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REVIEW ARTICLE

Spinel ferrite nanoparticles as potential materials in chlorophenol removal from wastewater

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Abstract

Persistent organic pollutants (POPs) including chlorophenols (CPs) are increasing in water effluents, creating serious problems for both aquatic and terrestrial lives. Several research attempts have considered the removal of CPs by functionalised nanomaterials as adsorbents and catalysts. Besides the unique crystal structure, spinel ferrite nanomaterials (SFNs) own interesting optical and magnetic properties that give them the potential to be utilised in the removal of different types of CPs. In this review, we highlighted the recent research work that focused on the application of SFNs in the removal of different CP substances based on the number of chlorine atom attached to the phenolic compound. We have also discussed the structure and properties of SFN along with their numerous characterisation tools. We demonstrated the importance of identifying the structure, surface area, porosity, optical properties, etc. in the efficiency of the SFN during the CP removal process. The reviewed research efforts applied photocatalysis, wet peroxide oxidation (WPO), persulfate activated oxidation and adsorption. The studies presented different paths of enhancing the SFN ability to remove the CPs including doping (ion substitution), oxide composite structure and polymer composite structure. Experimental parameters such as temperature, dosage of CPs and SFN structure have shown to have a major effect in the CP removal efficiency. More attention is needed to investigate the different properties of SFN that can be tailored through different techniques and expected to have major role in the removal mechanism of CPs.

Keywords Spinel ferrites · Chlorophenols · Hazardous impacts · Photocatalysis · Degradation · Oxidation · Adsorption

Introduction

The scarcity of water resources that coeval with water pollution emerged as a crisis threatening environmental ecosystems and human health (Alexandratos et al. 2019)(Mir et al. 2022).

Along with the excessive industrial activities worldwide, water effluents become highly polluted with different types of organic and inorganic substances. Inorganic pollutants are mainly heavy metals ions such as lead, cadmium, chromium, copper and arsenic and also acids. In the other hand, most of organic pollutants that found in water are called persistent organic pollutants (POPs) that are extremely stable and resistant to degradation in nature (Nair and Kurian 2017b). Their molecules are easily transporting through water and air and tend to accumulate in fatty tissue, creating a serious intimidation to quality of life in Earth (Fei et al. 2022). POPs are related to significant health disorders including hypersensitivity, allergies, cancers and disease of endocrine, immune, reproductive, central and peripheral nervous systems (Sahoo and Prelot 2020) (Wang and Zhang 2020) (Mota et al. 2021). They are also causing abnormalities in land and sea wildlife species (Zhao et al. 2019) (Tkaczyk et al. 2020). POPs include organochlorine pesticides (OCPs) (Bersuder et al. 2020), polychlorinated biphenyls (PCBs) (Castiglioni et al. 2022) and polybrominated diphenyl ethers (PBDEs) (Rodriguez-Narvaez

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et al. 2019). The existence of a conventional water remediation tool of POPs is still a challenging issue; hence, researchers are investigating different and efficient pathways to eliminate POPs. The functionalisation of nanomaterials (NMs) adsorbents and catalysts is one of the main potential and highly effective pathways (Fei et al. 2022).

NMs are grabbing a great interest of researchers around the world due to their small size (1 to 100 nm), high surface area and enhanced mechanical, optical and magnetic properties which make them more effective in several reactions and applications (Villaseñor and Ríos 2018). Most materials are powerful and efficacious in their nanoscale as metal oxides (Huang et al. 2020), iron oxides (Shah et al. 2021), graphene oxides (Lim et al. 2020) and carbon-based compounds (Z. Duan et al. 2020). Therefore, they are applied widely in medical applications such as controlled drug delivery (Hareendran et al. 2022) and diagnostic tools (Khizar et al. 2020). NMs are also functionalised effectively in energy harvesting (Bandala and Berli 2019), environmental sensing (Afzal et al. 2020) and water treatment applications (Chakhtouna et al. 2021).

Among NMs, spinel ferrites nanoparticles (SFNs) raised as promising and efficient oxides due to their low cost, low toxicity, easy and various synthesis methods. SFNs can be produced in different sizes and morphologies (Kefeni and Mamba 2020; Rashdan and Hazeem 2020; Y. jia Sun et al. 2017). They are well-known because of their improved mechanical structure (Manasa et al. 2018), high stability (Swathi et al. 2021), magnetic behaviour (Kmita et al. 2021) and optical responsiveness (Jyothish and Jacob 2021). Accordingly, SFNs have shown great effects in different applications and in particular the removal of different pollutants from wastewater (Nambikkattu et al. 2020; Tatarchuk et al. 2020b; Vinosha et al. 2022; Xiang et al. 2020; You et al. 2021). Recent research work considered SFNs, doped SFNs and SFN composites in the removal of heavy metals and organic pollutants through adsorption and oxidative photocatalytic processes. Adsorption process depends on the surface interaction between the adsorbent and the pollutant due to possible physical and chemical sorption (Tatarchuk et al. 2021b). Differently, oxidation process involved a series of chemical reactions caused by the electrons and holes that produced when the SFN atoms are excited. These chemical series depend on the generation of different radicals, called reactive oxygen species (ROS), in the aqueous solution that can degrade the organic compounds into less harmful molecules (Ariza-Tarazona et al. 2020). For instance, $ZnFe_2O_4$ nanoparticles has been applied efficiently in the degradation of methylene orange and methylene blue organic dyes under visible irradiation in seawater (Al-Najar et al. 2022) while Mg-doped $ZnFe_2O_4$ were applied to adsorb Cr^{+6} and Ni^{2+} ions from wastewater samples with maximum adsorption capacity of 30.49 g/mg (Tatarchuk et al. 2021a). $NiFe_2O_4$, $CoFe_2O_4$ and $MnFe_2O_4$ nanoparticles were also used for successful adsorptive removal of Cr^{+6}, Pb^{2+}, Cd^{2+} and Zn^{2+} from wastewater (Asadi et al. 2020; Khoso et al. 2021). In addition, polymer @ SFN composites are functionalised as heterogenous structures that provide higher surface area and more electron-hole yield that assist the oxidation process. Nickle-zinc spinel ferrite linked to graphene oxides was recently applied as visible light driven photocatalyst (Javed et al. 2019) as well as zinc-cobalt ferrite and silver halide composite (Chnadel et al. 2020). Moreover, SFNs have shown great effect in degradation and adsorption of other complex chemical structures such as antibiotics (Chakhtouna et al. 2021; Y. Xiang et al. 2020) and phenolic compounds (Camacho-González et al. 2019; Othman et al. 2019). Recently, some research work investigated the effect of SFNs and their composites on the removal of chlorinated phenolic compounds, chlorophenols (CPs), which are very stable POPs. The potential of applying SFNs in removing such persistent molecules is not only because of their outstanding outcome in water remediation process, it is because of the uniqueness of the SFNs' structure that can be easily optimised to meet the efficiency, economic and environmental considerations of the process.

In this review, we present SFNs as one of the sustainable and environmental materials that can be utilised efficiently in water remediation applications. We shall discuss the unique structure and controllable properties of the SFNs and the different experimental aspects affecting their efficiency in the removal of CPs from aqueous solutions.

Chlorophenols

Chlorophenols (CPs) are one of the significant classes of POPs that have been used widely in different industrial products including paper, textiles, pesticides, pharmaceuticals and dyes (Garba et al. 2019). They are formed by adding chlorine atoms to the phenol structure. There are 19 possible combinations that settle the chlorine atoms within the phenol structure depending on the number and the position of attached chlorine atoms. Figure 1 shows some examples of the possible CPs' structure. All of these types are considered dangerous and toxic as they are related to several health and environmental risks (X. Duan et al. 2019) and they are found in air (Kayan et al. 2021), surface water (Gallego et al. 2018), ground water, soil, urine (Kallawar et al. 2021) and in animals' bodies (Zada et al. 2021). As per the US Environmental Protection Agency and WHO, the amount of CPs must be lower than 0.5 µg/L in drinking water and 100 µg/L in industrial wastewater (Abu-Alsoud and Bottaro 2021). The toxicity of CPs is affected by the temperature (higher temperature increase inhale process), pH (increase in low pH) and sunlight which makes them occur in variable forms in nature (Zada et al. 2021).

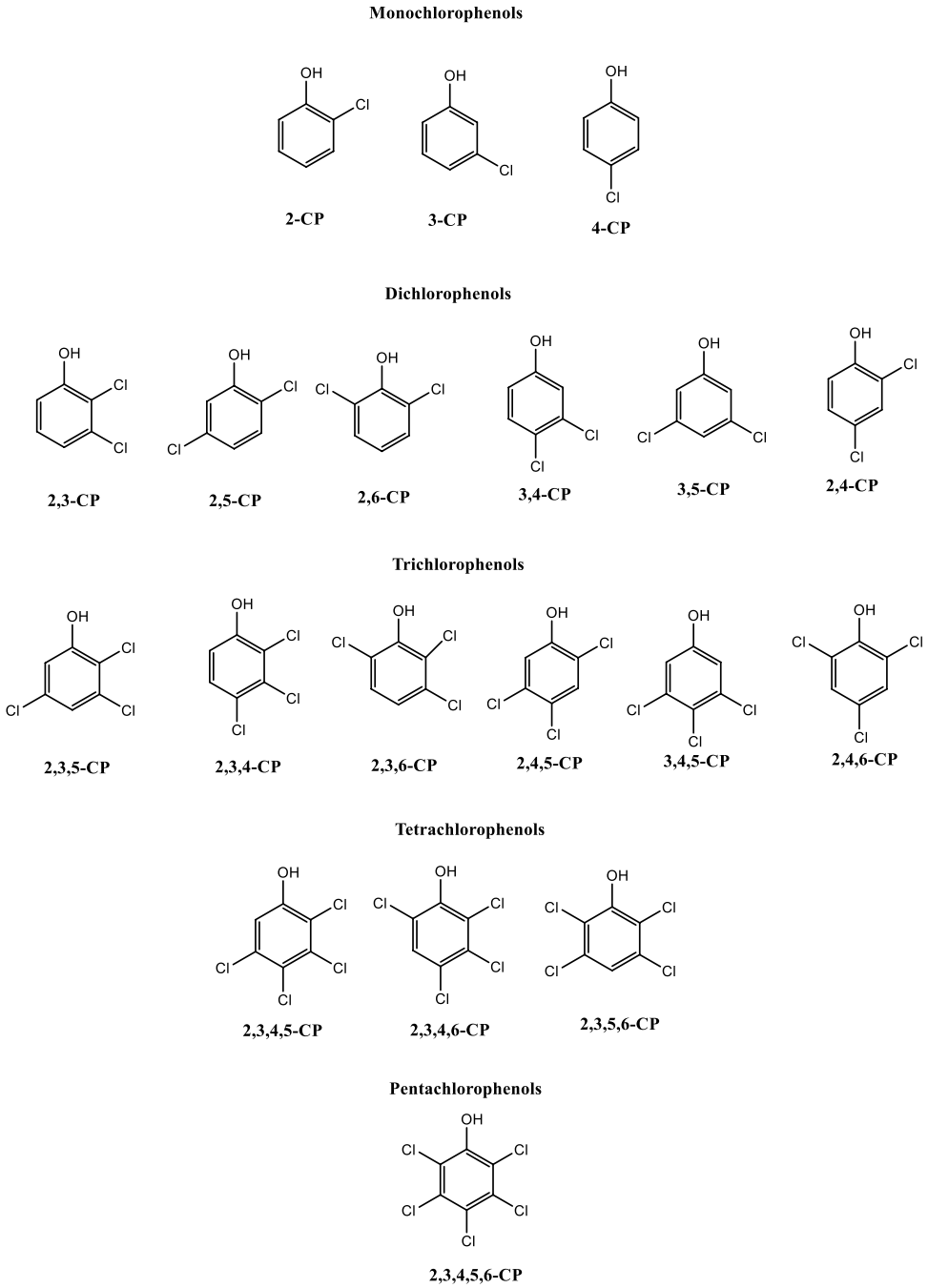

Fig. 1 Examples of some CP compounds

Furthermore, CPs such as 2,4-dichlorophenol are highly transportable and persistent in water, and it is very difficult to be degraded due to its chemical stability. Reports considered them to be carcinogenic and endocrine-disrupting chemicals. They can get through food chain, causing serious harms to human health, animals and other species (Nair and Kurian 2017a). Reports also confirmed that CPs can cause serious damage to the human nervous system (Choi et al. 2019) and to the gene expression and pancreas of zebra fish embryos (Wilson et al. 2023). Most of CPs are found in water as a result of diffused pesticides; however, some CP compounds such as tris(4-chlorophenyl) methanol (TCPMOH) are found in water without a certain source which makes them very dangerous, and applying more toxicity assays is essential. Traces of TCPMOH have been found in human breast milk, which creates a great risk for developing infants (Navarrete et al. 2021). Therefore, researchers are investigating different ways of removing these hazardous compounds from different mediums.

Specifying aqueous medium, there are several techniques that applied to remediate wastewater from CPs including

adsorption (Garba et al. 2019; Rangabhashiyam et al. 2022; Rezaei et al. 2021), filtration (Kim et al. 2022; Kotlhao et al. 2019), coagulation (Matin et al. 2020) and oxidation (Choi et al. 2019; Jiang et al. 2022; Kavitha et al. 2021; W. Li et al. 2021; Soltani and Lee 2017). Adsorption and oxidation are mainly governed by functional materials that attach with the pollutants or host the oxidation process on their surfaces. In the following section, we will discuss the structure and properties of SFNs that make them good candidates for CPs' removal applications.

Spinel ferrites: structure and properties

The spinel ferrite structure has a formula of MFe_2O_4, (M = Co, Ni, Mn, Mg, Cu and Zn) and a face-centred cubic (fcc) crystal where oxygen and other metal ions are positioned in tetrahedral (A) and octahedral (B) sites, as shown in Fig. 2. In a single ferrite unit cell, there are a total of 64 A sites and 32 B sites, while the cations only occupy 8 and 16 position respectively. Thus, the positions of metals within the A and B sites of the ferrite structure own different affinities depending on crystal size, energy levels and even the synthesis route (Aisida et al. 2020a; Al Maashani et al. 2020; Bhushan Das et al. 2021) The cation distribution of the divalent and trivalent ions in a few representative spinel ferrites is shown in Table 1.

SFNs are well-known for the variety, easiness and low cost of their synthesis routes. They can be synthesised through different chemical routes including co-precipitation, sol-gel, microemulsion, solvo(hydro)thermal method and template method template. Physical routes such as microwave assisted and mechanical milling were also applied (Soufi et al. 2021). Applying different routes led to different size and shapes of SFNs including spheres (Yong Lee et al. 2022), rods (Sarac 2020), tubes (Maleki et al. 2019), think films (Soe et al. 2020) and flowers (Sanna Angotzi et al. 2020). The hierarchal structure of the $ZnFe_2O_4$ composite has also shown to improve its photocatalysis efficiency (Gu et al. 2020). Also, $NiFe_2O_4$ flower-like 3D design grains were synthesised through facile hydrothermal approach (B. Xiang et al. 2017), providing a great surface area that allows high adsorption for water pollutants. Budhiraja et al. (2019) have reported a strategy to synthesise different shapes

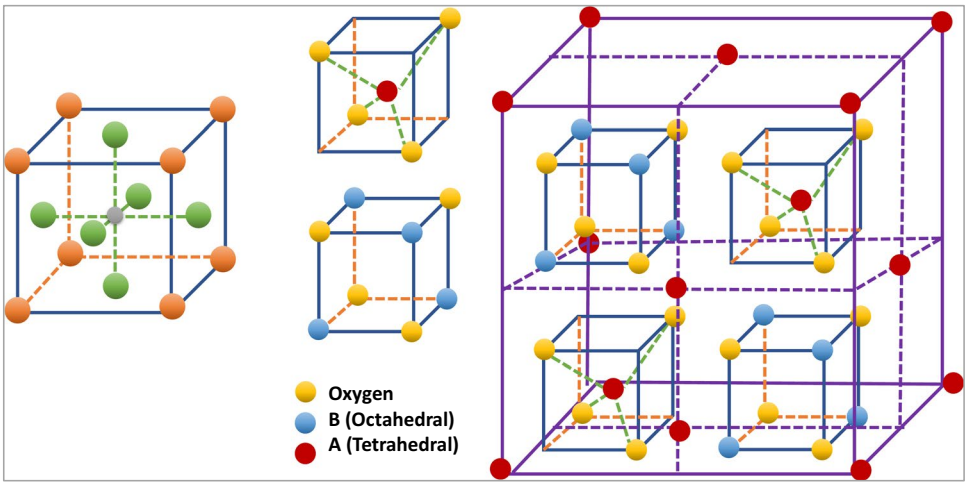

Fig. 2 Crystal structure of spinel ferrites, the diagram reproduced from Hwang et al. (2020)

Table 1 Structural cation distribution in different types of spinel ferrites

Spinel ferrite	Cation distribution		Spinel structure
	Tetrahedral sites (A)	Octahedral sites (B)	
$CdFe_2O_4$	Cd^{2+}	$Fe^{3+} + Fe^{3+}$	Normal
$ZnFe_2O_4$	Zn^{2+}	$Fe^{3+} + Fe^{3+}$	Normal
$MgFe_2O_4$	Mg^{2+}	$Fe^{3+} + Mg^{2+}$	Inverse
$NiFe_2O_4$	Ni^{2+}	$Fe^{3+} + Ni^{2+}$	Inverse
$CoFe_2O_4$	Co^{2+}	$Fe^{3+} + Co^{2+}$	Inverse
	$(Co^{x}Fe^{1-x})$	$(Co^{1-x}Fe^{1+x})$	Mixed
$CuFe_2O_4$	Cu^{2+}	$Fe^{3+} + Cu^{2+}$	Inverse
Fe_3O_4	Fe^{3+}	$Fe^{2+} + Fe^{3+}$	Inverse
$(Mn_{0.8}Fe_{0.2}$ $(Mn_{0.2}Fe_{1.8}O_4))$	$Mn_{0.8}Fe_{0.2}$	$Mn_{0.2}Fe_{1.8}O_4$	Mixed

of $ZnFe_2O_4$ whereas spheres, rods and flowers were successfully synthesised by applying certain chemical routes. Consequently, this results varies the morphology, band properties, surface area and also magnetic properties of the $ZnFe_2O_4$ structure (Budhiraja et al. 2019).

Furthermore, the size of SFNs showed to be sensitive to the synthesis route and its parameter conditions. As size is a very critical factor within the nonorange, researchers have been investigating the effect of the synthesis parameters of the SFNs on their size, along with their shape. For instance, the annealing temperature has a direct impact on the crystal growth and hence the grain size of the ferrite structure. As the annealing temperature increases, the SFN crystal grows, causing different cation locations within the unique cubic structure and accordingly affecting their magnetic and optical properties (Al-Najar et al. 2022; Amir et al. 2018). Moreover, other factors such as pH tuning and ammonia addition caused considerable variation in the SFNs' grain size that led to different magnetisation and absorption values (Ait Kerroum et al. 2019; Al-Najar et al. 2016).

When the size of SFNs is varied, exchange interaction occurs between the valence electrons of cations located at A and B sites. Consequently, the cation composition and their distributions over A and B sites influence the optical, electrical, mechanical and magnetic properties of the spinel (Algarou et al. 2020; Fayazzadeh et al. 2020; Rahman et al. 2021; Soufi et al. 2021; Xie et al. 2021) Therefore, SFNs own unique structure and controllable properties that have been utilised in wide range of applications including medicine (Somvanshi et al. 2020)(Bououdina et al. 2019), environment (Taqvi et al. 2022) and industry (B. Verma and Balomajumder 2020b).

Considering environmental applications, SFNs were applied widely in sensors (Akhlaghi and Najafpour-Darzi 2021) (Wu et al. 2019a) and wastewater remediation from different pollutants (Mmelesi et al. 2021). Highlighting the water pollution issue, recent research work has shown a great involvement of SFNs in the removal of different pollutants. SFNs own high surface area, high stability and good optical properties which makes them suitable candidates for adsorption (Tatarchuk et al. 2021b) (Niu et al. 2020) (Narayana et al. 2021) and oxidation processes (Kefeni and Mamba 2020)(Ismael 2021)(Park et al. 2019). (Soufi et al. 2021). SFNs can be utilised as enhanced pure phase structure (Swathi et al. 2021) or as a part of composite which involves metal oxides (Tatarchuk et al. 2020a), graphene oxides (Park et al. 2019), carbon nanotubes (B. Verma and Balomajumder 2020a), biochars (Xiang et al. 2021) and polymers (Aisida et al. 2020b).

For instance, pure $ZnFe_2O_4$ was applied to degrade dyes under harsh environmental conditions by the aid of solar irradiation (Al-Najar et al. 2022). Also, green synthesised $CoFe_2O_4$ and $ZnFe_2O_4$ were used to degrade bisphenol under sunlight (Rani and Shanker 2020). $MgFe_2O_4$ nanoparticles were used as efficient adsorbent for Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} metal ions (Ivanets et al. 2021a). Moreover, $CoFe_2O_4$@TiO_2 nanoparticles were successfully applied to adsorb Congo red dye (Tatarchuk et al. 2020a). In addition, graphene oxide-based $NiFe_2O_4$ (Narayana et al. 2021) and $MnFe_2O_4$ (M. Verma et al. 2020) showed great ability to adsorb Pb(II) ions. Based on these vast applications on organic and inorganic pollutants removal, SFN has raised as a potential structure to eliminate more persistent pollutants such as CPs.

As mentioned before, SFNs are good candidates for photocatalysis applications. Photocatalysis is a physiochemical process that depends on semiconductor materials to initiate a series of chemical reactions that cause degradation of POPs. As shown in Fig. 3, the semiconductor atoms consisted of optical energy gap (E_g) that exists between the conduction band (CB) and valance band (VB). The amount of the E_g controls the absorption properties of the material, as the absorbed radiation should be more or equal to the energy gap of the material. When the radiation is absorbed, the electrons will be excited from VB to CB, as shown in Fig. 3, leaving holes (h+) in the CB while the VB will contain the electrons. The flow of these electrons and the abundancy of holes are considered as the trigger of the oxidation process within the water molecules that eventually causes different possible reactions that led to pollutant degradation.

The efficiency of the photocatalysis process in removing pollutants depends on the amount of energy absorbed by the material as well as the number of electrons and holes generated. The recombination between the electrons and holes is the main cause of the photocatalysis suppression. Therefore, different approaches are applied to tune the energy levels within the materials to make them absorb the desired radiation as well as maintain the abundancy electron-hole pairs.

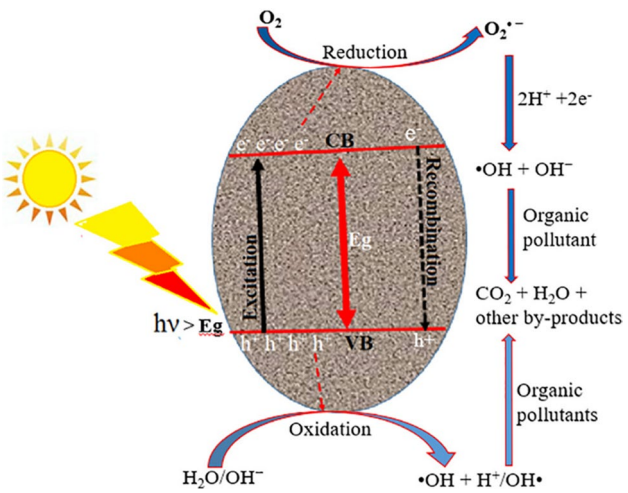

Fig. 3 Photocatalysis mechanism by SFN structure (Kefeni and Mamba 2020)

Considering the case of SFN, their relatively narrow energy gap can absorb larger irradiation spectrum including visible light. Figure 4 shows the optical band gaps of SFNs and other different semiconductors that can be functionalised efficiently in photocatalysis applications. Among them, TiO_2 emerged as one of the most effective and widely use photocatalysis. We can notice here that it owns the largest bandgap of around 3.2 eV which means that electrons in its atoms can be excited from the CB to the VB with an amount of energy larger than 3.2 eV which corresponds to the UV region (3 to 124 eV). Therefore, TiO_2 shows outstanding photocatalysis performance under UV irradiation.

It is very important to note that the energy of electrons coming out from this reaction will carry at least 3.2 eV, which is the minimum excitation energy of TiO_2. This gives the TiO_2 good ability to degrade organic compounds as the dissociation energies of most organic compounds are in the range of 1 to 2 eV (Khatymov et al. 2003; Vannatta et al. 2020). However, solar light cannot be applied efficiently to activate TiO_2 nanoparticles. This is because most of solar spectrum lay in the visible light range with wavelength of (0.4–0.7 µm, corresponding to energy range of 2–2.75 eV). Hence, it is difficult to activate the TiO_2 bandgap through solar spectrum. With the recent consideration of energy efficiency and utilizing renewable energy, SFN ferrites become good candidates for solar photocatalysis as they own smaller bandgap than TiO_2. As shown in Fig. 3, $CaFe_2O_4$, $MgFe_2O_4$ and $ZnFe_2O_4$ own band gaps of 1.9, 2.18 and 1.92 eV respectively. Such a small bandgap can be excited by lower energy visible light as well as UV. This gives them the privilege of conducting more sustainable water remediation process. However, the small band gaps allow faster recombination between holes and electrons and hence; efforts are made to tune the energy levels within the ferrites to create a slower path for electrons to re-join with holes. This is mainly done through metals defects (doping), self-defects (lattice vacancies) and creating heterogenous structure (composite) (Huang et al. 2020; Sahel et al. 2016; A. Sarkar and Khan 2019; Serpone 2018).

Generally, other factors such as SFN size, surface area, porosity and surface charge affect the removal ability (Ivanets et al. 2021b). The optimisation of all these factors is necessary to approach the optimum removal to certain pollutants. For the removal of CP substances from water, higher energy is required to overcome the persistent bonds in the CP molecules; hence, most conducted research considered doping to tune the SFN lattice. Moreover, additional factors were introduced to enhance the catalytic process such as oxidation substances and applying heat.

Characterisation of SFNs is very essential to choose the optimum sample for the application and to explain the removal mechanism. Most characterisation techniques include imaging using transition and scanning electron microscopes (TEM) and (SEM), crystal structure using X-ray diffraction spectroscopy (XRD), Fourier transform infrared (FTIR), Brunauer-Emmett-Teller (BET) analysis, vibrating sample magnetron (VSM), photoluminescence (PL) and ultraviolet visible light spectroscopy (UV-vis) spectroscopy. In the following sections, we shall discuss the recent research work that applied SFN structure in the removal of CP substances.

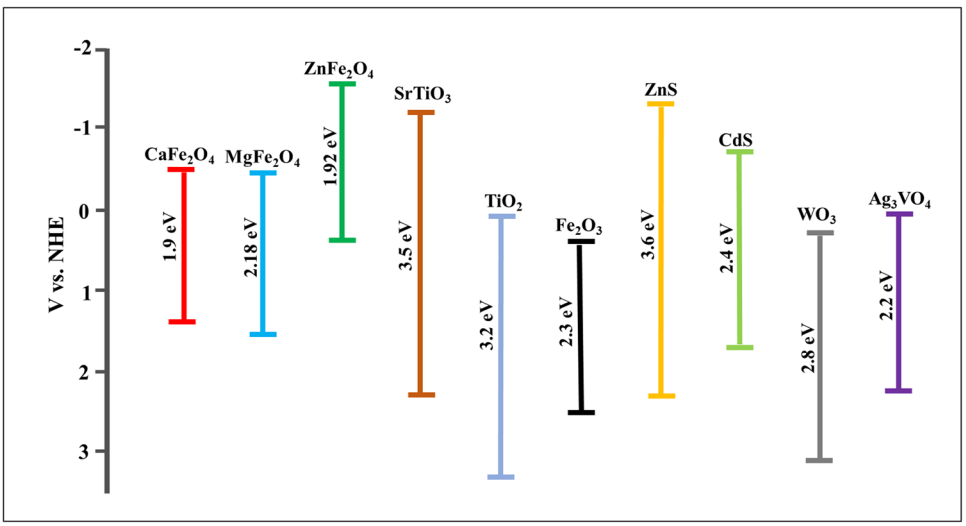

Fig. 4 Energy gaps for selected metal oxides and spinel ferrites, the diagram reproduced from Casbeer et al. (2012)

Chlorophenol removal applying spinel ferrite nanoparticles

In spite of the limited research attempts that related the spinel ferrites to chlorophenol removal, most of these efforts have shown high removal efficiency reaching almost 100% for different types of chlorophenol compounds. Authors demonstrated the influence of the ferrite structure and the experimental parameters on the chlorophenol removal efficiency. Table 2 includes details about types of ferrites applied, type of chlorophenol, removal efficiency and the optimum experimental conditions. The following sections will discuss some notable research work that successfully applied ferrite nanostructure to remove chlorophenols from aqueous solution samples.

Mochlorophenol removal

Among different types of monochlorophenol structure, 4-chlorophenol 4-CP is the most widely type investigated in literature. Most of recent research work applied the catalytic wet peroxide oxidation (WPO) to degrade 4-CP. Kurian and Nair (2015) applied the WPO for the degradation of 4-CP using Ni-dopped zinc ferrite ($Ni_xZn_{1-x}Fe_2O_4$ where $x = 0.0, 0.25, 0.5, 0.75, 1.0$) that synthesised by sol-gel auto combustion method. Their studies demonstrated the effect of the ambient parameters (temperature, catalyst dose, H_2O_2 dose) on the removal of 4-CP as well as the COD reduction, which is a strong indication of the pollutants' destruction. Interestingly, samples with different doping amount demonstrated different removal rates and efficiencies. This was also shown for the COD reduction and residual amount of H_2O_2 in the reaction. Authors had suggested a possible reaction mechanism, as shown in Fig. 5. They proposed two pathway mechanisms based on the intermediates obtained and the attack of $OH^{\cdot}$ radicals. The first pathway showed substitution of Cl by the attacked $OH^{\cdot}$ forming p-hydroxyphenol or hydroquinone. The obtained hydroquinone immediately forms 1,4-benzoquinone. The formed 1,4-benzoquinone is attacked by more hydroxyl radicals forming open-chain carboxylic acid derivatives and finally forming CO_2 and H_2O. In the second pathway, the hydroxyl radical first attacks on the ortho position to form 4-chlorobenzene-1,2-diol, which on dichlorination forms 2-hydroxyphenol or pyrocatechol in the second step. The pyrocatechol forms 2-hydroxy-1,4-benzoquinone which, under the attack of more $OH^{\cdot}$ radicals, forms CO_2 and H_2O.

Zinc ferrite dopped with nitrogen and sulphur nanostructure was applied to remove 4-CP from water through oxidation process assisted by $K_2S_2O_8$. Conventionally, $ZnFe_2O_4$ nanoparticles were prepared by sol-gel method with the addition of nitrogen and sulphur atoms during the preparation (Hareendran et al. 2022). The catalysis experiment showed a major role of persulfate in comparison to the applied $ZnFe_2O_4$ catalyst. Under certain experimental conditions (temperature = 30 °C, 4-CP/persulfate ratio = 1:3, catalyst dosage = 0.1 g, 4-CP concentration = 1 g/L, time = 60 min), the 4-CP conversion was found to be 87.25% with the absence of catalyst, while no conversion was obtained in the absence of persulfate (Hareendran et al. 2022).

A previous work has showed a better role of $ZnFe_2O_4$ as a part of the nanocomposite $ZnFe_2O_4$-Fe_2O_3-CeO_2 that is fabricated through several chemical steps including green walnut hull extract (Shafiee et al. 2017). The authors applied the fabricated nanocomposite with the aid of irradiation of 500-W halide lamp and the addition of a certain amount of H_2O_2 activator. Under optimised parameters, 100% of 4-CP molecules were degraded within 250 min. Such an outstanding degradation behaviour was related to heterogenous structure that provides abundant electron-hole yield that initiates oxidative radicals that break the persistent chemical bonds in the 4-CP compound with the aid of H_2O_2. The addition of H_2O_2 is very important to establish enough radical yield for the degradation process, as results revealed almost no effect when the nanocomposites were applied alone (without H_2O_2). Furthermore, experiments showed that the single CeO_2 did not initiate any degradation, even with the addition of H_2O_2 while $ZnFe_2O_4$ and Fe_2O_3 showed considerable removal efficiency, under the same condition.

Cobalt ferrites ($CoFe_2O_4$) doped with zirconium, nitrogen and sulphur were also applied to remove 4-CP (Kavitha et al. 2021). Authors investigated the effect of different experimental parameters on the efficiency of the degradation. As previous reports confirmed, temperature and the amount of H_2O_2 are very important to be introduced into the ferrite structure and 4-CP reaction. In this reported study, raising temperature from 30 to 50 °C has shown to enhance the removal efficiency of Zr-dopped $CoFe_2O_4$ from 48 to 100% respectively. The reaction also was enhanced as the molar ratio of 4-CP/H_2O_2 was increased, reaching its optimum at 1:15. With no ferrites applied, only 23% of 4-CP were degraded while the removal efficiency increased gradually with the amount of doped cobalt ferrite, reaching its maximum at 0.5 g/L. Under these optimum conditions, 100% degradation of 4-CP was obtained within 75 min. Authors have also demonstrated the effect of Zr doping within the $CoFe_2O_4$ lattice in the reaction. As seen in Fig. 6a, b, different amounts of Zr doping (25, 50 and 75% w/w) lead to different rates of 4-CP removal as faster rates are obtained with increasing the Zr doping amount, reaching its maximum rate at pure phase of $ZrFe_2O_4$. Furthermore, radical scavenging

Table 2 SFNs applied for the removal of different CP compounds under certain experimental conditions

	Type of spinel	Chlorophenol substance	Mechanism of removal	Removal efficiency	Optimum experimental conditions		Ref.
1	$ZnFe_2O_4$-Fe_2O_3-CeO_2	4-CP	Photocatalytic degradation and H_2O_2 activation	100%	**Catalyst dose:** **CP dose:** **Irradiation: Temperature:** **Activation:** **Time:**	0.025 g of in 10 mL 20 mg/L 500-W visible light Not applied H_2O_2 250 min	(Shafiee et al. 2017)
2	$Co_{1-x}Zr_xFe_2O_4$ (x = 0, 0.25, 0.5, 0.75 and 1)	4-CP	WPO	100%	**Catalyst dose:** **CP dose:** **Irradiation: Temperature:** **Activation:** **Time:**	0.5 g/L 1 g/L Not applied 50 °C 4-CP/H_2O_2, 1:15 75 min	(Kavitha et al. 2021)
3	Nitrogen- and sulphur-doped $ZnFe_2O_4$	4-CP	Persulfate activated oxidation	100%	**Catalyst dose:** **CP dose:** **Irradiation:** **Temperature:** **Activation:** **Time:**	0.1 g 1 g/L Not applied 30 °C CP/potassium persulphate, 1:3 60 min	(Hareendran et al. 2022)
4	$Mn_xZn_{(1-x)}Fe_2O_4$ (x = 0.0, 0.25, 0.5, 0.75, 1.0)	4-CP	WPO	100%	**Catalyst dose:** **CP dose:** **Irradiation: Temperature:** **Activation:** **Time:**	500 mg/L 1 g/L in 25 mL Not applied 70 °C H_2O_2 (30% v/v) 4 mL 120 min	(Kurian and Nair 2015)
5	$Co_xZn_{(1-x)}Fe_2O_4$ (x = 0.0, 0.25, 0.5, 0.75, 1.0)	4-CP	WPO	100%	**Catalyst dose:** **CP dose:** **Irradiation:** **Temperature:** **Activation:** **Time:**	500 mg/L 1 g/L (25 mL) Not applied 70 °C H_2O_2 (30% v/v) 4 mL 120 min	(Kurian and Nair 2014)
6	$CoFe_2O_4$	2,4-DCP	Persulfate activated oxidation	100%	**Catalyst dose:** **CP dose:** **Irradiation: Temperature:** **Activation:** **Time:** **pH:**	0.2 g/L 50 mg/L **Not applied** **25 °C** Peroxymonosulfate, 1g/L 90 min 6.8 was	(Zhou et al. 2020)
7	$Zn_xNi_{1-x}Fe_2O_4$ (x = 0.0, 0.25, 0.5, 0.75, 1.0)	2,4-DCP	WPO	100%	**Catalyst dose:** **CP dose:** **Irradiation:** **Temperature:** **Activation:** **Time:**	0.5 g/L 0.3 g/L in 25 mL Not applied 343 K CP/H_2O_2, 1:15 120 min	(Nair and Kurian 2017a)

Table 2 (continued)

	Type of spinel	Chlorophenol substance	Mechanism of removal	Removal efficiency	Optimum experimental conditions		Ref.
8	$Cr_xZn_{1-x}Fe_2O_4$ ($x = 0.0, 0.25, 0.5, 0.75, 1.0$)	2,4-DCP	WPO	100%	**Catalyst dose:** **CP dose:** **Irradiation:** **Temperature:** **Activation:** **Time:**	0.5 g/L 0.7 g/L Not applied 343 K CP/H_2O_2, 1:17 120 min	(Nair and Kurian 2018)
9	Ag_3PO_4/NrGO/$CuFe_2O_4$	2,4-DCP	Photocatalysis	95.3%	**Catalyst dose:** **CP dose:** **Irradiation: Temperature:** **Activation:** **Time:**	0.03 g 15 mg/L in 100 mL 250 W visible light RT Not applied 60 min	(Wei et al. 2021)
10	$Co_xZn_{1-x}Fe_2O_4$ ($x = 0.0, 0.25, 0.5, 0.75, 1.0$)	2,4-DCP	WPO	94.84%	**Catalyst dose:** **CP dose:** **Irradiation:** **Temperature:** **Activation:** **Time:** **pH:**	0.5 g/L 1 g/L in 25 mL Not applied 333 K CP/H_2O_2 1:14 90 min 6.78–7.03	(Nair and Kurian 2017b)
11	Nickel ferrite nanoparticles modified with poly(aniline-co-o-toluidine)	2,4-DCP	Adsorption	83% adsorption capacity of 162 mg/g	**Adsorbent dose:** **CP dose:** **Irradiation:** **Temperature:** **Activation:** **Time:** **pH:**	0.03g in 50 mL 30 mg/L Not applied RT Not applied 120 min 4	(Fathy et al. 2022)
12	gCN/$ZnFe_2O_4$/Bi_2S_3	TCP	Photocatalysis	100%	**Catalyst dose:** **CP dose:** **Irradiation:** **Temperature: Activation:** **Time:** **pH:**	0.25 g/L 50 mg/L 80 W visible light 35 °C Peroxymonosulfate 1g/L 60 min 7	Sarkar et al. (2022)

They are bold as they are representing the experimental parameters of the work

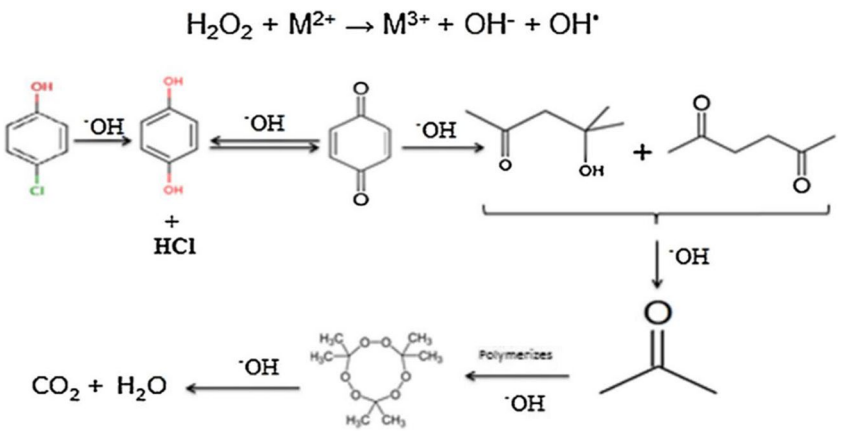

Fig. 5 Proposed mechanism of 4-CP degradation by H_2O_2 on the surface of the spinel ferrite catalyst. Copyrights are obtained from Elsevier (Kurian and Nair 2015)

tests suggested that the hydroxide OH· radical has a major role in the reaction. Nevertheless, the COD removal was also affected by the doping amount as $Co_{0.5}Zr_{0.5}Fe_2O_4$ caused the highest rate of COD removal (Kavitha et al. 2021). It is very essential to assure the conversion of 4-CP to less harmful substances in order to achieve the objective of environmental remediations to pollutants. Therefore, the doping process and varying the lattice structure of the ferrite showed to play an important role in the enhancement of the 4-CP degradation process.

Dichlorophenol removal

Copper ferrite ($CuFe_2O_4$) was utalised with Ag_3PO_4, NrGO and $CuFe_2O_4$ to form a novel nanocomposite applied effveintly to degrade 2,4-dichlorophenol through photocatalysis process (Wei et al. 2021). Due to their unique optical properties and in particular the size of their optical band gap, ferrite nanoparticles own great response to visible light. The composite was synthesised through three main chemical steps that combine the three oxides together. The optical band gap calculated from the absorption function curve decreased in the composite Ag_3PO_4/NrGO/$CuFe_2O_4$ composite (1.44 eV) in comparison to Ag_3PO_4 (2.3 eV) and $CuFe_2O_4$ (2.1 eV) alone, indicating an improved visible light absorption ability. The photoluminescence spectra also showed lower emission from the composite Ag_3PO_4/NrGO/$CuFe_2O_4$, in comparison with the oxides separately which led to better separation to electron-hole pairs. Therefore, photocatalysis experiments reflected the optical characterisations of each material, as the Ag_3PO_4/NrGO/$CuFe_2O_4$ demonstrated the maximum degradation rate of the 2,4-dichlorophenol under visible light source of 250 W (Wei et al. 2021). The authors of this work proposed the

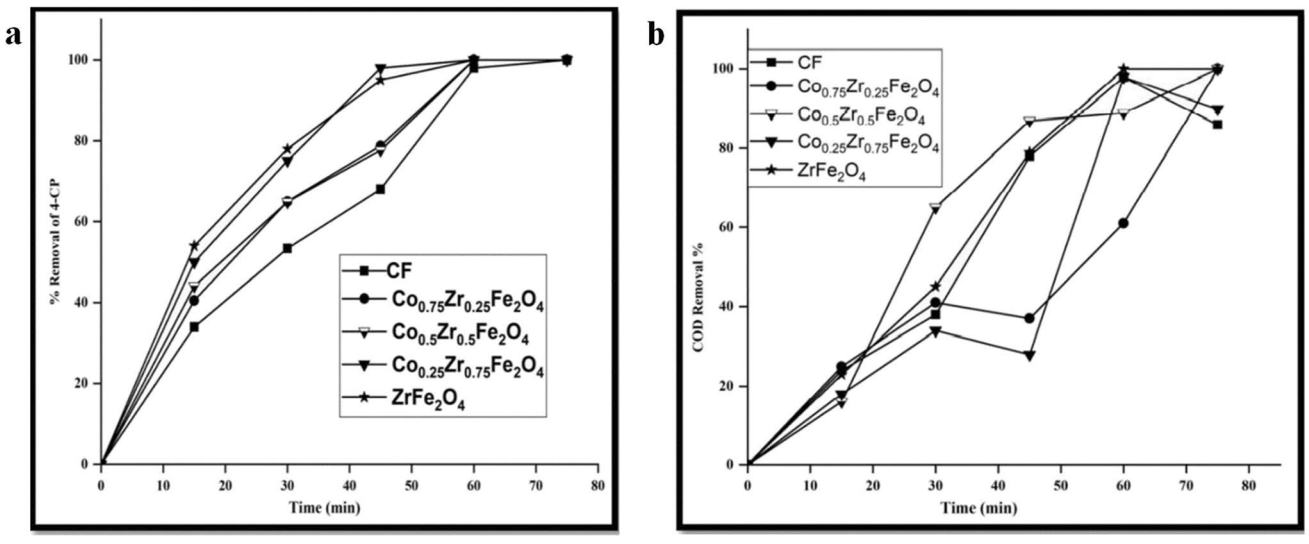

Fig. 6 Effect of Zr doping in the (**a**) WPO of 4-CP and (**b**) the removal of COD under reaction parameters: 4-CP/H_2O_2 1:15, temperature 50 °C, 4-CP 1 g/L, catalyst 0.5 g/L and time 75 min. Copyrights are obtained from Elsevier (Kavitha et al. 2021)

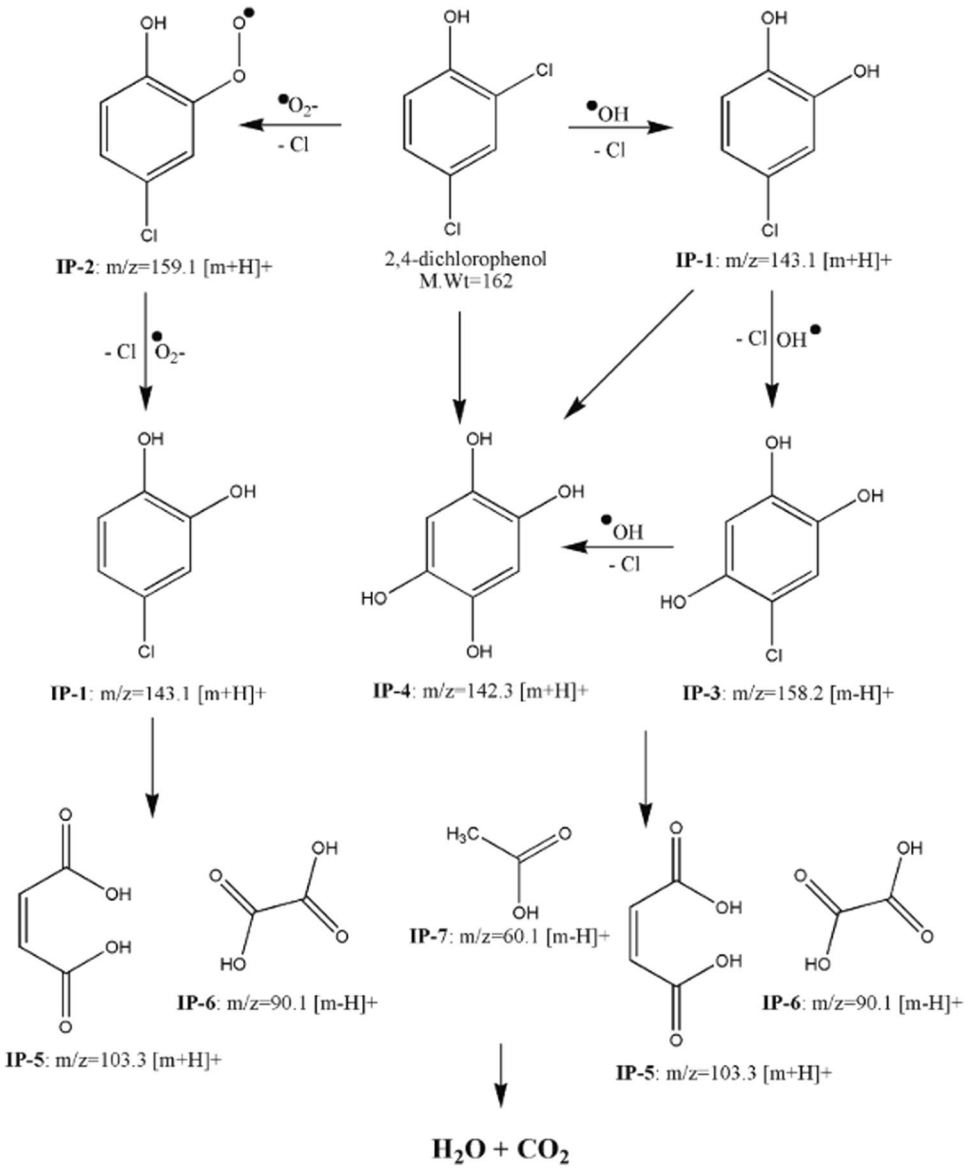

Fig. 7 Proposed degradation mechanism of 2,4 DCP applying Ag_3PO_4/NrGO/$CuFe_2O_4$ nanocomposite under visible light. Copyrights are obtained from Elsevier (Wei et al. 2021)

mechanism shown in Fig. 7 for the degradation process. Initially, one chloride atom is removed from the 2,4-DCP structure as a result of OH radical occurrence, generating 4-chlorocatechol. The latter will be subjected to OH attack too, producing 5-chlorobenzen-1,2,4-triol. •OH radicals will further degrade the product into benzene-1,2,4,5-tetrol and eventually produce maleic acid, oxalic acid and acetic acid (Wei et al. 2021).

In addition, different sets of $CoFe_2O_4$ were fabricated through hydrothermal method and investigated for 2,4-DCP degradation with the aid of peroxymonosulphate (PMS) (Zhou et al. 2020). The authors aimed to create iron and oxygen vacancies within the spinel structure, in order to alter their properties and enhance their ability to create radicals during the degradation process. The alteration in crystal structure was confirmed by the XRD pattern as well as the d-spaces in the TEM images that are shown in Fig. 8a, b respectively. Raman spectra revealed oxygen vacancy-related bands in the samples (604, 991 and 1024 cm^{-1}) which indicates the existence of peroxide (O_2^{2-}), and superoxide complexes (O_2^-), that plays a vital role in oxidation process. This was further confirmed by XPS spectra. By optimizing oxidation experiment parameters, the researchers expressed the dual role of PMS and the spinel catalyst in the degradation of 2,4-DCP. As shown in Fig. 8c, d, both catalyst dose and concentration influence the degradation process, along with pH and 2,4-DCP concentration. At optimum conditions, the degradation of 2,4-DCP reached almost 100%; however, the existence of other inorganic anions, including CO_3^{2-}, HCO_3^-, Cl^-, NO_3^- and SO_4^{2-}, demonstrated a considerable

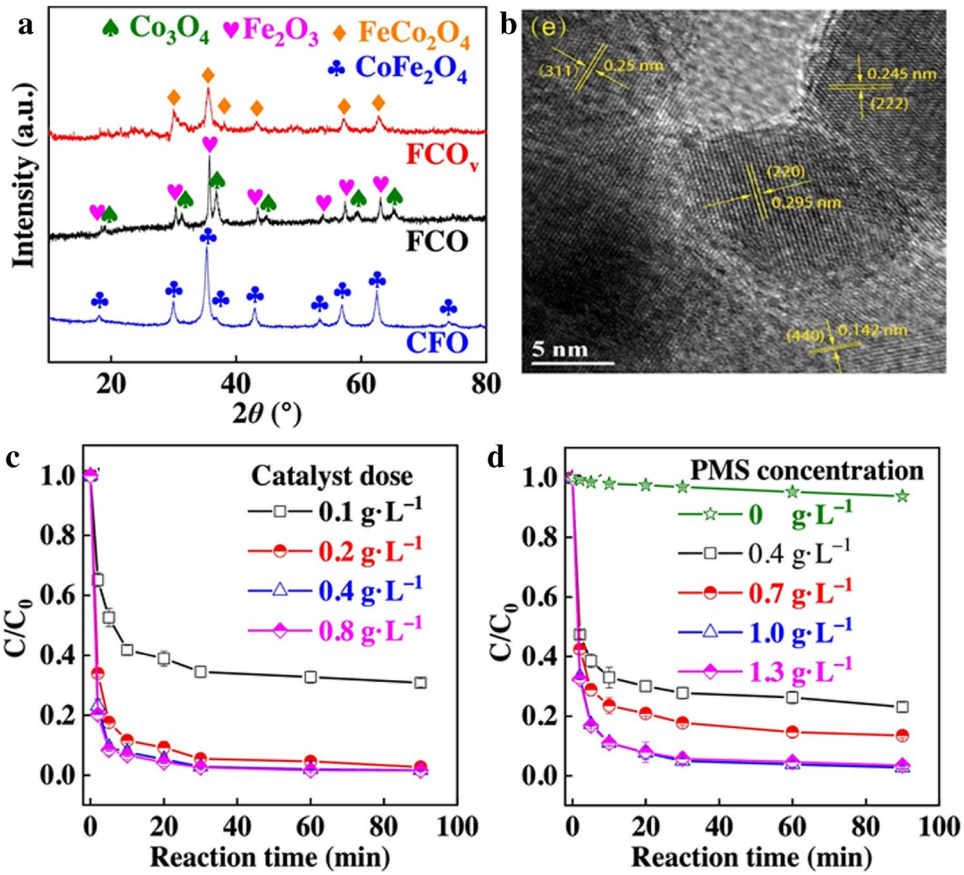

Fig. 8 **a** XRD spectra of $FeCo_2O_{4-x}$ spinel. **b** TEM image of $FeCo_2O_{4-x}$ spinel. **c** Effect of $FeCo_2O_{4-x}$ spinel dose on the degradation of 2,4-DCP. **d** Effect of PMS concentration on the degradation of 2,4-DCP. Copyrights are obtained from Elsevier (Zhou et al. 2020)

inhibition of the degradation process. This was explained by the low oxidation potential of these anions that eradicate the oxidation potential of the radicals created by the catalyst and PMS (OH and SO_4^-) (Zhou et al. 2020).

Furthermore, zinc ferrite nanoparticles were prepared by sol-gel autocombustion method and doped with different amounts of cobalt ($Co_xZn_{1-x}Fe_2O_4$ with $x = 0.0, 0.25, 0.50, 0.75, 1.0$) that were prepared by sol-gel method. It showed efficient removal of 2,4 dichlorophenol from aqueous solutions (Nair and Kurian 2017b). Along with the increase of cobalt contribution within the zinc ferrite lattice, the crystallite size was found to change considerably from 14.4 to 25.3 nm, as confirmed by XRD analysis. A typical catalysis experimental setup was conducted, where a certain amount of catalyst was introduced to the 2,4-dichlorophenol solution with addition of H_2O_2 and applying heat that ranges from 298 to 353 K. Further increase in temperature to 353 K resulted in a drop in reaction efficiency to 72%. Such high influence of temperature in the wet peroxide reaction was confirmed for all samples of doped $Co_xZn_{1-x}Fe_2O_4$. It is very essential to emphasise the role of the nanoparticles combined with raising temperature in the reaction, as the experiments confirmed that only 21.81% of 2,4 dichlorophenol was removed in the absence of nano catalyst (Nair and Kurian 2017b). The same group have also investigated the effect of chromium-dopped ferrite in 4-CP degradation (Nair and Kurian 2018). Similarly, the temperature and H_2O_2 addition influenced the reaction, greatly. They considered the effect of the structure of $ZnFe_2O_4$ as different doped chromium zinc ferrite $Cr_xZn_1^-{}_xFe_2O_4$ ($x = 0.0, 0.25, 0.5, 0.75, 1.0$) was applied under ambient conditions as the 4-CP and 2,4 DCP removal rate increased gradually with chromium substitution and $CrFe_2O_4$ catalyst demonstrated 100% removal. On the other hand, the study also showed that the effect of temperature is not the same for all doped composites as well as the type of pollutants (4-CP and 2,4 DCP). The study included a large set of data that investigated ambient condition of temperature, pollutant type, pollutant dose, catalyst dose and catalyst type. This revealed the complexity of the degradation reaction of such organic pollutants as it needs several factors to be achieved (Nair and Kurian 2018). Nickle-doped zinc ferrite was also investigated by the same group under the same conditions, confirming the effect of doping and ambient conditions on the WPO process (Nair and Kurian 2017a)(Kurian and Nair 2015).

Ultimately, a recent study investigated the effect of combining novel polyaniline-co-o-toluidine (POAT) with

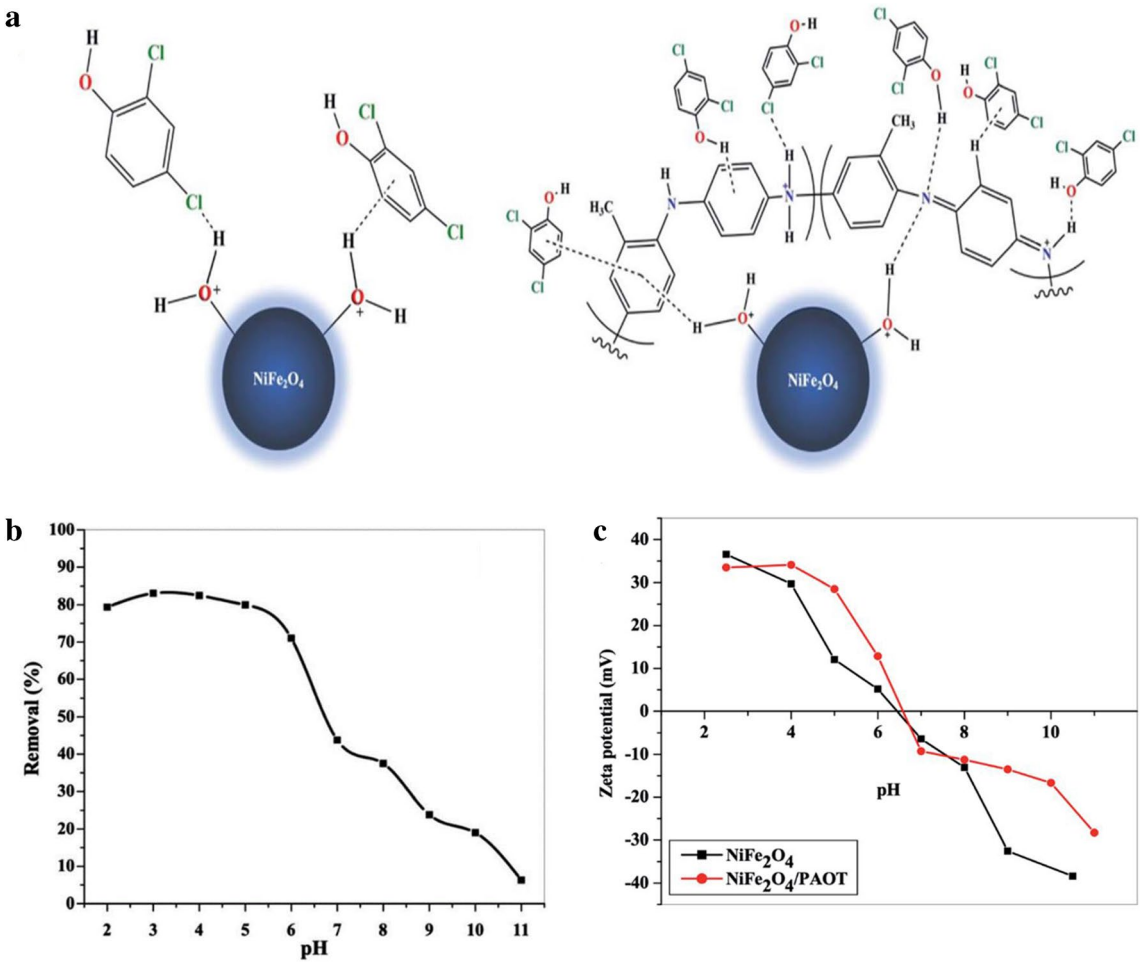

Fig. 9 Schematic 2D simulation for the adsorption mechanism of 2,4-DCP on $NiFe_2O_4$ nanoparticles and $NiFe_2O_4$/PAOT nanocomposite (Fathy et al. 2022)

$NiFe_2O_4$ in 2,4-DCP adsorption (Fathy et al. 2022). $NiFe_2O_4$ nanoparticles were prepared through conventional chemical routs and then combined with POAT through chemical polymerisation method. The formation of the composite was confirmed through XRF, FTIR and HRTEM. $NiFe_2O_4$/PAOT nanocomposite showed enhanced removal of 2,4-DCP reaching 83% in 120 min, in comparison with only 24% for the pristine $NiFe_2O_4$. The adsorption experimental data were fitted to both Langmuir and Freundlich isotherms indicating the formation of non-ideal monolayer on the adsorbent surface. The process showed high sensitivity to the medium pH as it worked only in acidic medium (pH from 2 to 4) as shown in Fig. 9a. This was related to the abundancy of the nitrogen atoms of the amine and imine groups that created in lower pH medium. It was also related to the surface charge of the composite as higher values of charges were obtained at lower pH values, as shown in Fig. 9b. The authors suggested a possible mechanism for the adsorption as illustrated in Fig. 9c (Fathy et al. 2022)

Trichlorophenol removal

Recently, a nanocomposite including $ZnFe_2O_4$ has been applied successfully to degrade 2,4,6-TCP in water (P. Sarkar et al. 2022) The graphitic g-C_3N_4?/$ZnFe_2O_4$/Bi_2S_3 composite was prepared through a facile microwave-assisted synthesis method that combines the previously prepared $ZnFe_2O_4$/g-C_3N_4 (facile thermal polycondensation method) to different weights of Bi_2S_3 (5, 10, 15 and 20 wt%). As shown in Fig. 10a, TEM images confirmed the production of the nanocomposite as the related lattice spaces were identified in the image. All samples (along with single gCN, $ZnFe_2O_4$ and Bi_2S_3) were intensively characterised, and the foremost sample was chosen for the PMS mediated degradation experiment. In terms of optical properties, g-C_3N_4/$ZnFe_2O_4$/Bi_2S_3 (10 wt%) showed the strongest photocurrent response in the light radiation cycle and weakest PL intensity among samples indicating a high response to radiation and high electron hole separation which are important factors in

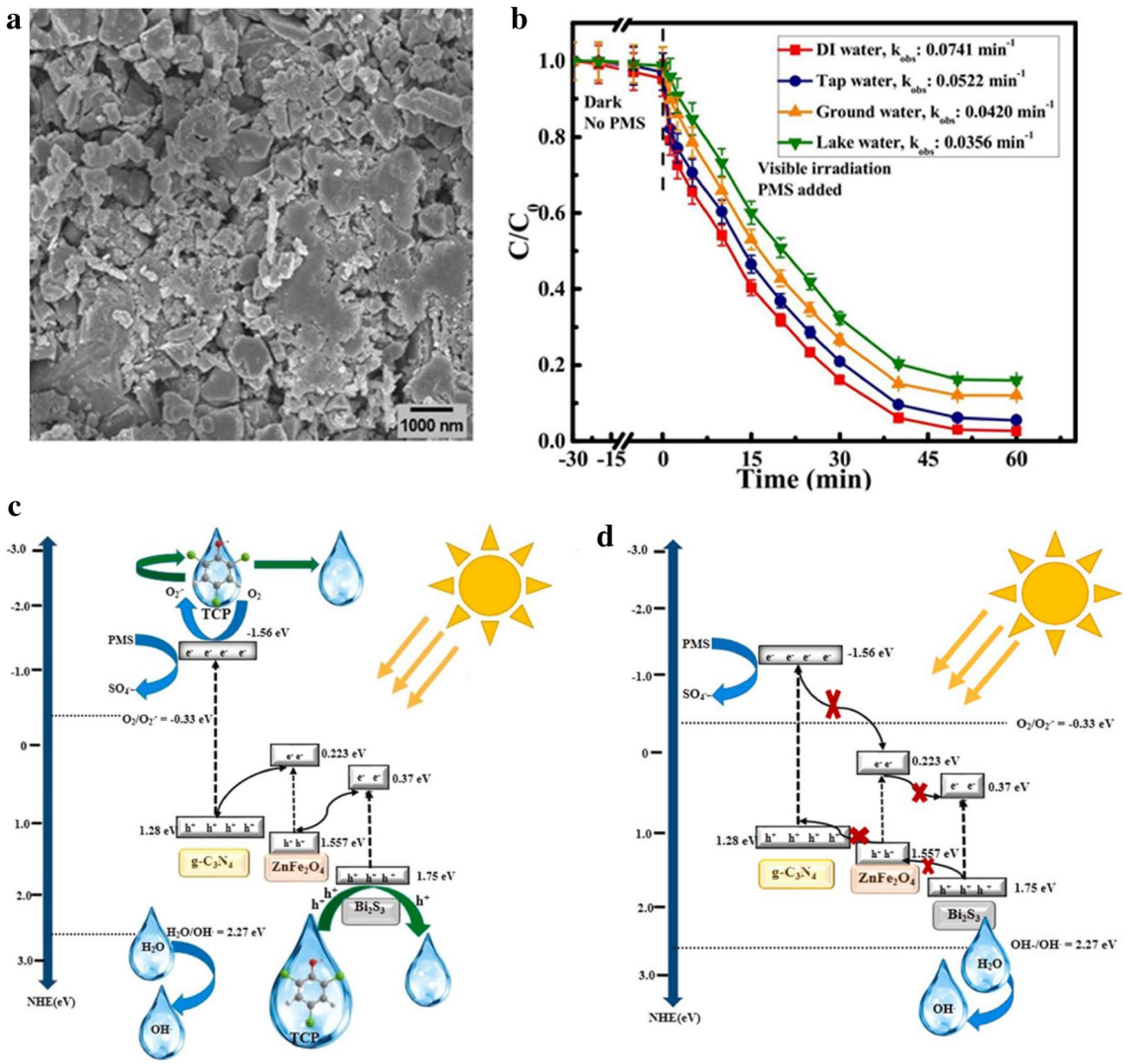

Fig. 10 **a** TEM images of gCN/$ZnFe_2O_4$/Bi_2S_3 nanocomposite and its **b** degradation efficiency of 2,4,6-TCP in different type of aqueous solutions. **c** The mechanism of photocatalysis process. Copyrights obtained from Elsevier (P. Sarkar et al. 2022)

photocatalytic reaction. BET surface area calculations also showed that g-C_3N_4/$ZnFe_2O_4$/Bi_2S_3 (10 wt%) owns the highest surface area (10.6 m^2 g^1) among the prepared samples which is an important factor too, as reaction active sites are expected to increase with surface area. PMS-assisted photocatalysis experiment was carried out under visible light intensity of 80 W only. As the best nanocomposite was chosen carefully in this study, an efficient result was obtained resulting in 100% removal of 2,4,6-TCP within 1 h. Typical degradation parameters were adjusted, and the reaction showed a good efficiency in tap water, groundwater and lake water as shown in Fig. 10b. This study also highlighted the importance of adjusting the PMS dose to the catalyst dose to get the optimum reaction, as excessive PMS dose may decrease the reaction efficiency (P. Sarkar et al. 2022). The authors suggested the mechanism of 2,4,6-TCP degradation with the aid of PMS and visible light on the surface of the ferrite catalyst as follows:

$$OH^{\bullet}(aq) + OH^{\bullet}(aq) \rightarrow H_2O_2(aq) \quad (1)$$

$$SO_4^{\bullet -}(aq) + OH^{\bullet}(aq) \rightarrow HSO_5^{-}(aq) \quad (2)$$

$$SO_4^{\bullet -}(aq) + HSO_5^{-}(aq) \rightarrow HSO_4^{-}(aq) + SO_5^{\bullet -}(aq) \quad (3)$$

$$2SO_4^{\bullet -}(aq) \rightarrow S_2O_8^{2-}(aq) \quad (4)$$

The mechanism of the photocatalysis process is also represented in Fig. 8c, d where two configurations of electron transfer are presented. Figure 10c shows dual type II heterojunction

where the electrons are excited as a result of solar irradiation and takes the path from the CBs of both g-C_3N_4 and $ZnFe_2O_4$ to the CB of Bi_2S_3. Such electron path configuration prevents the electron-hole recombination that occurs in the general type heterojunction as shown in Fig. 10d. With the aid of scavenging, the dual type II heterojunction has more affinity to occur causing considerable degradation to the 2,4,6-TCP molecules (P. Sarkar et al. 2022). This study confirms the influence of heterogenous structure that involves ferrites to assure wide range of irradiation absorption that includes solar radiation where the electron-hole recombination can be reduced/prevented.

Challenges and considerations

The exiguous literature resources that discussed the effect of SFNs in the removal of CPs have shown almost similar removal approaches and considerations which will be discussed as follows:

Enhancement of SFN structure

As per our search in the literature, no work on pure phase SFNs for the removal of CPs has been reported recently. SFNs own relatively small bandgap that makes them absorb radiation with wavelengths that range within the visible light region (R. Li et al. 2020)(Khadgi and Upreti 2019)(Jahanara and Farhadi 2019) and hence can be excited easily through visible light. However, due to the small band gap, the electron hole recombination occurs faster, which lead to lower oxidation ability. Therefore, enhancing SFN structure by including it as a part of metal oxide or polymeric composite is very essential to obtain good oxidation properties (M. Verma et al. 2020)(J. Sun et al. 2020). Within the composite, the ration of the combined chemical structure has shown to alter the composite properties (Dippong et al. 2020). Moreover, researchers are adopting the doping strategy (creating lattice defects) of the SFNs by introducing another metal ion substitution within the SFN crystal, to create additional subenergy levels that provide more electron-hole separation (Yang et al. 2019). These defects are rather internal such as oxygen vacancies (Wu et al. 2019b) or by adding a certain amount of metals to create the lattice defect (Jyothish and Jacob 2021). Accordingly, the behaviour of the ferrite within the application could be altered or controlled based on the required scenario. It is very important to mention here that doping SFN has shown effects not only on the mechanism route, but also on the COD removal during the oxidation process (Kavitha et al. 2021). The unique structure of ferrite allows wide variety of structure arrangements that still have not been fully investigated experimentally and specifically, in the removal of CP application. Further research in different strategies in enhancing the SFN structure and its effect on CPs' removal process is essential to create a platform of the optimum features of SFNs that are needed to degrade CPs. Recent reviewed studies included a remarkable SFNs' characterisation profile; however, stronger link between the properties of SFNs and their application in CP removal is indispensable.

Ambient experimental parameters

Research attempts on SFNs for CP removal emphasised the role of ambient parameters in the efficacy of CP degradation. As shown in Table 2, detailed work of varying all ambient parameters including temperature, catalyst dose, CP dose and pH was investigated, confirming the importance of tuning all of these parameters (Kurian and Nair 2015). This indicates the complexity of achieving degradation of CPs (Barzegar et al. 2018), as even the mount of activation radicals (H_2O_2 and PM) has noticeable effect on the degradation process. In some research attempts, temperature seems to have a great effect during the oxidation process (Nair and Kurian 2017b), while other work did not apply any temperature, taking the advantage of other parameters such Fenton's (Kavitha et al. 2021) and/or complex heterogenous structure (P. Sarkar et al. 2022) (Fathy et al. 2022). All the reviewed studies attempt a combination of external experimental enhancers as well as structure enhancement to ferrite chemical phase itself, as shown in Table 2.

Removal approach for different chlorophenols

Most of reported research work focused on degradation of CPs applying SFN structure through photocatalysis and oxidation process. These two processes showed great efficiencies in CP removal reaching 100%. However, additional heat, chemicals and irradiation are required to maintain robust and efficient degradation process, which is considered to be cost and energy consumable. In the other hand, very few reports considered the adsorption of CPs on the surface of SFNs (Fathy et al. 2022), though SFNs are generally well-known for their good adsorption ability in terms of surface charges and chemical groups (Amrutha et al. 2023; Lingamdinne et al. 2018; Punia et al. 2022; Xiang et al. 2021). Therefore, there is a great potential to apply SFNs, or/and composites including SFNs, as efficient adsorbents to CPs.

As shown in our review, 4-CP substance removal was mostly fulfilled through WPO route, while 2,4-CP substances were degraded through PMS activation and photocatalysis. This might be related to the mechanism of degradation of both CPs, as 4-CP depends more in OH radicals in its degradation (Hareendran et al. 2022), while 2,4-CP needs both O and OH radicals (Wei et al. 2021). The mechanism of other CP substances that can be degraded applying

SFNs still needs to be investigated, as research attempts only considered 4-CP for monochlorophenols and 2,4-CP for dichlorphenols. Other oxide nanoparticles such as ZnO, TiO_2, SnO_2, and Fe_3O_4 (Chen et al. 2022; Choi et al. 2017; X. Duan et al. 2019; Kotlhao et al. 2019) were applied to degrade other types of phenols such as 2-CP and 3-CP (Soltani and Lee 2017). Thus, there is a wide research possibility in this aspect, considering that SFN composites own potential properties to remove different types of CPs.

In view of the above aspects, it seems that all of them are essential to achieve CP removal, starting from the choice of SFN structure until the strong effect of ambient parameters. Therefore, more research in this area, investigating more SFN structure, more types of CPs and more removal approaches are highly recommended to create a solid understanding to this specific research area.

Toxicity and environmental considerations

As the use of NPs is spreading into wide range of applications, the toxicity and environmental aspects become very important. Mainly, the chemical composition, morphology, size and concentration of the NPs are the main factors that affect their toxicity toward certain biological cells (Samei et al. 2019). Though most of the reviewed research efforts have described SFNs as environmentally friendly, excessive sets of cytotoxicity assays are very essential to assure safety of the synthesised SFNs that vary in morphology and chemical composition. The assays include structural and functional investigations on a certain biological cell line. As the SFNs are effective in water remediation applications, their toxicity into aquatic life is a great concern. Therefore, most of research experiments are conducted using marine organism cell line models, to provide an indication of the SFNs' effect on marine species (Saxena et al. 2020). Toxicity assessment including growth and oxidative stress shows negligible toxicity effect of $ZnFe_2O_4$-Ag/rGO composite of the cells of Daphnia magna, a marine organism (Khadgi and Upreti 2019). Also, $SnFe_2O_4$/$ZnFe_2O_4$ structure was confirmed to be non-toxic based on the *Escherichia coli* bacterial growth (Wang et al. 2020). Furthermore, it is reported that different ferrites (Zn, Cr, Cu, Ni and Co) that have a particle size ranging from 30 to 50 nm caused different inhibition rates of the growth of *Picochlorum* sp. marine microalgae. Within a certain concentration, the toxic effect of these SFNs can be neglected (Rashdan and Hazeem 2020). The size is a very important factor too, as smaller size may cause more toxic effect. Smaller sizes of $ZnFe_2O_4$ structure (10 to 12 nm) have shown to cause more oxidation stress than larger $ZnFe_2O_4$ (20 to 25 nm). This is attributed to the ability of the smaller size particles to invade the cell membrane of the microalgae species (Al-Najar et al. 2022). Mainly, the concern is more related to the SFNs that contain heavier metallic components such as $CoFe_2O_4$ have shown to cause toxic reactions in organisms. $CoFe_2O_4$ can cause noticeable oxidative reactions in organism cells which led to cell membrane destruction as well as genotoxicity (Mmelesi et al. 2021).

In general, though some SFNs are considered as environmentally friendly, not all the SFNs can be considered as completely safe and non-toxic, and more investigations should be conducted. Aspects of size, concentration and chemical composition should be taken into account. The evaluation of the suitable SFNs for water treatment application should consider toxicity to marine and human life as an important factor along with its efficiency in removing pollutants. The size of NPs has a great role in initiating the oxidative stress within the biological cells, and hence, the size should be optimised not only for the efficient application but also for less harmfulness to environment and health.

Conclusion

Chlorophenols (CPs) are extremely hazardous and persistent organic compounds (POPs) that threat human life. Removal of such compounds is therefore very urgent and requires the fabrication of new functional nano-photocatalysts to deal accordingly. Their removal is further regarded in the presence of different soluble salts usually present in the effluents of many industries. It is therefore highly required to direct future research towards the fabrication of novel photocatalysts to deal with all these problems. Ferrite materials (spinel/inverse spinel or perovskite) have attracted significant scientific attention in heterogeneous photocatalyst research thanks to their excellent properties such as relatively small bandgaps, eco-friendly and low cost. Combination of ferrites with other photocatalysts leads to enhance photocatalytic activity performance. The synergistic effect and the efficient charge separation offered by the formation of the heterojunction structure are responsible for the photocatalytic activity improvement, resulting in increasing their photocatalytic activity. Besides, ferrite photocatalysts are suggested to be an effective photocatalyst when applied alone or with oxidants such as H_2O_2 in the presence of electromagnetic radiations such as UV/visible for the degradation of various organic pollutants.

In this review, we tried to elaborate the removal of different chlorophenols using ferrite nanoparticles either by photodegradation or adsorption. However, huge research is underway and every day, new literatures are introduced in different journals dealing with the different removal methods of chlorophenols from wastewater. Therefore, the day is not far away that advancement will be made in the field of photocatalysis to effectively remove toxic pollutants and safeguard environment for the future generation. The thermal and chemical stability of ferrite-based materials is less

tackled, and future research should focus on ferrite stability, which will be the main challenge for the development of photocatalysts. All published articles which deal with photocatalysis application of ferrites operated at the lab scale and showed an excellent photocatalytic activity; their functional applicability on an industrial scale has not yet been published. This field, therefore, involves engineering action to establish the correct configuration of the reactor that will fit for realistic operation on an industrial scale. We hope that this review will provide a sound knowledge to the viewers about the importance of using ferrites and their role in the removal of chlorophenols in the environment.

Author contribution Hereby, I declare that the author contribution in this manuscript is as follows: Dr. Basma Al-Najar: writing the first draft of the manuscript. Prof. Ayman H Kamel: the idea, design and structure of the manuscript. Dr. Hanan Albuflasa: supervision and revision. Dr. Nicholas P. Hankins: supervision and revision.

Data availability I hereby consent that this manuscript did not use any data.

Declarations

Ethics approval I hereby consent that this manuscript is not applicable for ethical approval as it does not contain any human or animal material and data.

Consent to participate I hereby consent that this manuscript is not applicable for consent to participate as it does not contain any human or animal material and data.

Consent for publication I hereby consent that this manuscript is not applicable for consent for publication as it does not contain any human or animal material and data.

Conflict of interest The authors declare no competing interests.

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