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Review Article

Iron Oxide Heterojunction Structure for Photodegradation of Emerging Pollutants

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ABSTRACT

Recently, the rise in the number of emerging pollutants (EPs) being released in the aquatic environment has been a significant global concern. The contaminants are produced in large volumes daily and are illicitly discharged into water resources. However, conventional wastewater treatment facilities are failing in eliminating these pollutants. Hence, a substantially more sustainable and effective removal technique such as photodegradation is demanded to deal with this concern. The photodegradation of wastewater using a semiconductor photocatalyst has been demonstrated to be an effective method due to its efficiency, affordability and simplicity. Iron oxide-based heterojunction is one of the photocatalysts that is more plausible for the treatment of contaminated materials from industrial, pharmaceutical, agricultural, and dyes effluent. Due to their low band gap of 2.2 eV, iron oxide-based materials were identified to have good photocatalytic activity in the presence of ultraviolet (UV) and visible light. This enables iron oxide-based to absorb much of the visible solar spectrum (absorbance edge-alternatively, 600nm). It is also a promising material for photocatalytic treatment and water division applications because of its excellent chemical stability in aquatic media, low cost, abundance and non-toxic nature. In short, iron oxide-based features are useful as a photocatalyst due to its tolerable band gap, wide harvesting of visible light, good stability and recyclability. In this review, the characteristics of iron oxide, iron oxide heterojunction with various morphologies and iron alterations to improve its photocatalytic performance in emerging pollutants will be discussed. Also, we will discuss the integrate procedure of iron oxide with supporting materials and the formation of iron heterojunction with other semiconductive materials. In a nutshell, this article informs about the research to shed some lights on the insight of the potential and basic limitations of iron oxide-based photocatalysts in the treatment of emerging pollutants.

Keywords: Iron Oxide, Nanocomposite, Chlorella vulgaris, Waste black toner ink

1. INTRODUCTION

Anthropogenic sources of emerging pollutants are dispersed throughout the environment from human activities have resulted in environmental pollution. The effluent is considered as hazardous due to the presence of vat dyes, sulphur, acetic acid, naphthol, soaps, nitrates, chromium compounds, and heavy metals for instance arsenic, copper, lead, mercury, cadmium, cobalt, and nickel, besides various auxiliary chemicals (Carolin et al., 2023). Disposing of this waste or emerging pollutant will lead to numerous health and environmental hazards for humans and the ecosystem even though several effective treatment processes have been implemented to preserve the environment. Due to the continuous of specific advancement techniques, a wide range of unidentified contaminants that are becoming an increasing source of environmental concern needs to be recognised and quantified in some environmental components as well as biological tissues. Numerous effective treatment processes have been implemented to protect the environment (Abdelsamad et al., 2018).

Various studies present several treatments such as biological treatment, chemical precipitation, ion exchange, membrane processes, chemical oxidation or reduction, coagulation or flocculation, reverse osmosis, and adsorption, but each one has a few shortcomings (Es-Sahbany et al., 2022). For instance, the ion exchange method requires renewing expensive ion exchange resins, while chemical reduction and precipitation methods can produce hazardous by-products, such as nitrite and ammonia, during nitrate removal (Vievard et al., 2023). Thus, the photocatalysis method is one of the most suitable methods to treat contaminated water and less harmful to the environment.

Photocatalysts function by using light energy to drive chemical reactions (Yang et al., 2018). In this process, at least two reactions occur simultaneously; an oxidation reaction from the photogenerated holes and a reduction reaction from the photogenerated electrons. In other words, the photocatalytic mechanism occurs with the following steps which is the absorption of energy photons incident above or equal to the photocatalyst band gap, the generation of photo-excited conduction band (CB) electrons and the same number of valence band (VB) holes (Hitam & Jalil, 2020). According to Li and Tang (2014), the holes formed absorb electrons from absorbed pollutants or react with H_2O to form OH. CB electrons, on the other hand, reduce the absorbed oxygen to form O_2 which can then be disproportionately reduced to form OH via chain reactions.

TiO_2 was extensively used as a well-known photocatalyst to photocatalytically remove dyes and organic pollutants due to its high activity, chemical stability, low price, non-toxic and high resistance to photography and chemical corrosion (Armaković et al., 2022). The widespread application of TiO_2 technology is slightly hampered by a wide band gap (anatase, 3.2 eV), which necessitates the employment of photocatalytic ultraviolet irradiation and, as a consequence, results in very low energy consumption from solar lights (Zhang et al., 2018). Aside from the wasteful use of visible light, due to the following restrictions practical implementation was also banned; 1) low adsorption capacity to hydrophobic pollutants; 2) high aggregation tendency; 3) separation and recovery difficulties (Osman et al., 2023). In addition, TiO_2 nanoparticles settle dependent on the pH, ionic force, and natural organic matter, which can result in active sites becoming clogged (blocked) and reduce the efficacy of photocatalysis (Lee et al., 2019). A large number of studies have taken place in order to improve the photocatalytic efficiency of TiO_2 to eliminate the above limitations. TiO_2's photoactivity can typically be improved through one of the three approaches. These include modifying the band gap or using photosensitizers to increase the amount of light absorbed, enhancing the separation of carriers, and promoting the adsorption of photocatalyst surface reactants (Tinoco & Jaroslav, 2023). These include the carbonate compound coupling, nobles metal surface adjustment, ion doping and combination with other semiconductors (Majeed et al., 2022).

Apart from various TiO_2 modifications, it is of great interest to explore a new potential catalyst to meet the visible-light reaction requirement for photocatalytic applications such as iron oxide which is easily produced in large quantities using standard reaction conditions. Due to its numerous applications in various fields, such as data storage, photocatalysis, biosensors, targeted drug delivery, pigments, magnetic resonance imaging, and catalysis, magnetic iron oxides have recently attracted a great deal of interest from researchers and environmentalists (Palden et al., 2019). The most widely used and promising magnetic minerals for water treatment are α-Fe_2O_3 (hematite), γ-Fe_2O_3 (maghemite), Fe_3O_4 (magnetite), and FeO (wustite) amongst the eight known phases of iron oxides. Hematite iron (III) oxide is found in the phases α-Fe_2O_3, β-Fe_2O_3, γ-Fe_2O_3, and ε-Fe_2O_3, of which the stable forms are α-Fe_2O_3 and γ-Fe_2O_3 (Malika et al., 2017). It has been noted that the separation of electron-hole pairs in iron oxide combined with its high conductivity and appropriate energy band structure can improve the photocatalytic performance of composite photocatalysts (Afkari et al., 2023).

The purpose of this review is to provide a general overview of the integration process of iron oxide with supporting materials as well as the creation of iron heterojunction with other semiconductive materials for emerging pollutants. The primary focus is on the latest advancements in iron oxide integrated photocatalysts' ability to address developing pollutants through photocatalytic activity. In the first section, type, basic properties and various methods to enhance the photocatalytic of iron oxides are discussed. The second section contains various modifications of iron oxide photocatalysts. The modifications of iron oxide photocatalysts with supporting materials and the formation of iron heterojunction with other semiconductive materials are classified and discussed in five subsections: (i) iron oxide Fe_xO_y heterojunction with nobles metal, (ii) iron oxide Fe_xO_y heterojunction with polymer, (iii) iron oxide Fe_xO_y heterojunction with metal oxide, (iv) iron oxide Fe_xO_y heterojunction with carbon material and (v) iron oxide Fe_xO_y (iron rush) heterojunction with other materials.

2. IRON OXIDE AS PHOTOCATALYST

Iron oxide is one of the alternative materials that can be used as a photocatalyst. Iron oxide is a transition metal oxide with various stoichiometric and crystalline structures, including FeO, α-Fe_2O_3, γ-Fe_2O_3 and Fe_3O_4 (Wahyuningsih et al., 2019). Due to the narrow band gap of 2.2 eV, it can be activated by visible light up to 600 nm, has excellent stability, is earth-abundant, recyclability and has been reported to be an important part of visible-light responsive semiconductor photocatalysts (Dai et al., 2019). Nevertheless, the use of iron oxide as a photocatalyst alone has some drawbacks, including poor electrical conductivity and difficulty of isolating photo-induced electrons and holes to stop their rapid recombination (Nasirian et al., 2017). Various methods and techniques have been introduced such as doping, morphology control, co-doping, heterojunction with other materials and surface modification techniques to increase the effective photocatalyst activity (AlSalka et al., 2019).

Thus, iron oxide is the best choice to combine with other nanocomposites to enhance the photocatalytic process. Many studies have shown that modified α-Fe_2O_3 with TiO_2 can greatly boost photocatalytic activity (Li et al., 2015). Moreover, α-Fe_2O_3 makes it a strong prospect for coupling with g-C_3N_4 and enhancing its catalytic activity for the photodegradation of aqueous organic compounds due to the good properties of iron oxide (Paquin et al., 2015). Thus, this review will explain how to improve the photocatalytic activity of emerging pollutants by modification of the iron oxide structure.

3. MODIFICATION OF Fe_xO_y PHOTOCATALYST

Many modifications and alterations of a photocatalyst are reported to be necessary for enhancing its surface and active site and for suppressing charge combination and hence increasing performance. This includes the use of supporting material, as well as the design of a heterojunction of iron oxide with other materials such as metal oxide, noble metal, polymer, and carbon compound and by using recycling and reuse of waste rush iron for degradation of emerging pollutants. The next part explains the details of iron oxide heterojunction with other photocatalyst materials.

3.1. Iron Oxide Fe_xO_y Heterojunction with Nobles Metal

Nanomaterials are becoming increasingly important in many technological fields due to their availability of numerous surface active sites, high surface area, and small size (Mamba & Mishra, 2016). Noble metal nanoparticles, such as platinum (Pt), gold (Au), palladium (Pd), and silver (Ag), significantly enhance photocatalytic activity by acting as cocatalysts, photosensitizers, good visible light absorbers, and electron sinks based on Schottky barriers (Fang et al., 2021). This is possible because of the unique properties of these noble metals (Lopes et al., 2016). Furthermore, it is possible to create nanomaterials that respond to visible light and have a long photogenerated charge carrier lifetime by using noble metals such as Au, Pt and Ag. The structural and chemical stability of these noble metal nanoparticles, on the other hand, is extremely low. This is because the unprotected plasmonic nanoparticles have a high surface energy and are subject to van der Waals forces, which render them susceptible to irreversible aggregation in the reaction medium while the synthesis is taking place (Li & Tang, 2014). Furthermore, if metal oxide such iron oxides are coupled with noble metal, the light absorption range of wide band gap iron oxide can be extended. It has been shown that immobilising noble metal NPs on magnetic Fe_3O_4 support prevents agglomeration and produces highly active composites (Mishra et al., 2019). Nobles metal-metal oxide nanostructures can be classified into five categories based on their geometrical configuration: (1) noble metal/metal oxide core/shell nanostructures; (2) noble metal-decorated metal oxide nanoarrays; (3) noble metal-decorated metal oxide nanoparticles; (4) noble metal–metal oxide nanostructures; and (5) noble metal/metal oxide yolk/shell nanostructures.

Several review articles reported on the NM–MOs, focusing on their synthesis, composition, characteristics, and applications. It is particularly relevant to be able to integrate NMs with MOs since this enables us to understand the interaction between NMs and MOs, which is necessary for obtaining metal–semiconductor heterostructures with the properties that are sought. Moreover, because of their controllable shape and size, flexible surface chemistry, adjustable optical properties, and biological inertness (Liu et al., 2017), Au nanoparticles are widely used as biomedical probes and drug carriers (Ankudze et al., 2018). Au nanorods (GNRs), nanoshells, and nanospheres (AuNPs) are used in laser-induced photothermal therapy (PTT) of cancers because of their favourable photothermal performance (Xing et al., 2018). In addition, because of their high reflexivity and contrast effect, superparamagnetic iron oxide nanoparticles (IONPs, commonly Fe_3O_4 NPs) are often used as contrast agents in magnetic resonance imaging (MRI) (Wang et al., 2018). It is not only the unique properties of AuNP or FeNP that make Au-Fe_3O_4 heterostructures so appealing, but also their complementary function and synergistic effect. For instance, two distinct nanoparticle domains can each be changed for multi-anchoring functionalization, enhancing the catalytic activity and thermal performance of the Au-Fe_3O_4 heterostructures (Kang et al., 2018). Biogenic Fe_3O_4/Au nanocomposites were tested for photocatalytic activity using an organic dye and two pharmaceutical substances. According to the Mirsadeghi et al. (2020) conducted an adsorption experiment on nanocomposite materials in the dark before UV–visible light irradiation to determine their adsorption efficiency. This proves that, under UV–visible light irradiation for 120 minutes, the photocatalytic activity of Fe_3O_4/Au nanocomposite to degrade contaminations was observed of pharmaceutical waste and dyes. Fe_3O_4/Au nanocomposite degraded methyl orange, imipenem, and imatinib (pharmaceutical waste) to a maximum degradation rate of 99 percent after 1800 s, 96 % after 1200 s, and 92% after 1200 s, respectively, under UV radiation, and 84% and 82% after 3600 seconds under visible radiation, for imipenem and imatinib, respectively, according to the study (Mirsadeghi et al., 2020). Increasing the surface area of Au-Fe_3O_4 heterostructures enhances AuNP and Fe_3O_4 catalytic activity. Combining these two heterostructures provides an excellent "all-in-one" system that includes enhanced catalytic activity, multimodal imaging, and combination therapy (Liu et al., 2018).

3.2. Iron Oxide Fe_xO_y Heterojunction with Polymer

Extensive research has been conducted on polymeric materials due to their remarkable properties, including durability, mechanical stability, large surface area, and stability (Riaz et al., 2015). By combining polymeric materials with iron oxide, researchers have achieved desirable properties, such as enhanced UV and sunlight performance and reduced pollutant levels in photodegradation during the photocatalytic process. In addition to being efficient electron donors and good hole transporters, polymeric materials are also good conductors when exposed to visible light. Compared to pure polymer and iron oxide, polymer heterostructure with iron oxide showed a higher photocatalytic activity, most likely due to a more efficient charge carrier separation due to the synergistic role of both catalysts (Tran et al., 2021). Non-metallic semiconducting materials have similar efficiencies to metal oxide photocatalysts because of their low material costs and a similar range of light absorption (Reddy et al., 2019). In addition to synthetic photosynthesis, polymeric graphitic carbon nitride g-C_3N_4 has been extensively studied for environmental remediation, such as wastewater treatment, and degradation of emerging pollutants.

In addition, it possesses an anisotropic nanosheet structure, allowing it to direct charge transfer in the in-plane direction, increasing photocatalytic activity, and speeding up the separation of photogenerated electrons and holes (Ma et al., 2020). Recently, g-C_3N_4 in combination with iron oxide is effective in the degradation of rhodamine B g-C_3N_4/ Fe_2O_3. Moreover, developed g-C_3N_4/Fe_2O_3 photocatalyst using large-scale g-C_3N_4 nanosheets synthesized by calcining guanidine hydrochloride found that the heterojunction materials performed well and improved the photocatalytic activity in 4-NP(4-nitrophenol) degradation. Iron oxide was impregnated with porous polymeric graphitic carbon nitrides, a method known as in wet impregnation. Furthermore, Lin et al. (2017) in Figure 1 shows the photodegradation of 4-NP(4-nitrophenol) in the solution conducted in a quartz reactor under visible-light irradiation, using a 400-nm cutoff filter and a 300-W Xe lamp. After 40 minutes under visible light irradiation, it was found that 0.5 wt% of g-C_3N_4/ Fe_2O_3 was the most effective for the photocatalytic degradation with 90% degradation of 4-NP(4-nitrophenol) in the presence of H_2O_2 at pH 3.5. The excellent photocatalytic performance of heterojunction g-C_3N_4/Fe_2O_3 was attributed to its unique two- dimensional layered structure, easy separation of photogenerated charge carriers and high surface oxygen adsorbed species concentration.

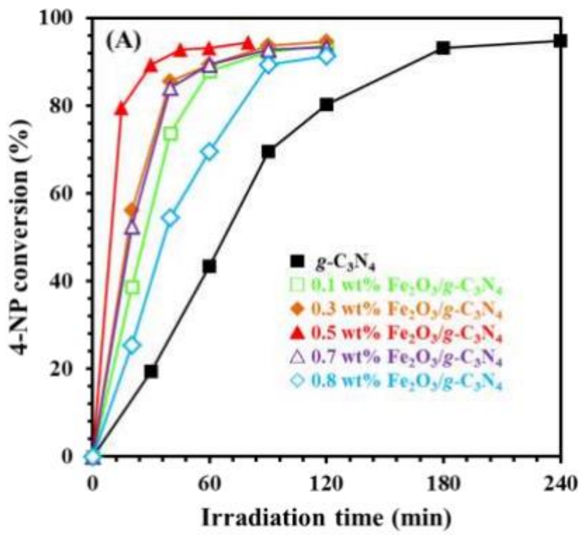

Figure 1. Degradation efficiency for the degradation of 4-NP (Lin et al., 2017).

3.3. Iron Oxide Fe_xO_y Heterojunction with Metal Oxide

Fe_2O_3 was utilised in the photodegradation of a wide variety of dyes and organic pollutants due to its superior performance as a photocatalyst. Under the influence of visible light and UVA irradiation, TiO_2 NPs caused microalgal cells to experience oxidative stress due to producing reactive oxygen species (ROS) (Baniamerian et al., 2020). Its photocatalytic efficacy was further enhanced by incorporating a Fe_2O_3 with a narrower band gap, which was used to construct an effective heterojunction (Ren et al., 2019). The incorporation of Fe_2O_3 into the TiO_2 structure results in the introduction of new levels within the band gap of TiO_2 and results in an increase in the light absorption wavelength. This results in more effective utilisation of visible light, or solar irradiation, for practical application (Demirel et al., 2018). This heterojunction catalyst TiO_2 nanoparticles with 2.5% w/w Fe_2O_3 by ultrasonic-assisted co-precipitation method was used in photodegradation of *Chlorella vulgaris* for freshwater, seawater and artificial seawater. Moreover, it was recorded that the remarkable performance of the Fe_2O_3 - TiO_2 heterojunction could be attributable to the narrow band gap, which allowed prolonged usage of visible light. They found that the heterojunction of photocatalyst TiO_2 nanoparticles with 2.5% w/w Fe_2O_3 effectively reduced the viability of green microalgae *Chlorella vulgaris* in freshwater and seawater when exposed to visible light irradiation. This was the plausible conclusion they drew from their research. After 24 hours of exposure to the photocatalyst at a concentration of 0.25 g/L in visible light at 55 W/m^2, a clearance of up to 99% of the algae was observed (Baniamerian et al., 2020).

Additionally, according to the Ren et al. (2019), tetracycline's photocatalytic degradation rate can reach 99.3% in 50 minutes by heterostructure of $\gamma Fe2O3$/b-TiO_2 , which is much higher than the degradation rate of αFe_2O_3- TiO_2 heterojunctions. In addition, this is due to the narrow bandgap of γFe_2O_3/b-TiO_2 heterojunctions, which extends photo response to visible light and near infrared regions, and the disordered layer caused by self-doping of Ti^{3+}, which promotes the separation of the photogenerated electron hole pairs and accelerates the e-catalytic reaction rate. In another study, a heterostructure of Ag_2O/Fe_2O_3heterojunction degraded RhB (Rhodamine B) by almost 85.3%, exhibit higher activity than pure Fe_2O_3 and a strong *p-n* heterojunction between Ag_2O and Fe_2O_3 could significantly enhance the photocatalytic activity, based on this information (Li et al., 2017).

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3.4. Iron Oxide Fe_xO_y Heterojunction with Carbon Material

Carbon material catalysts made from activated carbon, graphene, carbon nanotubes and carbon quantum dots have attracted much attention as a new-fire strategy for transferring photoinduced charge carriers and increasing its functioning period during the photocatalytic activity, according to a study recently published by Mohd Adnan et al. (2019). Due to their chemical stability, large surface area, and high electron conductivity, carbon nanotubes (CNTs) are considered as intelligent supports for photocatalysts. Moreover, CNTs have improved photocatalytic performance through their excellent electron transport capability and increased separation rate of charge carriers (Bellamkonda et al., 2019). The surface of nanotubes must be connected to nanostructure materials or other functional groups to optimise their maneuvering in different applications. In photocatalytic applications, hematite (or α Fe_2O_3) has a narrow band gap of about 2.0–2.2 eV. Other than that, hematite is a potential photoanode material for photodegradation of pollutant due to the band gap value of αFe_2O_3 (2.1 eV) and its valence band (VB) edge is substantially lower than the water oxidation potential. Many approaches have been used to control the αFe_2O_3 anomalies, including developing nanostructures based on carbon to lower the recombination rate, boosting conductivity by doping the proper metals and enhancing charge transfer efficiency (Li et al., 2022). The defect sites and oxygen-containing functional groups of carbon nanotubes (CNTs) in the carbon nanotube αFe_2O_3 (CNTs/ αFe_2O_3) heterostructure can significantly increase the interface charge separation efficiency and prevent -Fe2O3 aggregation (Xu et al., 2021).

Furthermore, the CNTs/ $\alpha-Fe_2O_3$ has better photocurrent and hole–electron separation rates, and the narrower band gap has been measured to be 2.8 eV with high visible-light absorption performance. All of these benefits can be attributed to the fact that the band gap has been narrowed. Compared to αFe_2O_3, the CNT/ αFe_2O_3 nanohybrid with 50% mesoporous CNTs demonstrated the highest photocatalytic efficiency (Ismail et al., 2019). The photodegradation process of carbon nanotube heterostructure with αFe_2O_3 was demonstrated by the degradation of RhB when subjected to irradiation from a 500 W spherical Xenon lamp (Zhao et al., 2015). In another case, almost 80% degradation of RhB (Rhodamine B), 58% for MB (Methylene Blue), 38% for phenol, 30% for MO(Methyl Orange) and 17% for CR(Congo Red) has been recorded with heterostructure of αFe_2O_3/ CNTs composites (Xu et al., 2021). Furthermore, Figure 2 shows that 50%CNT-$\alpha-Fe_2O_3$ demonstrates reusability up to 5 sequences times of photocatalytic oxidation of BBR (Bismarck Brown R) dye (Ismail et al., 2019).

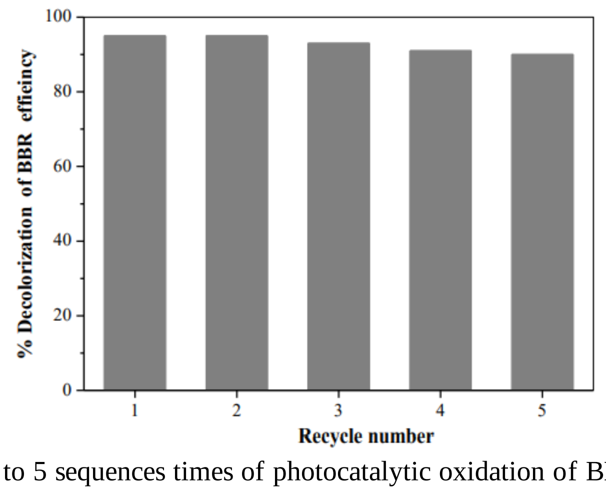

Figure 2. Reusability up to 5 sequences times of photocatalytic oxidation of BBR dye (Ismail et al., 2019)

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3.5. Iron Oxide Fe_xO_y (Iron Rush) Heterojunction with Other Materials

Corrosion happens when iron comes into contact with moisture in the atmosphere. Iron corrosion is a lengthy and intricate process influenced by humidity, pH, and pollution (Malel & Shalev, 2013). Hence, numerous anti-corrosion techniques have been developed to safeguard iron components in potentially corrosive settings (Leppaniemi et al., 2018). However, these methods do not completely terminate the corrosion, causing rust to form at a slower rate. Babar et al. (2018) found out that, few studies have been conducted on recycling and refurbishing waste iron rust into potentially useful Fe_2O_3 NPs. Concurrently, it is possible to combine magnetite iron oxide Fe_2O_3, (n-type) with g-C_3N_4, (n-type), and thus form a heterojunction of iron oxide Fe_2O_3, (n type) from waste rust, and g-C_3N_4. This can improve photocatalytic performance, as well as facilitate magnetic separation of the catalyst under an external magnetic field (Peng et al., 2017).

To date, there have been no reports on the use of waste iron rust to synthesise Fe_2O_3 nanoparticles and their coupling with g-C_3N_4 for photocatalysis applications, which would simultaneously address waste management and water contamination. Under sunlight irradiation, the photocatalytic performance of the g-C_3N_4 - Fe_2O_3 composite derived from rust was evaluated for degradation of methyl orange (MO) and textile effluent (TE). A simple grinding and calcination method to convert waste iron rust into Fe_2O_3 nanoparticles for the synthesis of magnetically separable g-C_3N_4 - Fe_2O_3 composite photocatalyst. Under natural sunlight, this study demonstrated for the first time that rust-derived of Fe_2O_3 nanoparticles could be used to combine with g-C_3N_4 - Fe_2O_3 composite for the photodegradation of MO and TE as a model pollutant. Owing to its high photodegradation efficiency, the g-C_3N_4 - Fe_2O_3 composite exhibits outperforms of photodegradation efficiency which is (TE=98% and MO = 99%) compared to pure g-C_3N_4 (TE = 43 % and MO = 44 %) and Fe_2O_3 (TE = 13% and MO = 7) (Babar et al., 2018). The researchers confirmed that, the high absorption of visible light, synergistic effect, and well-established heterojunction between the g-C_3N_4 and Fe_2O_3 were responsible for the amplified photodegradation efficiency.

Waste black toner ink (black ink) for fabrication of doped nano-carbons could also be a better option in this condition (Figure 3). The widespread availability of toner ink is a key factor in its popularity. According to the Jujun et al. (2013), nano-particle polymers containing iron, copper, silicon and manganese oxides are now used in toner ink. An environmentally friendly method for fabricating self-doped iron oxide nanocarbons from residual waste ink is described in the paper. It highlighted that toxic azo dye Congo Red was degraded using functionalized iron oxide nanocarbons (f-FeO-NC). Nonbiodegradable Azo dyes containing the azo groups (-N=N) have a wide range of adverse effects on aquatic life and humans. Waste black toner ink from printer is collected and then carbonised at 600 °C in muffle furnace. To make f-FeO-NC, the iron oxide was further oxidised with nitric acid. For the photocatalytic application of toxic organic azo-dye as Congo red, the f-FeO-NC were used under natural sunlight illumination. As a photocatalytic material, waste black toner ink showed a high rate of photocatalytic activity towards Congo Red degradation, and its availability, stability, and reusability made this pollutant f-FeO-NC a reassuring alternative material.

This is proven from the photocatalytic activity where under 150 minutes of sunlight exposure, the photocatalytic activity of f-FeO-NC is 99 %, compared to 15 % when in the dark (Saini et al., 2019).

Figure 3. Diagram illustrating the separation of the functionalized version (f-FeO-NC) from the control (waste black toner ink) and its application to the degradation of the poisonous Congo red dye in the presence of natural sunlight (Saini et al., 2019).

4. CONCLUSION

Recent research on the use of iron oxide for photocatalytic degradation of emerging contaminants is summarised in this review article. Iron oxide is modified by adding support materials, forming heterojunctions by combining it with other photocatalysts such as noble metal, metal oxide, polymer, carbon material and the iron rust from waste product were rigorously discussed. For a typical heterojunction to be successful, it is important to choose a photocatalyst with a suitable band gap that can be coupled with iron oxide. Their improved visible light harvesting suggests a favourable design of both heterojunctions due to changed band gap, reduced charge recombination, and more effective charge carrier separations to increase photocatalytic activity in destroying emerging contaminants. Furthermore, in the studies listed above, the majority of researchers focused on the utilisation of iron oxide for photocatalytic degradation of dyes, rather than emerging contaminants. Photocatalytic removal of developing contaminants such as pesticides, pharmaceuticals waste, insecticides, solvents, organic compounds and the removal of microorganisms should be examined with this flexible photocatalyst.

In the future, the water and wastewater treatment systems may benefit more from the integration of iron oxide photocatalyst with supporting materials and the creation of iron heterojunction with other semiconductive materials. Reusing the photocatalysts could potentially mitigate their high cost, when viewed from an economic standpoint. In this context, the magnetism of various iron-based materials integrated in core-shell structures is advantageous. With a magnetic core that facilitates simple particle separation and a shell that offers the required functionality, the resulting hybrid materials are unique. It is possible to escalate the activity of iron-based materials and reduce the well-known photocorrosion caused by them when combined with other photocatalysts.

Conflict of Interest
The authors declare no conflicts of interest.

Author Contribution Statement
Muhammad Shaiful Aidil Mohd Syafaruddin: Conceptualization, Writing – Original Draft. Mohamad Saufi Rosmi: Writing – Reviewing and Editing. Siti Munirah Sidik: Investigation, Writing – Review and Editing. Ong Suu Wan: Investigation, Formal Analysis. Mohamad Azuwa Mohamed:

Investigation, Writing – Review and Editing. Suriani Abu Bakar: Formal Analysis. Lulu'atul Hamidatu Ulya: Investigation.

Data Availability Statement
The authors confirm that the data supporting the findings of this study are available within the article.

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