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Synthesis, structural, optical and magnetic properties of NiFe₂O₄/MWCNTs/ZnO hybrid nanocomposite for solar radiation driven photocatalytic degradation and magnetic separation

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Abstract

Novel multifunctional NiFe₂O₄/MWCNTs/ZnO hybrid nanocomposite has been successfully synthesized via the hydrothermal and the co-precipitation methods at 210 °C and 90 °C, respectively, to be used as a solar radiation driven photocatalytic material. The hybrid nanocomposite exhibits enhanced photocatalytic activity compared to NiFe₂O₄ and ZnO for decolorization of Methylene Blue (MB) dye - as a model pollutant- from aqueous solutions under solar radiation. Different complementary analytical tools were used to investigate the structural, optical and magnetic properties of the photocatalyst which possess good light response ability, photocatalytic stability, magnetic separation performance and reproducibility. The results from optical degradation confirmed the synergistic effect between the NiFe₂O₄, the ZnO and the MWCNTs. Suppressed recombination of electron-hole pairs mean more efficient charge separation and enhanced photocatalytic activity. The apparent rate constant (k_{app}) of the MB decolorization for a duration of 300 minutes using NiFe₂O₄/MWCNTs/ZnO, NiFe₂O₄ and ZnO photocatalysts were found to be 0.00438 min⁻¹, 4.12857E⁻⁴ min⁻¹ and 0.002 min⁻¹, respectively. The removal efficiency was also investigated for different pH values. Due to the magnetic properties of the nanocomposite, it was possible to separate it after degradation experiments and hence re-usability is possible. In view of the enhanced solar radiation driven photodegradation, the present composite can present a robust alternative as a solar radiation driven photocatalyst.

Key words: Magnetic carbon nanotubes (Mag-CNTs); NiFe₂O₄ nanoparticles; Photocatalytic degradation, Magnetic separation.

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1. Introduction

The process industry is developing at an extremely rapid pace however one of the great challenges faced are the environmental pollution effects [1-7]. Most synthetic dyes employed in textile, cosmetics and other products have high contents of colored components, salts, organic contaminants and high chemical oxygen demand. They cannot be eliminated efficiently by conventional chemical oxidation and traditional biodegradation methods due to their stable complicated aromatic molecules [8]. Carbon nanotubes (CNTs) have been proven to acquire a great potential as a superior adsorbent for eliminating many kinds of inorganic and organic pollutants from aqueous solutions, due to their small pore size, large specific surface area, hollow and layered structures [9]. Functionalization of the CNTs surface with different materials like polymers, metals, metal oxides and complex metal oxides can develop CNTs features and will possess potential applications as magnetic data storage [10], electric devices [11] and heterogeneous catalysis [12].

It is believed that a remarkable improvement of the photocatalytic activity can be achieved via the combination of CNTs and a suitable semiconductor due to the synergistic effect [13-16]. The semiconductors alone display some photocatalytic effect, but the limitations diminish their wider applicability. The anchoring of semiconductors with multi-walled carbon nanotubes (MWCNTs), overcome such limitations and make semiconductor composites better photocatalyst materials [17].

Among the many semiconductors used in the field of photocatalysis are TiO_2 , ZnO and CdS [18-23]. ZnO is widely used in photocatalytic degradation of organic pollutants [7]. It is well known as an excellent photocatalyst due to its superior features such as non-toxicity, lower cost synthesis possibilities and chemical stability [24, 25]. Most semiconductors basically absorb ultraviolet light [26, 27] which accounts for only 3%–5% of sunlight [19]. ZnO has a wide band gap (~ 3.37 eV) [7, 28], which is unfavorable for the absorption of solar visible light. However, ZnO possesses point defects that fills the band gap and enable the emission and absorption of the light energy in the visible range. To further improve the ZnO performance, several attempts have been made to increase the shift of its absorption band from UV to the visible light region by different approaches such as e.g. doping or coupling ZnO with metals, nonmetals, and metal oxides. The difficulty in isolating the ZnO and CNTs - based photocatalysts from aqueous solutions after usage limits their application in treatment of water polluted with dyes [24]. Although centrifugation, precipitation, filtration and other methods have been used to separate the photocatalysts from the reaction solution, the separation process is generally complex and time-consuming. Therefore, to solve the problem, and in order to separate the

photocatalysts conveniently after the reaction, magnetic carriers are introduced into the photocatalyst to prepare a good recyclable magnetic photocatalyst, for example, coupling of ZnO or CNTs with strong magnetic materials as spinel ferrites [29]. This is an alternative option for isolation by filtration or centrifugation [13, 30]. Furthermore, decoration of CNTs by spinel ferrites nanoparticles (NPs) which are very important magnetic materials, can improve the optical, electrochemical and magnetic properties of the CNTs [31]. In some investigations, MWCNTs decorated with NiFe_2O_4 NPs ($\text{NiFe}_2\text{O}_4/\text{MWCNTs}$) have proven to be an appropriate mediator in electrochemical processes [32]. Previous studies have clearly demonstrated that the synergistic effect through the decoration of CNTs by NiFe_2O_4 can improve the optical, electrochemical and magnetic properties of the CNTs [13, 33]. It is clearly demonstrated that it is possible to further promote the activity of the photoinduced charge separation leading to high photocatalytic efficiency due to the synergistic effect through the combination of ZnO [34-36] or NiFe_2O_4 [13, 33, 37] with CNTs to make hybrids for effective elimination of dye contaminants from aqueous solutions.

Likewise, coupling among ZnO and NiFe_2O_4 creates a semiconductor photocatalyst which enhances the photocatalytic activity under visible light [24, 38]. Theoretically, when ferrite composites are coupled with ZnO, a heterojunction is created and then the photoinduced electrons and holes are separated effectively, give rise to enhancement in the photocatalytic efficiency [39]. Zhu et al. [38] used $\text{NiFe}_2\text{O}_4/\text{ZnO}$ hybrid prepared by the hydrothermal method for Congo red (CR) dye removal by adsorption and photocatalysis, then the magnetic hybrid was easily and effectively separated from the aqueous solution by an external magnet. Jamarun et al. [24] used the solvothermal method to prepare the same composite for photocatalytic Rhodamine B dye degradation under solar light. The two previous studies i.e. [24] and [38] reported that the photocatalytic activity of the synthesized nanocomposites were higher than pristine ZnO and pristine NiFe_2O_4 . Zhu et al. [13] used $\text{NiFe}_2\text{O}_4/\text{MWCNTs}$ hybrid prepared by the hydrothermal method to investigate its photocatalytic activity for the removal of Congo red (CR) dye from aqueous solutions under simulated solar light irradiation. It was found that the activity was 2.18 times higher than that of NiFe_2O_4 . Seffah et al. [40] synthesized the same nanocomposite by hydrolysis using refluxing for 45 minutes which have been used for the elimination of methyl orange dye from polluted water.

In this study, novel multifunctional $\text{NiFe}_2\text{O}_4/\text{MWCNTs}/\text{ZnO}$ photocatalyst has been synthesized via the hydrothermal and co-precipitation methods (two-steps process) and was investigated as an efficient visible light driven photocatalyst. The as-prepared composites were characterized using, UV-

visible spectrometry, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), energy dispersive x-ray spectroscopy (EDX), transmission electron microscope (TEM), Ultraviolet–visible diffuse reflectance spectroscopy (UV-Vis DRS), vibrating sample magnetometer (VSM) and electrochemical impedance spectroscopy (EIS).

2. Materials and methods

2.1. Chemicals

Multi-walled carbon nanotubes (+95% Pure, Outer D: 30 ~ 50 nm, Length: 10-30 μm), were purchased from M K Impex Corp, (Mississauga, Ontario Canada). $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sodium Hydroxide (NaOH) and Nitric acid (HNO_3 , 65%) were obtained from S D Fine-CHEM Limited (SDFCL). All reagents were of analytical grade and were used without further purification. Methylene Blue (MB) dye was supplied by the National Center for Leather- Khartoum, Sudan.

2.2. Oxidation of MWCNTs

The MWCNTs were oxidized to facilitate good attachment with the other nano-materials such as NiFe_2O_4 NPs on its outer walls [41]. For oxidation of the MWCNTs, 0.5 g of pristine MWCNTs was sonicated in deionized water for 3 hours before adding them to a nitric acid solution (300 mL, 4 mol/liter) in an oil bath (refluxing at 110-120 $^\circ\text{C}$ for 7 hours). The suspension was washed several times until the pH was neutral. Then they were dried for later usage.

2.3. Preparation of NiFe_2O_4 /MWCNTs/ZnO

NiFe_2O_4 /MWCNTs/ZnO hybrid nanocomposite was prepared by the hydrothermal and the co-precipitation methods (Fig. 1). First 0.2 g of nitric acid treated MWCNTs was dispersed in 50 ml deionized water. 1 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were added slowly to the solution under vigorous stirring for 10 minutes to obtain a homogenous solution. The pH of the mixture was adjusted to 13 by adding NaOH solution (6 M) drop-wise. Then the solution was subjected to stirring for 20 minutes at room temperature. After that the mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave and maintained at 210 $^\circ\text{C}$ in an oil bath for 5 hours. After the container is left to cool naturally, the resulting precipitate was washed several times by deionized water. NiFe_2O_4 /MWCNTs hybrid nanocomposite was then formed.

In the next stage, the as-synthesized $\text{NiFe}_2\text{O}_4/\text{MWCNTs}$ (wet precipitate) was decorated on its outer surface by ZnO NPs using the co-precipitation method. In details, the resulting washed precipitate ($\text{NiFe}_2\text{O}_4/\text{MWCNTs}$) was added to a 350 ml deionized water under vigorous stirring for 10 minutes. After that 3.2 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is dissolved in the solution for also 10 minutes, and then NaOH solution (0.6 M) was added drop-wise to the solution until the precipitate appears when the color of the dark brown solution changes to be light brown, which means that zinc oxide NPs are achieved. Finally, the solution was heated at 70 °C for one hour, and then a $\text{NiFe}_2\text{O}_4/\text{MWCNTs}/\text{ZnO}$ hybrid nanocomposite is formed. It was then washed several times and dried for later usage. Pure NiFe_2O_4 nanocomposite was synthesized by the same way as the method used for the $\text{NiFe}_2\text{O}_4/\text{MWCNTs}$ hybrid nanocomposite except that for the NiFe_2O_4 preparation, the Teflon-lined stainless-steel autoclave was kept 3 hours only in the oil bath.

During the hydrothermal operation, in the first step, the MWCNTs act as a substrate for the growth of the spinel ferrites because of the interaction between the Ni, Fe precursors and the functional groups on the surface of the MWCNTs which covalently attach the molecules.

The mechanism for the formation of the $\text{NiFe}_2\text{O}_4/\text{MWCNTs}/\text{ZnO}$ nanocomposite is as follows: Firstly, the chemical treatment (oxidation) of the MWCNTs by the HNO_3 acid introduced a considerable carboxyl groups on the outer walls of the MWCNTs as indicated by the FTIR results. The functional groups that are negatively charged make the MWCNTs active for interaction with metal ions. With introducing functionalized MWCNTs into the solution containing the metal salts, the Ni^{2+} and Fe^{3+} ions are attached by electrostatic interactions to the carboxylic groups that function as nucleation sites. Then, the NaOH reacts with the metal ions that precipitate down after converting them into metal hydroxides. After heating for one hour at 100 °C, this precipitates is transformed into ferrite NPs.

Fig. 1. Schematic diagram of the preparation of the NiFe₂O₄/MWCNTs/ZnO hybrid nanocomposite.

2.4. Characterization of the NiFe₂O₄/MWCNTs/ZnO

XRD patterns of the composites were recorded using x-ray powder diffraction XRD-7000S/7000L, SHIMADZU equipped with Cu $k_{\alpha 1}$ ($\lambda = 1.5406 \text{ \AA}$). UV-Vis diffuse reflectance spectrometer (DRS) Jasco-V-570, Japan was used to record the absorbance spectra of samples. UV-Vis spectrophotometer UV-1800, SHIMADZU was used to record the changes in the absorbance of the MB dye solution. The morphology was characterized using scanning electron microscopy (SEM) TESCAN MIRA 3 equipped with the energy dispersive spectroscopy analysis (EDS) attached part, and high-resolution transmission electron microscopy (HR-TEM) JEM-2100, JEOL, Japan. Room temperature magnetic properties were measured using a vibrating sample magnetometer (VSM) 7410-Lake Shore, USA. Fourier transform infra-red (FTIR) spectra were recorded using a SHIMADZU 8400S FTIR spectrometer. Cole-Cole semicircles were performed using electrochemical impedance spectroscopy (EIS) at room temperature in a dry nitrogen atmosphere through Novocontrol turnkey concept 40 System in the frequency range from 0.1 Hz to 20 MHz. The specimens were scanned through sandwiching between two copper electrodes ($r = 0.5 \text{ cm}$).

2.5. Photocatalytic experiments

The activity of the NiFe₂O₄/MWCNTs/ZnO photocatalyst was evaluated by photocatalytic decolorization of the MB dye under solar light irradiation at ambient temperature. All experiments were conducted with a constant catalyst dosage (1.0 g L⁻¹) and constant initial dye concentration (20 mg L⁻¹). Typically, 50 mg of NiFe₂O₄/MWCNTs/ZnO was added to 50 mL of MB dye solution. During the reaction, at given time intervals, 3 mL of solution was drawn and the catalyst was separated immediately by a magnet from the drawn solutions and the dye concentration was analyzed at $\lambda_{\text{max}} = 658$ nm using UV–Visible spectrophotometer. Three repeated experiments were performed (the average was taken) made the experimental data more reliable. The decolorization efficiency (η) (%) of the MB dye by the photocatalyst at time t was calculated by the equation:

$$\eta (\%) = ((C_0 - C_t) / C_0) \times 100\% \quad (1)$$

taking A_0 and A_t to represent the absorbance of the MB dye solution before and after the solar light irradiation at any time t , respectively, such that $A_t/A_0 = C_t/C_0$, where C_0 is the initial MB dye concentration (mg L⁻¹) and C_t is the MB dye concentration (mg L⁻¹) at any time t (min). The decolorization kinetics of MB dye solution have been further investigated. The photodegradation process was fitted for the pseudo-first-order kinetic model in order to describe the corresponding experimental data [42, 43] according to the following equation:

$$\ln(C_0 / C_t) = k_{\text{app}} t \quad (2)$$

where " t " is the reaction time (minutes), k_{app} is the apparent reaction rate constant (min⁻¹).

2.5.1. Recycling experiments

In the recycling experiments, after the initial photodegradation reaction, the remaining solids were recovered by the use of an external magnet and ultrasonically washed in ethanol for 30 min to remove the MB and other by-products. Afterward, the NiFe₂O₄/MWCNTs/ZnO photocatalyst was rinsed three times with deionized water and ethanol. The reproducibility of the catalyst was investigated by repeating the process five times at the normal pH (of the MB dye solution) and at high pH (11.55).

3. Results and discussion

3.1. Characterization of catalysts

3.1.1. Structural properties

Fig. 2 shows the XRD patterns of the pure NiFe₂O₄, MWCNTs, ZnO and NiFe₂O₄/MWCNTs/ZnO nanocomposites. It shows that the characteristic XRD patterns of the NiFe₂O₄, MWCNTs and ZnO are present in the NiFe₂O₄/MWCNTs/ZnO nanocomposite pattern. The characteristic peaks at $2\theta = 26.08^\circ$ and 43.08° are attributed to graphite structure belonging to the (002) and (100) planes of the MWCNTs [33, 44]. The diffraction peaks of the NiFe₂O₄ sample are observed at $2\theta = 30.34^\circ, 35.74^\circ, 37.35^\circ, 43.43^\circ, 53.90^\circ, 57.46^\circ$ and 63.11° , which can be indexed to (220), (311), (222), (400), (422), (511) and (440) planes of the face centered cubic structure of NiFe₂O₄, respectively, space group Fd-3m, which is consistent with the JCPDS data file no. 54-0964 [45, 46]. The diffraction peaks of the ZnO sample are observed at $2\theta = 31.75^\circ, 34.45^\circ, 36.25^\circ, 47.6^\circ, 56.54^\circ, 62.86^\circ, 66.18^\circ, 67.95^\circ$ and 69.08° , which correspond to the (100), (002), (101), (102), (110), (103), (200), (112) and (201) crystal planes of the hexagonal ZnO phase (JCPDS no. 79-0206) [24, 38, 47]. Fig. 2 shows that in the XRD pattern of the NiFe₂O₄/MWCNTs/ZnO sample no other peak related to impurities was detected which further confirms that the synthesized nanocomposite is of high purity and having good crystallinity. The average crystallite size of the nanocomposites was calculated from the most intense reflection using Debye–Scherrer's formula [48]:

$$D = 0.89 \lambda / (B \cos \theta) \quad (3)$$

where $\lambda = 0.154056$ nm, B: the full peak width at half maximum value, θ : the diffraction angle. The NiFe₂O₄ and the ZnO crystallite sizes were estimated to be 34.6 nm and 19.5 nm, respectively.

Fig. 2. XRD patterns of MWCNTs, ZnO, NiFe₂O₄, and NiFe₂O₄/MWCNTs/ZnO nanocomposites.

FTIR spectra (Fig. 3) were employed to further prove the formation of the above samples. The spectra of the raw and the oxidized MWCNTs are presented in Fig. 3(a) and the spectra of ZnO, NiFe₂O₄ and NiFe₂O₄/MWCNTs/ZnO are presented in Fig. 3(b). For the raw MWCNTs, there are no significant bands except the sharp band around 1540 cm⁻¹ corresponding to C=C stretch vibration originating from the surface of the tubes [49] and at 3452 cm⁻¹ corresponds to O–H stretching vibrations of adsorbed water molecules [12]. As a result of the oxidation process of the MWCNTs, the bands in the area 1000-1300 cm⁻¹ are attributed to C–O bending frequencies [50-52]. The band around 1730 cm⁻¹ are corresponding to C=O stretch vibration [53, 54]. Also, the bands between 2850-3000 cm⁻¹ correspond to the C–H stretching vibrations. This indicate that the –COOH group have been successfully introduced on the outer walls of the MWCNTs which make them active to attaching covalently with the decorated molecules.

Metal ions in ferrites are situated in two different sub-lattices designated as tetrahedral and octahedral according to the oxygen nearest neighbor's geometrical configuration. It has been reported that the band in the high frequency range from 650 to 550 cm⁻¹ is related to the tetrahedral A-site, while the band in the low frequency range from 450 to 385 cm⁻¹ is related to the octahedral B-site [55, 56]. In Fig. 3(b), the sharp peaks at 601 cm⁻¹ and 417 cm⁻¹ correspond to the intrinsic vibrations of tetrahedral and octahedral metal-O bounds, respectively. The peak in the area around 400–500 cm⁻¹ is assigned to

the Zn–O vibration [57], while the combination of the ferrite and the ZnO peaks appears at around 601 cm^{-1} [24]. The weaker band in the area 1100–1300 cm^{-1} corresponds to the vibration of the NO_3 ions which are generated during the preparation and appeared with a very less intensity [58].

Fig. 3. FTIR spectrum of: (a) Pristine and oxidized MWCNTs, (b) ZnO, NiFe_2O_4 and $\text{NiFe}_2\text{O}_4/\text{MWCNTs}/\text{ZnO}$ prepared nanocomposites.

3.1.2. Morphology and composition

The morphology of the samples was studied using SEM, EDX and TEM as shown in Figs. 4, 5 and 6. Fig. 4 (a-d) shows the pure NiFe_2O_4 and ZnO prepared NPs, and raw MWCNTs appear in the part e. The NPs sizes are estimated from the TEM images and were found to be in the nanoscale. As can be seen in Fig. 5, the surface of the MWCNTs is successfully decorated with the NiFe_2O_4 and the ZnO NPs. The NiFe_2O_4 and the ZnO NPs are bound as a hybrid and decorated the surface of the MWCNTs leading to the creation of the interaction between the NiFe_2O_4 and the ZnO NPs with each other and between them and the MWCNTs. The NiFe_2O_4 in the hybrid is much bigger than the ZnO NPs and the sizes of both pure NiFe_2O_4 and ZnO are smaller in the hybrid. The average size of the NiFe_2O_4 NPs on the surface of the MWCNTs is about 50 nm which is smaller than that of pure NiFe_2O_4 NPs (Figs. 4, and 5) indicating that the existence of MWCNTs has led to the crystallization of NiFe_2O_4 and ZnO NPs with smaller sizes. Hence, the introduction of MWCNTs as a good support will make the loaded NiFe_2O_4 and ZnO achieve a further enhancement of the charge separation and suppressing the electron-hole recombination in photocatalytic processes [13]. The elemental mapping images and EDS spectra (Fig. 6)

were also inspected and displayed. The sample contains O, Fe, Ni, Zn, C elements, further indicating that NiFe₂O₄/MWCNTs/ZnO nanocomposite is successfully prepared.

The work in ref. [13] is the most close example to our present study where a novel NiFe₂O₄/MWCNTs hybrid nanocomposite has been synthesized via the hydrothermal method to remove the CR dye from its solutions using solar radiation time of 300 minutes reaching an efficiency of up to 90%. We can observe the formation of NiFe₂O₄ NPs in a larger size compared to the sizes formed on the surface of CNTs in this work and the morphology was similar to the mixture. That is due to the nature of the formation of the NiFe₂O₄ NPs, which are formed in large sizes compared to e.g. Fe₃O₄ ferrite which is formed in smaller sizes, thus allowing for homogeneous decoration of the entire surface of the MWCNTs.

In this work, the defects that we have seen in the morphology were due to the relatively short time applied in the MWCNTs treatment (only 7 hours). Since the treatment process (oxidation) of the pristine MWCNTs is the first essential step to the success of any functionalization process for the carbon nanotube surface, the time required for efficient processing must be longer.

Fig. 4. (a), (b) SEM and TEM images of NiFe_2O_4 nanoparticles, respectively. (c), (d) SEM and TEM images of ZnO nanoparticles, respectively, and (e) SEM image of raw MWCNTs.

Fig. 5. (a) SEM, and (b) TEM images of $\text{NiFe}_2\text{O}_4/\text{MWCNTs}/\text{ZnO}$ nanocomposite.

Fig. 6. (a) SEM image and (b) Energy-dispersive x-ray diffraction (EDX) spectrum and (c, d) Map of the elements distribution of NiFe₂O₄/MWCNTs/ZnO hybrid nanocomposite.

3.1.3 UV–Vis Diffuse Reflectance Spectroscopy (DRS) and Electrochemical Impedance Spectroscopy (EIS)

The optical absorption technique can be employed for an examination of optically induced transitions and can give information about energy gap (E_g) in crystalline materials, non-crystalline materials and the bond structure [59]. In the absorption process an electron transition from a lower to higher energy state happens via the absorption of a photon of specified energy. Hence, changes in the radiation absorbed can decide possible electron transitions. Fundamental absorption shows a surprising change in absorption and can be used in the determination of the optical band gap (E_g) (see equation 4).

Reflectance spectroscopy technique is closely related to the UV/Vis spectroscopy, in that both of them use visible light to excite valence electrons to empty orbitals. The difference is that in diffuse reflectance, we measure the relative change in the amount of light reflected off of a surface, whereas in UV/Vis spectroscopy we measure the relative change of transmittance of light as it passes through a solution.

UV–Vis diffuse reflectance spectroscopy (DRS) was used to determine the optical absorption properties of the samples. Fig. 7(a) gives the UV-Vis DRS spectra of the NiFe₂O₄ and the NiFe₂O₄/MWCNTs/ZnO composites. ZnO has a sharp optical-absorption edge at about 386 nm, so it absorbs UV light to a degree higher than visible light. Fig. 7(a) showed that the NiFe₂O₄ absorbs the light in the whole region (200 to 800 nm) due to its small band gap (1.64 eV) which is consistent with the previous observations [13, 33]. However, NiFe₂O₄ is rarely applied as a visible light photocatalyst alone since the electrons could not survive long in the conduction band and it will return to the valence band (h^+). Consequently photodegradation processes do not occur as it should [60], but synergistic effect between NiFe₂O₄, ZnO and MWCNTs can lead to a significant enhancement in photo-activity due to the effective charge transfer from the NiFe₂O₄ to the ZnO and then to the MWCNTs and thus suppresses recombination of electron–hole pairs in the composite [33]. By extrapolating the linear portion near the commencement of absorption edge to x-axis, the optical band gap (E_g) of NiFe₂O₄ and NiFe₂O₄/MWCNTs/ZnO nanocomposites were found to be 1.64 eV and 2.3 eV, respectively. The band gap of the hybrid nanocomposite was calculated as the average value obtained from the absorption spectrum (equation 4 and Fig. 7a) and the Tauc plot (equation 5 and Fig. 7c). The estimated band gaps are obtained from Fig. 7a by dividing 1240 by the intersection point of the extension line of the tangent of the curve (NiFe₂O₄ and NiFe₂O₄/MWCNTs/ZnO) and the abscissa using the equation [24]:

$$E_g = hc / \lambda_g$$

$$E_g (eV) = 1240 / \lambda_g \quad (4)$$

where h is Planck constant and c is the speed of light. Results also were expressed from the plots $(\alpha h\nu)^2$ vs. photon energy ($h\nu$) as shown in Fig. 7(b, c) by Tauc equation [61-63]:

$$(\alpha h\nu)^2 = A (h\nu - E_g) \quad (5)$$

where A is a constant that depends on the transition probability, and α is the absorption coefficient [64].

Compared to the known absorption curves of zinc oxide, the bias of the absorption spectra of the hybrid compound in the visible light area indicates that the combination of the NiFe₂O₄, the MWCNTs

and the ZnO has enhanced the absorption efficiency of the light. This make the composite more effective and efficient in the photocatalytic processes to remove dyes contaminants under the sun's radiation.

In addition to the good light response ability of the light, good charge separation was supported by electrochemical impedance spectroscopy (EIS) to further characterize the transfer of the photogenerated electron-hole pairs. As showed in (Fig. 7d), the NiFe₂O₄/MWCNTs/ZnO hybrid photocatalyst showed much smaller semicircle than the NiFe₂O₄ and the NiFe₂O₄/MWCNTs, indicating that the NiFe₂O₄/MWCNTs/ZnO photocatalyst exhibited the lowest charge-transfer resistance. Therefore, the existence of the NiFe₂O₄ and the ZnO in the surface layer of the MWCNTs could effectively separate the photogenerated electron and photogenerated holes produced by the NiFe₂O₄ and the ZnO and subsequently, hindering the recombination process [19].

Fig. 7. (a) Absorption versus wavelength spectra of NiFe₂O₄ and NiFe₂O₄/MWCNTs/ZnO composites. (b, c) Plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for NiFe₂O₄ and NiFe₂O₄/MWCNTs/ZnO composites. (d) Electrochemical impedance spectroscopy (EIS) curves (Cole–Cole semicircles (M'' vs. M')) of the NiFe₂O₄, the NiFe₂O₄/MWCNTs and the NiFe₂O₄/MWCNTs/ZnO nanocomposites at room temperature.

3.1.4 Magnetic properties

The magnetic properties of the NiFe_2O_4 and the $\text{NiFe}_2\text{O}_4/\text{MWCNTs}/\text{ZnO}$ samples were performed by VSM at room temperature with an applied magnetic field up to 20 KOe. The saturation magnetization (M_s), remanence (M_r) and coercivity (H_c) of the samples are shown in Table I.

Table I. Magnetic parameters of NiFe_2O_4 and $\text{NiFe}_2\text{O}_4/\text{MWCNTs}/\text{ZnO}$ nanocomposites at room temperature.

Sample	Magnetization (M_s) (emu/g)	Coercivity (H_c) (Oe)	Remanence (M_r) (emu/g)
NiFe_2O_4	37.77	157.67	6.42
$\text{NiFe}_2\text{O}_4/\text{MWCNTs}/\text{ZnO}$	17.02	159.45	3.28

The hysteresis loops shown in Fig. 8 revealed that the NiFe_2O_4 and the $\text{NiFe}_2\text{O}_4/\text{MWCNTs}/\text{ZnO}$ nanocomposites have a superparamagnetic behavior at room temperature. The saturation magnetization (M_s) value of the $\text{NiFe}_2\text{O}_4/\text{MWCNTs}/\text{ZnO}$ hybrid (17.021 emu g⁻¹) is much lower than that of the pure NiFe_2O_4 (37.8 emu g⁻¹), which is ascribed to the existence of other nonmagnetic material, i.e. the MWCNTs and the ZnO [24, 38, 41]. Also, as we found before in the structural properties, the size of the NPs of nickel ferrite formed on the surface of the MWCNTs is smaller than that of the NiFe_2O_4 bare material. So, in this case, the spins on the surface of the NPs are canted and hence the magnetization is reduced [65, 66].

Mainly, the magnetic order in a spinel ferrites material such as NiFe_2O_4 is due to the super exchange interaction mechanism happening between the metal ions in the tetrahedral and the octahedral sublattices. The spinel can be of normal or inverse structure according to the distribution of the cations on the interstitial tetrahedral (A) and octahedral (B) sites [67]. In the normal structure all divalent A^{2+} (trivalent B^{3+}) cations occupy tetrahedral (octahedral) lattice sites exclusively, while in the inverse, the trivalent B^{3+} cations distributed equally across the tetrahedral (A) and octahedral (B) sites and the divalent A^{2+} cations only occupy the B sites. A mixture of both structures is quantified by the inversion parameter λ . Here, λ is the fraction of A^{2+} -cations occupying B sites. $\lambda = 0$ denotes a normal ($\text{A}^{2+}[\text{B}^{3+}\text{B}^{3+}]\text{O}_4$) and $\lambda = 1$ denotes a fully inverse spinel lattice ($\text{B}^{3+}[\text{A}^{2+}\text{B}^{3+}]\text{O}_4$) [67-70].

The net magnetization in the inverse spinel NiFe_2O_4 is the result of these two sub-lattices in which the Ni^{2+} ions incline to occupy the B-site, and Fe^{3+} ions occupy both A- and B-sites [71, 72] as the chemical composition formula $[\text{Fe}^{3+}][\text{Ni}^{2+}\text{Fe}^{3+}]\text{O}_4$ [72]. In the bulk inverse spinel NiFe_2O_4 , the distribution of the Fe^{3+} ions of high magnetic moment (5 μ_B) is equal on both the A- and the B-sites [68]. The magnetic moments of the Fe^{3+} cations is equivalent to the antiferromagnetic conjugation between the A- and B sites, only the Ni^{2+} cations is taken into account for the net magnetization of 2 μ_B /f.u [68].

The magnetic behavior of the NPs is determined by the structural, the magnetic and the surface properties of the individual NPs and the interactions among them. Practically, inter-particle interactions are inevitable mainly due to van der Waals forces and the interaction of magnetic dipolar of magnetic moments. By reducing the inter-particle distances in magnetic NPs, superparamagnetic relaxation, for instance, is affected remarkably [73, 74]. The mechanism can be explained in terms of spin-glass like state, spin canting and spin-disorder in the surface layers of NPs because of the broken exchange interaction, local chemical disorder and an unlike local symmetry for the surface atoms [71]. On the surface of the ferrite NPs, the spins can be in a disturbed state because of several reasons: (a) Differences in coordination of the surface cations can lead to a distribution of the net exchange fields, whether positive or negative with respect to a cations sub-lattice; (b) because an oxygen ion mediated the super exchange interaction, and if an oxygen ion is missing, the exchange bonds will be broken [75]. In magnetic NPs, the most studied finite-size effects are the superparamagnetic limit and the single domain limit [76]. The reduction of the grain size can strongly affects the magnetic properties of the materials because of the influence of the thermal energy over the ordering of the magnetic moment causing a paramagnetic relaxation phenomenon [74]. Depending on the magnetic domain theory, there is a critical size d_s of single domain particles. If the particle size D is larger than d_s , the magnetic particles are multi-domain particles and their coercivity (H_c) increases with the decrease of D . With reduced particle size to a critical diameter, the value of coercivity increases to a maximum value. When the particle size decreases furthermore below the critical size, the coercivity decreases toward zero and the particles become superparamagnetic [33, 77]. This may explain why the coercivity of the hybrid nanocomposites is slightly larger than that of the unsupported ferrite [33] as in Table I. Also, as in the table, the remanence (M_r) of both compounds is very small and almost equal to zero. The impermanent magnetization ($M_r=0$) after the magnetic field removal in superparamagnetic materials is an important feature for carriers in magnetic target [78].

Although the M_s value of the hybrid nanocomposite is much lower than that of the NiFe_2O_4 , it is still relatively high and ensures high magnetic response toward an external magnetic field. The $\text{NiFe}_2\text{O}_4/\text{MWCNTs}/\text{ZnO}$ hybrid composite showed strong attraction with a magnet, which is important for their applications in the biological field to eliminate organic pollutants and in for an economical approach for the treatment of industrial wastewater, as the nanocomposite can be reused.

Fig. 8. Magnetic hysteresis loops of NiFe₂O₄ and NiFe₂O₄/MWCNTs/ZnO nanocomposites at room temperature.

3.2. Photocatalytic activity of the NiFe₂O₄/MWCNTs/ZnO hybrid photocatalyst

The photocatalytic activity for decolorization of Methylene Blue (MB) dye (molecular formula: C₁₆H₁₈ClN₃S.3H₂O) as an example of the sun radiation driven photocatalytic activity using NiFe₂O₄/MWCNTs/ZnO hybrid nanocomposite catalyst compared with the adsorption process has been investigated (Fig. 9a). In addition, the photodegradation activity is compared with the performance of NiFe₂O₄ and ZnO under solar light irradiation for 300 minutes. Then, to describe the corresponding experimental data and to evaluate the mechanism of photocatalytic process, the pseudo-first-order kinetic model was applied to fit the data (see the correlation factors (R^2) of the catalysts in Fig. 9b).

With normal pH, the decolorization efficiency of the MB solution for 300 minutes under solar light irradiation using NiFe₂O₄/MWCNTs/ZnO, NiFe₂O₄ and ZnO catalysts were 73.02%, 11.48% and 43.78%, respectively, and the corresponding decolorization rate constants (k_{app}) were 0.00438 min⁻¹, 4.12857E⁻⁴ min⁻¹ and 0.002 min⁻¹, respectively, according to the pseudo first-order kinetic model (equation 2). The NiFe₂O₄/MWCNTs/ZnO hybrid showed a photocatalytic efficiency (η) of 73.02% at a pH = 6.66 (pH of the dye solution) and 98% with pH = 11.55 at the same conditions (the same irradiation time and the same concentration of the catalyst) (Fig. 10).

Fig. 9. (a) Adsorption and photocatalytic efficiency of MB dye degradation using $\text{NiFe}_2\text{O}_4/\text{MWCNTs}/\text{ZnO}$ photocatalyst for 300 min. (b) $\ln(C_0/C_t)$ versus irradiation time for MB degradation using $\text{NiFe}_2\text{O}_4/\text{MWCNTs}/\text{ZnO}$, ZnO , and NiFe_2O_4 nanocatalysts, where pseudo-first-order kinetic model was applied to describe corresponding experimental data. (Normal pH, catalyst concentration: 1.0 g/L, concentration of MB dye solution: 20 mg/L).

Fig. 10. (a) Photocatalytic efficiency of MB dye degradation as a function of solar light irradiation time using $\text{NiFe}_2\text{O}_4/\text{MWCNTs}/\text{ZnO}$ nanocomposite for 300 min with different pH values (3, 6.66 (normal) and 11.55). (b) Catalyst reuse for five cycles under the same conditions at pH = 6.7 (normal) and pH = 11.6.

Obviously, from Fig. 9b, in the presence of the NiFe₂O₄, there is no significant increase of the MB degradation, and ZnO has more excellent photocatalytic efficiency compared to NiFe₂O₄.

The reaction mechanism for the MB dye photo-degradation using the ZnO, the NiFe₂O₄ and the NiFe₂O₄/MWCNTs/ZnO photocatalysts is similar. The first step (before starting the exposure to the irradiation) begins by adsorbing the dye on the catalyst surface through stirring, which is an essential step before the photocatalytic interaction [13, 33, 38, 79] (Fig. 11). The good removal efficiency for the MB dye by the NiFe₂O₄/MWCNTs/ZnO corresponds to UV-Vis DRS results which showed a high absorption of the irradiation in the visible and ultraviolet regions. Fig. 11 illustrates the photocatalytic decolorization of the MB dye using the NiFe₂O₄/MWCNTs/ZnO photocatalyst under solar light irradiation and illustrates the magnetic separation. In order to compare the performance of the NiFe₂O₄/MWCNTs/ZnO photocatalyst to the other similar photocatalysts, the photocatalytic activity of other related magnetic carbon nanotubes (Mag-CNTs) and related ZnO/carbon nanotubes nanocomposites are shown in Table II.

Table II. Photocatalytic activity of related mediated composites.

Catalyst	Pollutant	Optimization conditions	Ref.
NiFe ₂ O ₄ /MWNTs	nitrophenols (phenol, o-nitrophenol, p-nitrophenol and picric acid)	0.85% degradation ratio ($k_{app} = 0.00468 \text{ min}^{-1}$) after 400 min irradiation time in the presence of H ₂ O ₂ under UV light irradiation.	[33]
NiFe ₂ O ₄ /MWNTs	Congo red (CR) dye	99% degradation ratio ($k_{app} = 0.01433 \text{ min}^{-1}$) after 300 min irradiation time in the presence of H ₂ O ₂ under visible-light irradiation.	[13]
NiFe ₂ O ₄ /MWCNT	recalcitrant sulfamethoxazole (SMX)	100% degradation ratio ($k_{app} = 0.041 \text{ min}^{-1}$) after 120 min irradiation time in the presence of H ₂ O ₂ under UV-A light.	[37]
ZnFe ₂ O ₄ /MWCNTs	methylene blue (MB) dye	99% degradation ratio after 6 hours irradiation time in the presence of H ₂ O ₂ under simulated solar light irradiation.	[80]
Ni _x Co _{1-x} Fe ₂ O ₄ /CNT NPs	methylene blue (MB) dye	88% degradation ratio after 50 min irradiation time under visible-light source (a 200W electric bulb).	[81]
MWCNTs-ZnO	methylene blue (MB) dye	92% degradation ratio after 120 min irradiation time under the visible light irradiation.	[34]
ZnO-Ag/MWCNT	Phenol	81% degradation ratio for 100 ppm phenol after 240 min irradiation time under UV-A light irradiation.	[82]
MWCNTs-ZnO	methyl orange (MO) dye	94% degradation ratio after 30 min irradiation time under UV irradiation.	[83]
nitrogen-doped carbon nanotubes (N-CNT/ZnO)	Phenol	Apparent constant (k_{app}) of the degradation = 0.260 min^{-1} after 30 min irradiation time under simulated solar light irradiation.	[35]
NiFe ₂ O ₄ /ZnO	Congo red (CR) dye	94.55% degradation ratio after 10 min irradiation time under simulated solar light irradiation.	[38]
Ce-doped ZnO/CNT	methylene blue (MB) dye	96.4% degradation ratio after 250 min irradiation time under UV irradiation.	[84]
(ZnO	reactive blue 203	99.1% degradation ratio after 20 min irradiation time under	[36]

(NPs)/MWCNTs	(RB203) dye	UV radiation intensity of 23 mW/cm ² .	
ZnO/MWCNT	methylene blue (MB) dye	93% degradation ratio after 40 min irradiation time under UV light irradiation (125 W mercury lamp).	[85]

Fig. 11. Diagram illustrates the photocatalytic decolorization of MB dye using NiFe₂O₄/MWCNTs/ZnO hybrid catalyst under solar light irradiation and illustrates the magnetic separation.

3.2.1. Reproducibility

Recycling can effectively reduce the waste of resources and environmental pollution [16, 86]. The reproducibility of the NiFe₂O₄/MWCNTs/ZnO photocatalyst for 5 cycles was displayed in Fig. 10b. It could be clearly seen that the photocatalyst could be used at least 5 cycles with a little loss of photocatalytic efficiency, indicating that it had good photochemical stability. The loss of photocatalytic efficiency after five cycles for MB dye degradation might be ascribed to the sample loss during the magnetic separation and recovery process.

3.2.2. Mechanism of photocatalytic decolorization process

Based on the experimental results and some previously submitted reports [2, 38] on the mechanism of the photocatalytic decolorization to remove organic pollutants, the presented mechanism can be described as follows: at first, the MB dye molecules are adsorbed on the outer surfaces of the NPs on the catalyst. By exposure to solar radiation, electrons (e⁻) in the valence band (VB) of NiFe₂O₄ and ZnO are excited to the conduction band (CB). This will simultaneously lead to generate gaps with positive charge in the VB. Due to the difference in energy bands between the nickel ferrite, the carbon

nanotubes and the ZnO, the photo-generated electrons (e^-) can be transferred to the ZnO and to the MWCNTs instantly. This causes charge separation and stabilization, subsequently hindering the recombination process [40, 41]. After that, the generated electrons react with O_2 contained in the solution to yield O^{2-} ions which will further react with H_2O forming $\cdot OH$ hydroxyl radical [24]. It is established that the photocatalytic reactive species are capable of attacking and degrading organic pollutants in the photocatalytic reaction [87-89] .

The VB potential of the ZnO is more positive than that of the $NiFe_2O_4$ while the CB potential of $NiFe_2O_4$ is more negative than that of the ZnO. Therefore, the photo-produced electrons (e^-) in the $NiFe_2O_4$ will be transferred across the interface of the $NiFe_2O_4/ZnO$ hybrid to the surface of ZnO [38] then to the MWCNTs. The active species included in the photocatalytic degradation reaction are photo-generated holes (h^+), hydroxyl radicals ($\cdot OH$) and superoxide radical anions ($O_2^{\cdot -}$). The surface-adsorbed MB molecules were attacked by the active species (free radicals) to become simple compounds such as CO_2 , H_2O and other byproducts.

For both zinc oxide and nickel ferrite in particular this low efficiency in the photocatalytic degradation is due to the recombination process of the photo-induced electron-hole pairs that happen immediately and does not allow the pairs to flow and interact with the dye solution. The high photocatalytic efficiency at the high values of the pH is due to the increase of the amount of hydroxide anions (OH^-) in the solution which contribute to the decolorization process and this is the same effect of other oxidizing agents such as hydrogen peroxide (H_2O_2).

According to the our control sample and as in shown in previous studies on other dyes [24], it is worth mentioning that the solar radiation alone contributes in the breakdown of the bonds in methylene blue dye with degradation efficiency up to 10% at the end of the irradiation time. This is due to the direct effect of photons of solar radiation. Just as photons directly generate electron-gap pairs by photocatalysis and then free radicals are created, photons directly break the bonds of the dye and also indirectly affect in increasing the kinetic energy of free radicals formed.

Fig. 12. Diagram of the proposed mechanism of MB dye removal by photocatalytic decolorization over NiFe₂O₄/MWCNTs/ZnO hybrid catalyst.

Based on these results, the most likely mechanism of the photocatalytic degradation is illustrated in Fig. 12 and equations 6- 9. The main process is as the following:

Based on the structural, optical and magnetic properties of the NiFe₂O₄/MWCNTs/ZnO photocatalyst, it is shown that the nanocomposite possesses good performance in the removal of the dyes from solutions through the processes of absorption and photocatalysis under solar radiation. Taking into account the need to prolong the time required to oxidize the carbon nanotubes; we can avoid those defects related to morphology and ensure a homogeneous decorating process on the entire surface of the carbon nanotubes, thus increasing the photocatalytic efficiency.

As a result, the NiFe₂O₄/MWCNTs/ZnO is a novel multifunctional photocatalyst for an economic treatment of dyed wastewater with the advantages of low cost, good adsorption, high photocatalytic activity with magnetically separation possibility.

4. Conclusions

Novel multifunctional NiFe₂O₄/MWCNTs/ZnO hybrid nanocomposite was synthesized by the hydrothermal and the co-precipitation methods and used as an efficient photocatalyst with good adsorption and photocatalytic activity. The NiFe₂O₄/MWCNTs/ZnO hybrid composite exhibited enhanced photocatalytic activity compared to the NiFe₂O₄ and to the ZnO for the decolorization of MB as a model pollutant under solar light irradiation for 5 hours. High removal efficiency was obtained at relatively high values of the pH, when the catalyst concentration was 1.0 g/L and the concentration of MB dye solution was 20 mg/L. Pseudo-first-order kinetic model was applied to demonstrate the corresponding experimental data. It was found that the combination of the NiFe₂O₄, the MWCNTs and the ZnO enhances the absorption efficiency of light with band gap of 2.3 eV for the NiFe₂O₄/MWCNTs/ZnO hybrid catalyst. In the photocatalytic degradation reaction, the $\cdot\text{OH}$, h^+ , $\text{O}_2^{\cdot-}$ free radicals attack the surface-adsorbed MB molecules and turn them to simple compounds such as CO₂, H₂O and other products. It was shown that the NiFe₂O₄/MWCNTs/ZnO hybrid nanocomposite is a super paramagnetic at room temperature with saturation magnetization (M_s) of 17.02 emu/g. The hybrid composite is of potential in the biological applications field specifically to remove organic pollutants and in economic treatment of the industrial wastewater. The decolorization efficiency of the MB solution for a duration of 300 minutes using the NiFe₂O₄/MWCNTs/ZnO, the NiFe₂O₄ and the ZnO catalysts were 73.02%, 11.48% and 43.78%, respectively, with corresponding apparent rate constant (k_{app}) of 0.00438 min⁻¹, 4.12857E⁻⁴ min⁻¹ and 0.002 min⁻¹, respectively.

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References

- [1] P. Zhang, B.Y. Guan, L. Yu, X.W.D. Lou, Facile synthesis of multi-shelled ZnS-CdS cages with enhanced photoelectrochemical performance for solar energy conversion, *Chem*, 4 (2018) 162-173.
- [2] Z. Lu, G. Zhou, M. Song, X. Liu, H. Tang, H. Dong, P. Huo, F. Yan, P. Du, G. Xing, Development of magnetic imprinted PEDOT/CdS heterojunction photocatalytic nanoreactors: 3-Dimensional specific recognition for selectively photocatalyzing danofloxacin mesylate, *Applied Catalysis B: Environmental*, 2019, doi: 10.1016/j.apcatb.2019.118433.
- [3] J. Byun, W. Huang, D. Wang, R. Li, K.A. Zhang, CO₂-Triggered Switchable Hydrophilicity of a Heterogeneous Conjugated Polymer Photocatalyst for Enhanced Catalytic Activity in Water, *Angewandte Chemie International Edition*, 57 (2018) 2967-2971.

- [4] Z. Lin, C. Du, B. Yan, C. Wang, G. Yang, Two-dimensional amorphous NiO as a plasmonic photocatalyst for solar H₂ evolution, *Nature communications*, 9 (2018) 4036.
- [5] T. Su, Q. Shao, Z. Qin, Z. Guo, Z. Wu, Role of interfaces in two-dimensional photocatalyst for water splitting, *Acs Catalysis*, 8 (2018) 2253-2276.
- [6] Z. Lu, F. He, C.Y. Hsieh, X. Wu, M. Song, X. Liu, Y. Liu, S. Yuan, H. Dong, S. Han, Magnetic Hierarchical Photocatalytic Nanoreactors: Toward Highly Selective Cd²⁺ Removal with Secondary Pollution Free Tetracycline Degradation, *ACS Applied Nano Materials*, 2 (2019) 1664-1674.
- [7] K. Chattopadhyay, S. Maiti, S. Pal, Recent advances in low temperature, solution processed morphology tailored ZnO nano-architecture for electron emission and photocatalysis applications, *CrystEngComm*, 17 (2015) 9264-9295.
- [8] H. Zhu, R. Jiang, L. Xiao, Y. Chang, Y. Guan, X. Li, G. Zeng, Photocatalytic decolorization and degradation of Congo Red on innovative crosslinked chitosan/nano-CdS composite catalyst under visible light irradiation, *Journal of Hazardous Materials*, 169 (2009) 933-940.
- [9] J. Xu, Z. Cao, Y. Zhang, Z. Yuan, Z. Lou, X. Xu, X. Wang, A review of functionalized carbon nanotubes and graphene for heavy metal adsorption from water: Preparation, application, and mechanism, *Chemosphere*, 195 (2018) 351-364.
- [10] T. Mühl, D. Elefant, A. Graff, R. Kozhuharova, A. Leonhardt, I. Mönch, M. Ritschel, P. Simon, S. Groudeva-Zotova, C. Schneider, Magnetic properties of aligned Fe-filled carbon nanotubes, *Journal of applied physics*, 93 (2003) 7894-7896.
- [11] V.D. Punetha, S. Rana, H.J. Yoo, A. Chaurasia, J.T. McLeskey Jr, M.S. Ramasamy, N.G. Sahoo, J.W. Cho, Functionalization of carbon nanomaterials for advanced polymer nanocomposites: A comparison study between CNT and graphene, *Progress in Polymer Science*, 67 (2017) 1-47.
- [12] M. Bahgat, A.A. Farghali, W. El Rouby, M. Khedr, M.Y. Mohassab-Ahmed, Adsorption of methyl green dye onto multi-walled carbon nanotubes decorated with Ni nanoferrite, *Applied Nanoscience*, 3 (2013) 251-261.
- [13] H.-Y. Zhu, R. Jiang, S.-H. Huang, J. Yao, F.-Q. Fu, J.-B. Li, Novel magnetic NiFe₂O₄/multi-walled carbon nanotubes hybrids: facile synthesis, characterization, and application to the treatment of dyeing wastewater, *Ceramics International*, 41 (2015) 11625-11631.
- [14] X. Cui, X. Yang, X. Xian, L. Tian, H. Tang, Q. Liu, Insights into highly improved solar-driven photocatalytic oxygen evolution over integrated Ag₃PO₄/MoS₂ heterostructures, *Frontiers in chemistry*, 6 (2018) 123.
- [15] Y. Guo, P. Wang, J. Qian, Y. Ao, C. Wang, J. Hou, Phosphate group grafted twinned BiPO₄ with significantly enhanced photocatalytic activity: Synergistic effect of improved charge separation efficiency and redox ability, *Applied Catalysis B: Environmental*, 234 (2018) 90-99.
- [16] Z. Lu, G. Zhou, M. Song, D. Wang, P. Huo, W. Fan, H. Dong, H. Tang, F. Yan, G. Xing, Magnetic functional heterojunction reactors with 3D specific recognition for selective photocatalysis and synergistic photodegradation in binary antibiotic solutions, *Journal of Materials Chemistry A*, 7 (2019) 13986-14000.
- [17] K.K. Gangu, S. Maddila, S.B. Jonnalagadda, A review on novel composites of MWCNTs mediated semiconducting materials as photocatalysts in water treatment, *Science of the Total Environment*, 646 (2019) 1398-1412.
- [18] Z. Lu, Z. Yu, J. Dong, M. Song, Y. Liu, X. Liu, Z. Ma, H. Su, Y. Yan, P. Huo, Facile microwave synthesis of a Z-scheme imprinted ZnFe₂O₄/Ag/PEDOT with the specific recognition ability towards improving photocatalytic activity and selectivity for tetracycline, *Chemical Engineering Journal*, 337 (2018) 228-241.
- [19] Z. Lu, J. Peng, M. Song, Y. Liu, X. Liu, P. Huo, H. Dong, S. Yuan, Z. Ma, S. Han, Improved recyclability and selectivity of environment-friendly MFA-based heterojunction imprinted photocatalyst for secondary pollution free tetracycline orientation degradation, *Chemical Engineering Journal*, 360 (2019) 1262-1276.
- [20] S. Liu, M. Zheng, R. Chen, Z. Wang, One-pot synthesis of an AgBr/ZnO hierarchical structure with enhanced photocatalytic capacity, *RSC Advances*, 7 (2017) 31230-31238.
- [21] M. Pelaez, P. Falaras, V. Likodimos, K. O'Shea, A. Armah, P.S. Dunlop, J.A. Byrne, D.D. Dionysiou, Use of selected scavengers for the determination of NF-TiO₂ reactive oxygen species during the degradation of microcystin-LR under visible light irradiation, *Journal of Molecular Catalysis A: Chemical*, 425 (2016) 183-189.

- [22] S. Fang, M. Sun, Y. Zhou, Q. Liang, Z. Li, S. Xu, Solvothermal synthesis of CdS QDs/MWCNTs nanocomposites with high efficient photocatalytic activity under visible light irradiation, *Journal of Alloys and Compounds*, 656 (2016) 771-776.
- [23] X. Song, Y. Li, Z. Wei, S. Ye, D.D. Dionysiou, Synthesis of BiVO₄/P25 composites for the photocatalytic degradation of ethylene under visible light, *Chemical Engineering Journal*, 314 (2017) 443-452.
- [24] N. Jamarun, S. Arief, Synthesis of ZnO-NiFe₂O₄ Magnetic Nanocomposites by Simple Solvothermal Method for Photocatalytic Dye Degradation Under Solar Light, *Oriental Journal of Chemistry*, 32 (2016) 1411-1419.
- [25] Q. Zhou, J.Z. Wen, P. Zhao, W.A. Anderson, Synthesis of vertically-aligned zinc oxide nanowires and their application as a photocatalyst, *Nanomaterials*, 7 (2017) 9.
- [26] S.M. El-Sheikh, T.M. Khedr, G. Zhang, V. Vogiazzi, A.A. Ismail, K. O'Shea, D.D. Dionysiou, Tailored synthesis of anatase-brookite heterojunction photocatalysts for degradation of cylindrospermopsin under UV-Vis light, *Chemical Engineering Journal*, 310 (2017) 428-436.
- [27] Z. Jin, Q. Zhou, Y. Chen, P. Mao, H. Li, H. Liu, J. Wang, Y. Li, Graphdiyne: ZnO Nanocomposites for High-Performance UV Photodetectors, *Advanced Materials*, 28 (2016) 3697-3702.
- [28] S. Sunitha, A.N. Rao, J. Karthikeyan, Synthesis of novel cobalt doped zinc oxide/carbon nano composite for the photocatalytic degradation of acid blue 113, *Oriental Journal of Chemistry*, 31 (2015) 107-112.
- [29] Z. Lu, M. He, L. Yang, Z. Ma, L. Yang, D. Wang, Y. Yan, W. Shi, Y. Liu, Z. Hua, Selective photodegradation of 2-mercaptobenzothiazole by a novel imprinted CoFe₂O₄/MWCNTs photocatalyst, *RSC Advances*, 5 (2015) 47820-47829.
- [30] H. Zhu, Y. Fu, R. Jiang, J. Yao, L. Liu, Y. Chen, L. Xiao, G. Zeng, Preparation, characterization and adsorption properties of chitosan modified magnetic graphitized multi-walled carbon nanotubes for highly effective removal of a carcinogenic dye from aqueous solution, *Applied Surface Science*, 285 (2013) 865-873.
- [31] Y. Liu, W. Jiang, Y. Wang, X. Zhang, D. Song, F. Li, Synthesis of Fe₃O₄/CNTs magnetic nanocomposites at the liquid-liquid interface using oleate as surfactant and reactant, *Journal of Magnetism and Magnetic Materials*, 321 (2009) 408-412.
- [32] A.A. Ensafi, A.R. Allafchian, Multiwall carbon nanotubes decorated with NiFe₂O₄ magnetic nanoparticles, a new catalyst for voltammetric determination of cefixime, *Colloids and Surfaces B: Biointerfaces*, 102 (2013) 687-693.
- [33] P. Xiong, Y. Fu, L. Wang, X. Wang, Multi-walled carbon nanotubes supported nickel ferrite: A magnetically recyclable photocatalyst with high photocatalytic activity on degradation of phenols, *Chemical engineering journal*, 195 (2012) 149-157.
- [34] Y. Prabhu, B. Sreedhar, U. Pal, Achieving Enhanced Photocatalytic Activity of ZnO Supported on MWCNTs towards Degradation of Pollutants Under Visible Light, *Materials Today: Proceedings*, 8 (2019) 419-426.
- [35] M. Sampaio, R. Bacsá, A. Benyounes, R. Axet, P. Serp, C.G. Silva, A. Silva, J.L. Faria, Synergistic effect between carbon nanomaterials and ZnO for photocatalytic water decontamination, *Journal of Catalysis*, 331 (2015) 172-180.
- [36] M. Bagheri, N.R. Najafabadi, E. Borna, Removal of reactive blue 203 dye photocatalytic using ZnO nanoparticles stabilized on functionalized MWCNTs, *Journal of King Saud University-Science*, (2019).
- [37] M. Nawaz, A. Shahzad, K. Tahir, J. Kim, M. Moztahida, J. Jang, M.B. Alam, S.-H. Lee, H.-Y. Jung, D.S. Lee, Photo-Fenton reaction for the degradation of sulfamethoxazole using a multi-walled carbon nanotube-NiFe₂O₄ composite, *Chemical Engineering Journal*, 382 (2020) 123053.
- [38] H.-Y. Zhu, R. Jiang, Y.-Q. Fu, R.-R. Li, J. Yao, S.-T. Jiang, Novel multifunctional NiFe₂O₄/ZnO hybrids for dye removal by adsorption, photocatalysis and magnetic separation, *Applied surface science*, 369 (2016) 1-10.
- [39] N.R. Su, P. Lv, M. Li, X. Zhang, M. Li, J. Niu, Fabrication of MgFe₂O₄-ZnO heterojunction photocatalysts for application of organic pollutants, *Materials Letters*, 122 (2014) 201-204.
- [40] K. Seffah, N. Bensacia, A. Skender, E. Flahaut, Synthesis and characterization of nano-magnetic material based on (carbon nanotubes/nickel ferrite): Application for the removal of methyl orange dye from contaminated water, *algerian journal of environmental science and technology*, 3 (2017) 45-53.
- [41] J. Deng, X. Wen, Q. Wang, Solvothermal in situ synthesis of Fe₃O₄-multi-walled carbon nanotubes with enhanced heterogeneous Fenton-like activity, *Materials Research Bulletin*, 47 (2012) 3369-3376.

- [42] H. Zhu, R. Jiang, Y. Fu, Y. Guan, J. Yao, L. Xiao, G. Zeng, Effective photocatalytic decolorization of methyl orange utilizing $\text{TiO}_2/\text{ZnO}/\text{chitosan}$ nanocomposite films under simulated solar irradiation, *Desalination*, 286 (2012) 41-48.
- [43] Y. Yu, C.Y. Jimmy, C.-Y. Chan, Y.-K. Che, J.-C. Zhao, L. Ding, W.-K. Ge, P.-K. Wong, Enhancement of adsorption and photocatalytic activity of TiO_2 by using carbon nanotubes for the treatment of azo dye, *Applied Catalysis B: Environmental*, 61 (2005) 1-11.
- [44] X.-j. FAN, L. Xin, Preparation and magnetic property of multiwalled carbon nanotubes decorated by Fe_3O_4 nanoparticles, *New Carbon Materials*, 27 (2012) 111-116.
- [45] X. Hou, J. Feng, X. Liu, Y. Ren, Z. Fan, T. Wei, J. Meng, M. Zhang, Synthesis of 3D porous ferromagnetic NiFe_2O_4 and using as novel adsorbent to treat wastewater, *Journal of colloid and interface science*, 362 (2011) 477-485.
- [46] K.C. Verma, V.P. Singh, M. Ram, J. Shah, R. Kotnala, Structural, microstructural and magnetic properties of NiFe_2O_4 , CoFe_2O_4 and MnFe_2O_4 nanoferrite thin films, *Journal of magnetism and magnetic materials*, 323 (2011) 3271-3275.
- [47] M. Sun, T. Li, Z. Zhang, N. Wang, A. Xie, X. Lv, Y. Wang, F. Wu, M. Wang, Natural biological template for ZnO nanoparticle growth and photocatalytic dye degradation under visible light, *RSC Advances*, 5 (2015) 84406-84409.
- [48] M. Mozaffari, J. Amighian, E. Darsheshdar, Magnetic and structural studies of nickel-substituted cobalt ferrite nanoparticles, synthesized by the sol-gel method, *Journal of magnetism and magnetic materials*, 350 (2014) 19-22.
- [49] N. Srinivasan, Y. Shiga, D. Atarashi, E. Sakai, M. Miyauchi, A PEDOT-coated quantum dot as efficient visible light harvester for photocatalytic hydrogen production, *Applied Catalysis B: Environmental*, 179 (2015) 113-121.
- [50] S. Arora, M.L. Singla, P. Kapoor, Evidence for monoalkoxide species on the surface of palladium nanoparticles synthesized in ethylene glycol, *Materials Chemistry and Physics*, 114 (2009) 107-112.
- [51] J. Zhang, H. Zou, Q. Qing, Y. Yang, Q. Li, Z. Liu, X. Guo, Z. Du, Effect of chemical oxidation on the structure of single-walled carbon nanotubes, *The Journal of Physical Chemistry B*, 107 (2003) 3712-3718.
- [52] Z. Li, G. Che, W. Jiang, L. Liu, H. Wang, Visible-light-driven CQDs@ MIL-125 (Ti) nanocomposite photocatalyst with enhanced photocatalytic activity for the degradation of tetracycline, *RSC Advances*, 9 (2019) 33238-33245.
- [53] Y. Zhan, R. Zhao, Y. Lei, F. Meng, J. Zhong, X. Liu, A novel carbon nanotubes/ Fe_3O_4 inorganic hybrid material: Synthesis, characterization and microwave electromagnetic properties, *Journal of magnetism and magnetic materials*, 323 (2011) 1006-1010.
- [54] I. Vergili, Z.B. Gönder, Y. Kaya, G. Gürdağ, S. Çavuş, Lead removal from battery wastewater using synthesized poly (ethyleneglycol dimethacrylate-methacrylic acid) gel bead and poly (methacrylic acid) hydrogel, *Polymer Bulletin*, 74 (2017) 2605-2624.
- [55] J. Jiang, L.-H. Ai, L.-C. Li, H. Liu, Facile fabrication and characterization of $\text{NiFe}_2\text{O}_4/\text{ZnO}$ hybrid nanoparticles, *Journal of alloys and compounds*, 484 (2009) 69-72.
- [56] R. Waldron, Infrared spectra of ferrites, *Physical review*, 99 (1955) 1727.
- [57] T. Arfin, S.N. Rangari, Graphene oxide-ZnO nanocomposite modified electrode for the detection of phenol, *Analytical methods*, 10 (2018) 347-358.
- [58] M. Hashim, S. Kumar, S.E. Shirsath, R. Kotnala, J. Shah, R. Kumar, Synthesis and characterizations of Ni^{2+} substituted cobalt ferrite nanoparticles, *Materials Chemistry and Physics*, 139 (2013) 364-374.
- [59] R. Mishra, S. Tripathy, D. Sinha, K. Dwivedi, S. Ghosh, D. Khathing, M. Müller, D. Fink, W. Chung, Optical and electrical properties of some electron and proton irradiated polymers, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 168 (2000) 59-64.
- [60] E. Casbeer, V.K. Sharma, X.-Z. Li, Synthesis and photocatalytic activity of ferrites under visible light: a review, *Separation and Purification Technology*, 87 (2012) 1-14.
- [61] H. Derikvandi, A. Nezamzadeh-Ejhi, Synergistic effect of pn heterojunction, supporting and zeolite nanoparticles in enhanced photocatalytic activity of NiO and SnO_2 , *Journal of colloid and interface science*, 490 (2017) 314-327.

- [62] A. Shirzadi, A. Nezamzadeh-Ejhi, Enhanced photocatalytic activity of supported CuO–ZnO semiconductors towards the photodegradation of mefenamic acid aqueous solution as a semi real sample, *Journal of Molecular Catalysis A: Chemical*, 411 (2016) 222-229.
- [63] L. Lin, J. Huang, X. Li, M.A. Abass, S. Zhang, Effective surface disorder engineering of metal oxide nanocrystals for improved photocatalysis, *Applied Catalysis B: Environmental*, 203 (2017) 615-624.
- [64] P. Chand, S. Vaish, P. Kumar, Structural, optical and dielectric properties of transition metal (MFe₂O₄; M= Co, Ni and Zn) nanoferrites, *Physica B: Condensed Matter*, 524 (2017) 53-63.
- [65] S. Joshi, M. Kumar, S. Chhoker, G. Srivastava, M. Jewariya, V. Singh, Structural, magnetic, dielectric and optical properties of nickel ferrite nanoparticles synthesized by co-precipitation method, *Journal of Molecular Structure*, 1076 (2014) 55-62.
- [66] R.H. Kodama, Magnetic nanoparticles, *Journal of Magnetism and Magnetic Materials*, 200 (1999) 359-372.
- [67] J.Z. Msomi, Synthesis, structural and magnetic properties of bulk and nanosized (Zn, Cd, Cu)_{0.5}Ni_{0.5}Fe₂O₄ and NiFe₂O₄ ferrites, in, 2010.
- [68] M. Hoppe, Magnetic, structural, and electronic properties of NiFe₂O₄ ultrathin films, *Reihe Schlüsseltechnologien / Key Technologies* 2015.
- [69] R.J. Tilley, *Crystals and crystal structures*, John Wiley & Sons, 2006.
- [70] A.M. Gismelseed, K. Mohammed, H. Widatallah, A. Al-Rawas, M. Elzain, A. Yousif, Structure and magnetic properties of the Zn_xMg_{1-x}Fe₂O₄ ferrites, in: *Journal of Physics: Conference Series*, IOP Publishing, 2010, pp. 012138.
- [71] M. Rashad, D. Rayan, A. Turkey, M. Hessien, Effect of Co²⁺ and Y³⁺ ions insertion on the microstructure development and magnetic properties of Ni_{0.5}Zn_{0.5}Fe₂O₄ powders synthesized using co-precipitation method, *Journal of Magnetism and Magnetic Materials*, 374 (2015) 359-366.
- [72] A. Globus, H. Pascard, V. Cagan, Distance between magnetic ions and fundamental properties in ferrites, *Le Journal de Physique Colloques*, 38 (1977) C1-163-C161-168.
- [73] E. Mosiniewicz-Szablewska, A.R. Clavijo, A.P. Castilho, L.G. Paterno, M.A. Pereira-da-Silva, J. Więckowski, M.A. Soler, P.C. Morais, Magnetic studies of layer-by-layer assembled polyvinyl alcohol/iron oxide nanofilms, *Physical Chemistry Chemical Physics*, 20 (2018) 26696-26709.
- [74] J.-H. Nam, S.J. Park, W.K. Kim, Microstructure and magnetic properties of nanostructured NiZnCu ferrite powders synthesized by sol-gel process, *IEEE transactions on magnetics*, 39 (2003) 3139-3141.
- [75] J. Duque, E. Souza, C. Meneses, L. Kubota, Magnetic properties of NiFe₂O₄ nanoparticles produced by a new chemical method, *Physica B: Condensed Matter*, 398 (2007) 287-290.
- [76] A.H. Lu, E.e.L. Salabas, F. Schüth, Magnetic nanoparticles: synthesis, protection, functionalization, and application, *Angewandte Chemie International Edition*, 46 (2007) 1222-1244.
- [77] S.P. Gubin, *Magnetic nanoparticles*, John Wiley & Sons, 2009.
- [78] G.-y. Li, Y.-r. Jiang, K.-l. Huang, P. Ding, J. Chen, Preparation and properties of magnetic Fe₃O₄–chitosan nanoparticles, *Journal of alloys and compounds*, 466 (2008) 451-456.
- [79] J. Qu, C. Luo, Q. Cong, Synthesis of carbon nanotube/ZnO nanocomposites using absorbent cotton and their photocatalytic activity, *Micro & Nano Letters*, 7 (2012) 1064-1068.
- [80] C.-H. Chen, Y.-H. Liang, W.-D. Zhang, ZnFe₂O₄/MWCNTs composite with enhanced photocatalytic activity under visible-light irradiation, *Journal of Alloys and Compounds*, 501 (2010) 168-172.
- [81] S. Iftikhar, M.F. Warsi, S. Haider, S. Musaddiq, I. Shakir, M. Shahid, The impact of carbon nanotubes on the optical, electrical, and magnetic parameters of Ni²⁺ and Co²⁺ based spinel ferrites, *Ceramics International*, 45 (2019) 21150-21161.
- [82] F. Hosseini, A. Kasaeian, F. Pourfayaz, M. Sheikhpour, D. Wen, Novel ZnO-Ag/MWCNT nanocomposite for the photocatalytic degradation of phenol, *Materials Science in Semiconductor Processing*, 83 (2018) 175-185.
- [83] N. Roozban, S. Abbasi, M. Ghazizadeh, Statistical analysis of the photocatalytic activity of decorated multi-walled carbon nanotubes with ZnO nanoparticles, *Journal of Materials Science: Materials in Electronics*, 28 (2017) 6047-6055.
- [84] M. Elias, M.K. Amin, S.H. Firoz, M.A. Hossain, S. Akter, M.A. Hossain, M.N. Uddin, I.A. Siddiquey, Microwave-assisted synthesis of Ce-doped ZnO/CNT composite with enhanced photo-catalytic activity, *Ceramics International*, 43 (2017) 84-91.

- [85] D. Chaudhary, S. Singh, V. Vankar, N. Khare, ZnO nanoparticles decorated multi-walled carbon nanotubes for enhanced photocatalytic and photoelectrochemical water splitting, *Journal of Photochemistry and Photobiology A: Chemistry*, 351 (2018) 154-161.
- [86] Z. Lu, F. Chen, M. He, M. Song, Z. Ma, W. Shi, Y. Yan, J. Lan, F. Li, P. Xiao, Microwave synthesis of a novel magnetic imprinted TiO_2 photocatalyst with excellent transparency for selective photodegradation of enrofloxacin hydrochloride residues solution, *Chemical Engineering Journal*, 249 (2014) 15-26.
- [87] S. Xun, W. Zhu, Y. Chang, H. Li, M. Zhang, W. Jiang, D. Zheng, Y. Qin, H. Li, Synthesis of supported $\text{SiW}_{12}\text{O}_{40}$ -based ionic liquid catalyst induced solvent-free oxidative deep-desulfurization of fuels, *Chemical Engineering Journal*, 288 (2016) 608-617.
- [88] Q. Liu, J. Shen, X. Yang, T. Zhang, H. Tang, 3D reduced graphene oxide aerogel-mediated Z-scheme photocatalytic system for highly efficient solar-driven water oxidation and removal of antibiotics, *Applied Catalysis B: Environmental*, 232 (2018) 562-573.
- [89] H. Yu, Y. Huang, D. Gao, P. Wang, H. Tang, Improved H_2 -generation performance of Pt/CdS photocatalyst by a dual-function TiO_2 mediator for effective electron transfer and hole blocking, *Ceramics International*, 45 (2019) 9807-9813.