2O$ and $Fe(NO_3)_3.6H_2O$ were applied as precursors for preparation of $CoFe_2O_4$ nanoparticles. Similar to the applied method for the synthesis of manganese ferrite, 5-mL fresh marshmallow extract was used for morphological engineering.

Photocatalytic test

The synthesized $MnFe_2O_4$ and $CoFe_2O_4$ nanoparticles were used for the photodegradation of methylene blue, methyl orange, and acid violet 7 under UV as well as visible light at room temperature and pressure. An aliquot of 0.005 g mL^{-1} synthesized nanostructures were mixed with 30 ppm of acid violet and methylene orange solutions. The obtained mixture stirred for one hour in a dark box to provide adsorption–desorption equilibrium between the $MnFe_2O_4$ and $CoFe_2O_4$ nanoparticles nanostructure as well as acid violet and methylene orange. Then, the mixture was exposed to the UV and visible light and at every period of time (10 min). In addition, 5-mL organic dyes solution were filtered for recording absorbance UV-Vis spectrophotometer. The photodegradation efficiency of $MnFe_2O_4$ and $CoFe_2O_4$ nanoparticles was determined via the following equation (1):

$$\text{Photocatalytic efficiency } \% = \frac{C_0 - C_t}{C_0} \times 100 \qquad \textbf{(1)}$$

where C_0 is the initial concentration of dyes and C_t is the concentration after the time interval.

RESULTS AND DISCUSSION

The X-ray diffraction (XRD) analysis was applied for determination crystallinity and structural properties of products. The XRD analysis confirmed that the synthesis of $MnFe_2O_4$ and $CoFe_2O_4$ nanostructures was successful and that both $MnFe_2O_4$ and $CoFe_2O_4$ were pure and crystalline. The presence of hematite phase in both $MnFe_2O_4$ indicated that Fe cation has replaced Mn one in the crystalline structure of $MnFe_2O_4$. The peaks location confirmed formation of cubic phase of $MnFe_2O_4$ with Fd-3m space group. Scherrer equation which was applied for determination grain size, calculated 38 nm as grain size of prepared $MnFe_2O_4$. In the case of $CoFe_2O_4$, the results confirmed formation of cubic phase with Fd-3m space group and 42.5 nm grain size. In summary, the XRD analysis provided crucial information about the composition and crystal structure of the synthesized nanostructures.

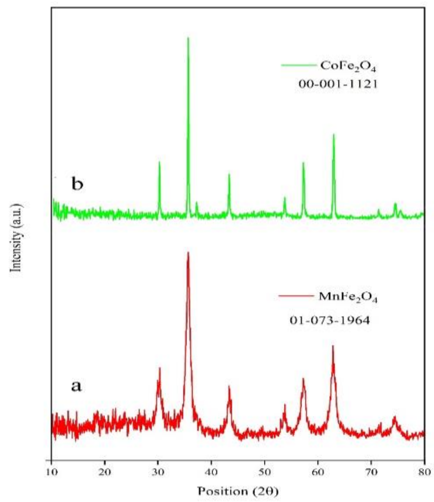

Fig. 1. X-ray diffraction patterns of prepared a) $MnFe_2O_4$ b) $CoFe_2O_4$ nanoparticles.

The SEM analysis was utilized to the studying morphological properties of products. Fig. 2a and Fig. 2b provide SEM images of prepared $MnFe_2O_4$ nanoparticles. It can be seen from SEM images that the uniform sphere-like particles are prepared. Also, the SEM images revealed that the marshmallow extract acts as excellent capping agent. This is the advantage of this work to use green capping agent instead of chemical capping one. Fig. 2c shows the EDS analysis of prepared $MnFe_2O_4$ nanoparticles. As shown in this Fig., the Mn, Fe, and O elements are presented in prepared nanoparticles. EDS analysis confirmed the formation of $MnFe_2O_4$ with any impurity. Figs. 3a and 3b present SEM images of prepared $CoFe_2O_4$ nanoparticles. It can be concluded that the uniform sphere-like $CoFe_2O_4$ nanoparticles with average diameter of 62 nm was formed via applied green synthesis route.

The EDS analysis of obtained $CoFe_2O_4$ nanoparticles confirmed presence of cobalt, iron, and oxygen elements in the sample. Figs. 4a and 4b provide TEM images of obtained $MnFe_2O_4$ nanoparticles. The obtained particles size with TEM images (52 nm) is in good agreement with SEM results. Also, TEM images confirm the uniform sphere-like morphology of prepared $MnFe_2O_4$ nanoparticles (Fig. 4).

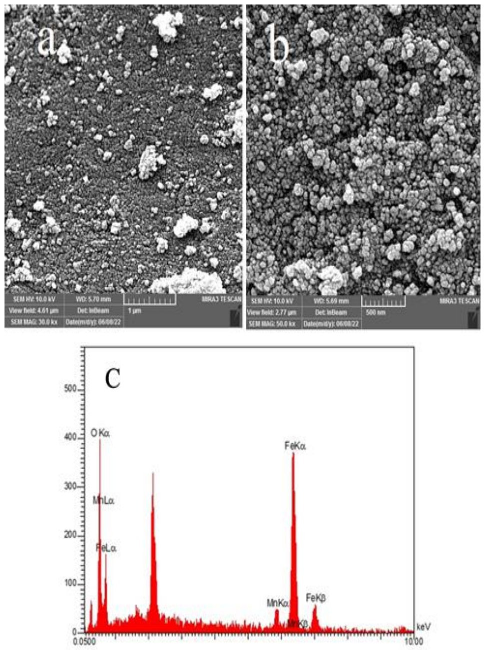

Fig. 2. a,b) SEM images c) EDS analysis of as-obtained $MnFe_2O_4$ nanoparticles.

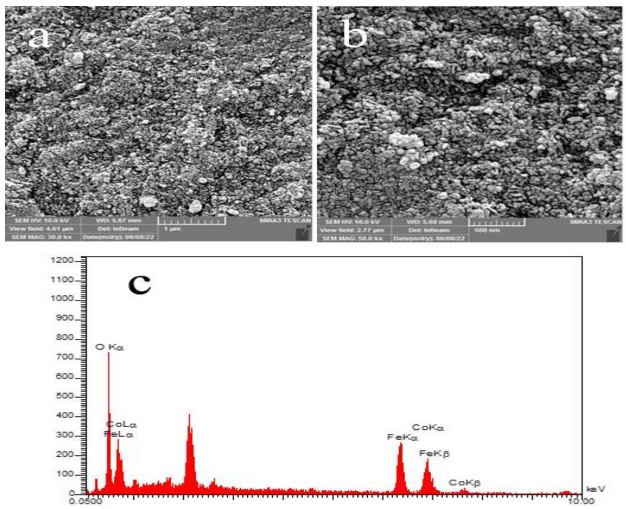

Fig. 3. a,b) SEM images c) EDS analysis of synthesized $CoFe_2O_4$ nanoparticles.

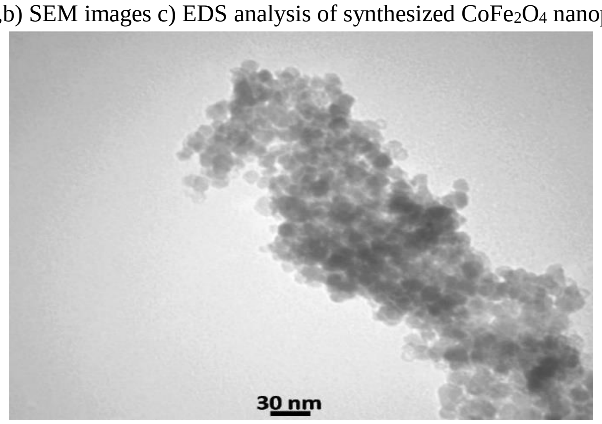

Fig. 4. TEM image of prepared $MnFe_2O_4$ nanoparticles.

Manganese ferrite and cobalt ferrite are well known to show magnetic behavior that can be determined with VSM. In $MnFe_2O_4$, the saturation magnetization (Ms), retentivity (Mr), and coercivity (Hc) were 41.50 emu/g, 2.30 emu/g and 6.76 Oe respectively (Fig. 5a). In the case of $CoFe_2O_4$, the saturation magnetization (Ms), retentivity (Mr) and coercivity (Hc) were 49.35 emu/g, 0.64 emu/g and 7.42 Oe respectively. The obtained results are in good agreement with previously reported papers (Liu *et al.* 2021). The results suggest that the prepared ferrites possess low magnetic strength, making it suitable for applications that require weak magnetic properties like catalysis. The measurements of Hc, Mr, and Ms are significant in comprehending the magnetic characteristics of prepared nanomaterials and can assist in advancing research and innovation in photocatalytic process (Chinnathambi *et al.* 2021).

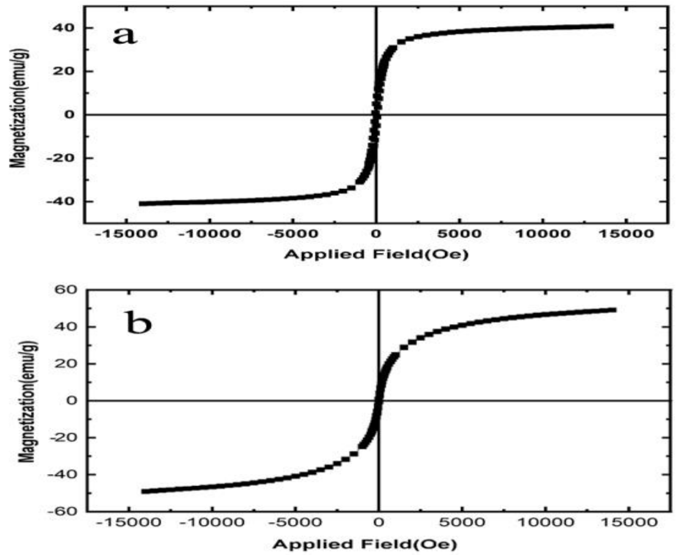

Fig. 5. VSM analysis of prepared a) $MnFe_2O_4$ b) $CoFe_2O_4$ nanoparticles.

Fig. 6a shows the manganese ferrite N2 sorption isotherm. By a type V isotherm, the isotherm displays an H3 hysteresis loop, suggesting that multilayer adsorption followed by capillary condensation exhibit in which way the adsorption of mesoporous manganese ferrite occurs. The surface area, pore volume, and pore diameter were measured 72.30 m^2 g^{-1}, 0.24 cm^3g^{-1} and 13.39 nm respectively. For $CoFe_2O_4$, the surface area, pore volume, and pore diameter were 65.85 m^2 g^{-1}, 0.21 cm^3 g^{-1}, and 13.28 nm respectively (Fig. 6b). It can be concluded from BET analysis that the applied green capping agent leads to the synthesis of high surface area ferrites. The higher surface area of prepared nanomaterials is vital for application of nanomaterials in photocatalytic field. Optical properties of materials play key role in photocatalytic activity. So, UV-Vis-diffuse reflectance spectroscopy (DRS) was applied for investigation optical properties of prepared samples (Fig. 7a and 7c). Also, the optical band gap was calculated via Tauc equation and extrapolating the linear part of the plot of $(\alpha h\nu)^2$ vs $h\nu$. In this manner, the optical band gap of synthesized manganese ferrite was 2.42 eV (Fig. 7b) while the optical band gap of obtained cobalt ferrite nanomaterials was 2.71 eV (Fig. 7d).

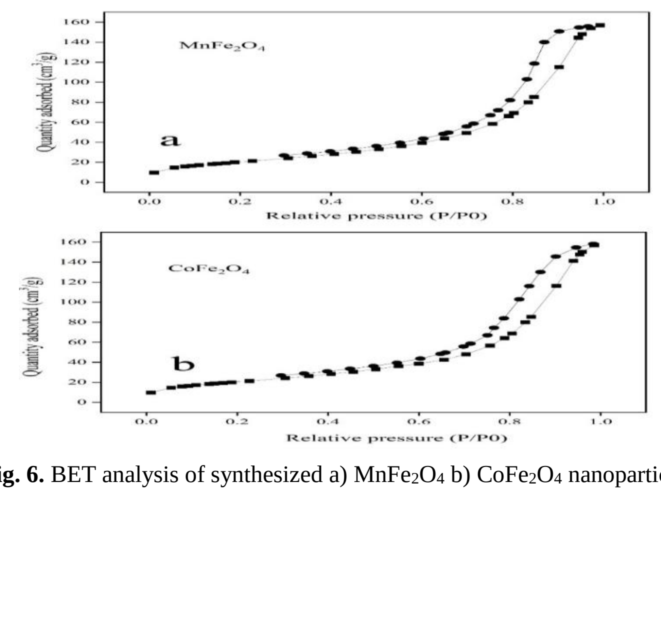

Fig. 6. BET analysis of synthesized a) $MnFe_2O_4$ b) $CoFe_2O_4$ nanoparticles.

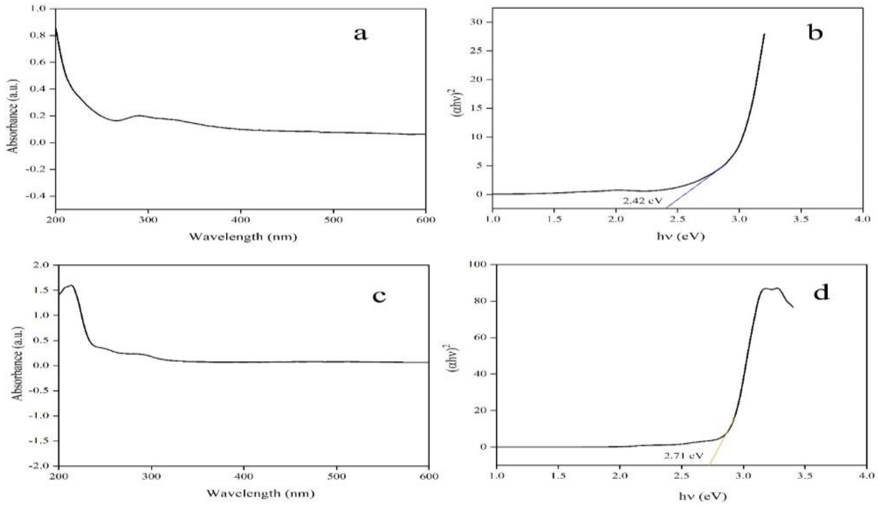

Fig. 7. a) DRS spectrum of $MnFe_2O_4$ nanoparticles b) optical band gap of $MnFe_2O_4$ nanoparticles c) DRS spectrum of $CoFe_2O_4$ nanoparticles d) optical band gap of $CoFe_2O_4$ nanoparticles.

The photocatalytic performance of prepared $MnFe_2O_4$ and $CoFe_2O_4$ was tested against methyl orange, methylene blue, and acid violet 7 dyes under UV irradiation for 80 min. The results showed that when $MnFe_2O_4$ was applied as photocatalyst, it can photodegraded 78, 84, and 92% of methyl orange, methylene blue, and acid violet 7 dyes, respectively, in 80 minutes (Fig. 8). The mechanisms behind the enhanced photocatalytic activity of manganese ferrite are not yet fully understood. However, it is believed that the high surface area of manganese ferrite plays a key role in enhancing photocatalytic activity. The high surface area provides a large number of active sites for the reaction to occur, which increases the efficiency of the process. The photodegradation mechanism of manganese ferrite can be defined as:

$$\text{Manganese ferrite nanoparticles (MnFe)} \xrightarrow{h\upsilon} \text{MnFe}\ (e^-_{CB}) + \text{MnFe}(h^+_{VB}) \quad \textbf{(1)}$$

$$O_2 + e^- \rightarrow \bullet O_2^- \quad \textbf{(2)}$$

$$\bullet O_2^- + H^+ \rightarrow \bullet HO_2 \quad \textbf{(3)}$$

$$2 \bullet HO_2 \rightarrow O_2 + H_2O_2 \quad \textbf{(4)}$$

$$H_2O_2 + e^-_{CB} \rightarrow 2 \bullet OH \quad \textbf{(5)}$$

$$h^+_{VB} + H_2O \rightarrow \bullet OH + 2H^+ \quad \textbf{(6)}$$

$$\text{acid violet (MB or MO)} + \bullet OH \rightarrow \text{Degradation of acid violet (MB or MO)} \quad \textbf{(7)}$$

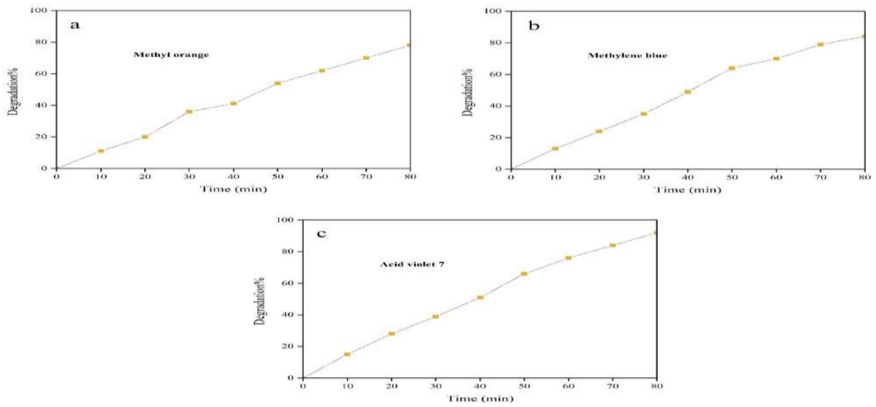

Fig. 8. Photocatalytic activity of prepared $MnFe_2O_4$ nanoparticles against a) methyl orange b) methylene blue c) acid violet 7 under UV irradiation.

It was expected that the photocatalytic activity of $CoFe_2O_4$ is lower than manganese ferrite. The result confirmed this prediction. $CoFe_2O_4$ could photodegraded 72, 81, and 86% of methyl orange, methylene blue, and acid violet

7 dyes, respectively, in 80 minutes (Fig. 9). It was found that manganese ferrite is more effective than cobalt ferrite in enhancing photocatalytic activity. This is due to the higher surface area of manganese ferrite, which provides more active sites for the reaction to occur. Manganese ferrite is also more stable than cobalt ferrite, which makes it more suitable for industrial applications. The effect of irradiation light on the photocatalytic activity was investigated. The results showed that the photocatalyst under visible light has a lower efficiency compared to UV irradiation in degradation of acid violet 7. The photocatalytic efficiencies were 49 and 41% for prepared $MnFe_2O_4$ and $CoFe_2O_4$ nanoparticles, respectively (Fig. 10). However, these visible light-induced photodegradation are very attractive and can promise the widespread use of these nanomaterials on industrial scale.

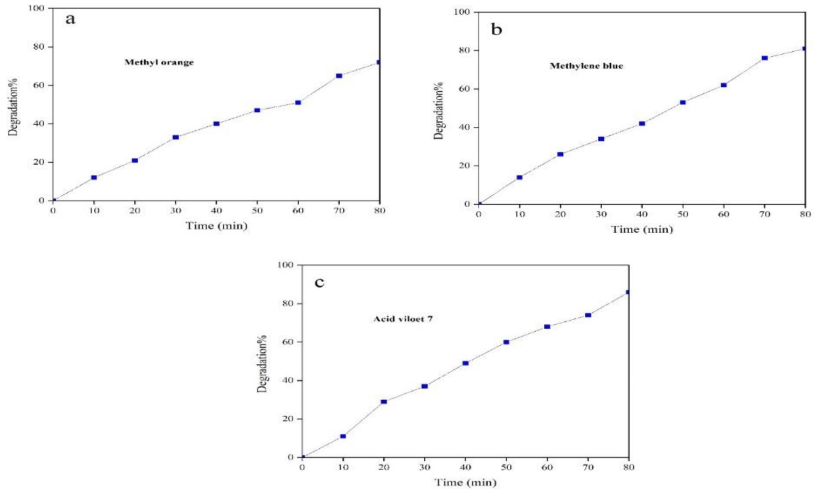

Fig. 9. Photocatalytic activity of prepared $CoFe_2O_4$ nanoparticles against a) methyl orange b) methylene blue c) acid violet 7 under UV irradiation.

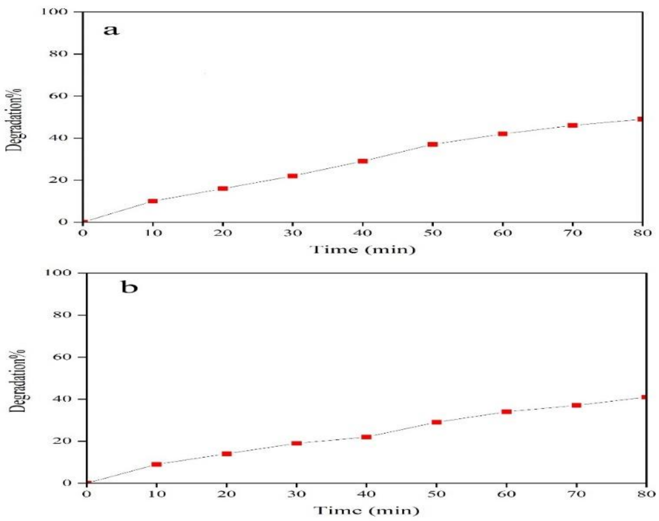

Fig. 10. Photocatalytic activity of prepared $MnFe_2O_4$ nanoparticles against acid violet 7 under visible light irradiation.

CONCLUSION

In conclusion, $MnFe_2O_4$ and $CoFe_2O_4$ nanomaterials were synthesized via green chemical route. The physical and chemical properties of samples were determined via SEM, TEM, XRD, and BET analyses. The results showed that marshmallow extract could act as promising capping agent for controlling shape and size of $MnFe_2O_4$ and $CoFe_2O_4$ nanomaterials. VSM analysis was applied for determination magnetic behavior of products. Results showed that prepared samples have excellent magnetic and morphological properties for photocatalytic application. The optical band gap of synthesized $MnFe_2O_4$ and $CoFe_2O_4$ were 2.42 and 2.71 eV, respectively. The photocatalytic tests showed that prepared magnetic nanomaterials can effectively photodegraded methyl orange, methylene blue, and acid violet 7 from wastewater. Also, it was found that manganese ferrite is a higher effective catalyst in enhancing photocatalytic activity rather than cobalt ferrite. It had a high surface area, which provides more active sites for the reaction to occur, and it is more stable than cobalt ferrite catalyst.

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