

## Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>/CNTs based nanocomposites incorporated with neodymium and samarium nanoparticles for efficient photocatalytic vitiation of organic pollutants

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Received 17 December 2021; Accepted 27 March 2022

### ABSTRACT

Neodymium and samarium based nanocomposites with efficient photocatalytic activity were synthesized and their structural and morphology were characterized using Fourier-transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy techniques. The SEM results of synthesized nanocomposites depict the flaked morphology of graphitic carbon nitride with interlinked stacked structure of metallic framework. UV-visible spectral studies revealed that the absorption edge has been shifted to longer wavelength in samarium and neodymium based samples which results in the decreased band gap of g-C<sub>3</sub>N<sub>4</sub> being used as main precursor. The photocatalytic activity of the synthesized catalysts was assessed by studying the degradation of Rhodamine B and Congo red dyes under visible light. The obtained results depict that Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>/CNTs/Sm<sub>2</sub>O<sub>3</sub> nanocomposite is more efficient with 86.1% degradation efficiency and 80.2% for Rhodamine B and Congo red as compared to Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>/CNTs/Nd<sub>2</sub>O<sub>3</sub>. Present studies revealed that superoxide ions and holes play significant role in the degradation of dye effluents. Further, the possible mechanism of the photocatalytic degradation of pollutants using samarium based nanocomposites is also proposed.

*Keywords:* Graphitic carbon nitride; CNTs; Neodymium; Samarium; Photocatalytic activity

### 1. Introduction

The entire world is facing the problems of pollution caused by rapid increase in numbers of industries, due to which living organisms especially human beings are badly affected. For this purpose, a lot of ways are adopted for degradation of harmful pollutants using economical materials.

For this purpose, researchers are keenly devoted for using efficient and eco-friendly materials as tool of cleaning major water bound pollutants. The choice of materials is focused on smaller sized large surface area with-holding properties.

Owing to innumerable properties like simple preparation, high chemical stability, use of visible light as source,

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low cost of the material and non-toxicity, graphitic carbon nitride ( $g\text{-C}_3\text{N}_4$ ) has been selected as a photo catalyst of choice [1,2]. The two dimensional (2D) graphitic carbon nitride ( $g\text{-C}_3\text{N}_4$ ) is an example of n-type semiconductor with a moderate band gap of 2.7 eV which causes it to absorb a narrow range of visible light [3].

Due to the appropriate valence Band (VB) and conduction band (CB) potential energy, Graphitic  $\text{C}_3\text{N}_4$  is widely accepted as photo catalyst for hydrogen production [4]. As compared to  $g\text{-C}_3\text{N}_4$ , CB band of metal oxides (ZnO) possesses lower energy. Hence the application of Sm doped-ZnO and  $g\text{-C}_3\text{N}_4$  could exert high photo activity due to their synergistic effect and proper matching of valence band (VB) and conduction band (CB) potential which could allow higher charge separation through the heterojunction [5,6]. Graphite carbon nitride polymer has a special electronic structure and is corresponding to graphite, which has resulted in the use of this material in optical sensor, light emitting devices and photo cathodes [7]. It can also be used as a visible-light-responsive and metal free photo catalyst in solar energy conversion field [8].

$\text{Fe}_2\text{O}_3$  has been widely used as an improved semiconducting material with average band gap of about 2.1 eV, excessively used as visible light driven photocatalyst but with short lifetime of excited state and high recombination rate of electron hole pairs. For this deficient nature,  $\text{Fe}_2\text{O}_3$  has been combined with  $g\text{-C}_3\text{N}_4$  as  $\text{Fe}_2\text{O}_3/g\text{-C}_3\text{N}_4$  to utilize the maximum efficiency of both materials in the field of photocatalysis [9,10].

Rare earth metals have been utilized in broad applications owing to suitability for sensors, solar cells, nano-optics, semiconductors and catalytic activities. Neodymium oxide ( $\text{Nd}_2\text{O}_3$ ) is naturally abundant, important and highly reactive element in the series of rare earth metal oxides [11,12].  $\text{Nd}_2\text{O}_3$  has numerous uses in dielectrics, magnetic devices and catalysts, to improve the electrical properties of materials [13]. Whereas samarium oxide due to the exceptional properties of lowered crystallite size, increased surface area; enhanced separation efficiency of charge carriers, lowering the band gap and availability of 4f level improves the performance of composite when incorporated [14].

CNTs have been used from last few decades due to their exceptional structural and fabricating properties, providing large number of spaces and surface area for better applications. In recent researches, metal oxides linked CNTs are being used in the fields of photocatalysis [15].  $\text{M}_2\text{O}_3/\text{CNTs}$  have been synthesized in this work and then attachment with  $g\text{-C}_3\text{N}_4/\text{Fe}_2\text{O}_3$  nanomaterial has been done as a different approach for studying photocatalytic degradation of dyes as application.

## 2. Experimental work

### 2.1. Materials used

The chemicals used for this work were all of analytical grade and no further purification was needed before their usage. Major chemicals being used are listed as; urea ( $\text{CH}_4\text{N}_2\text{O}$ ) (Sigma-Aldrich, USA), carbon nanotubes (CNTs) (Sigma-Aldrich), neodymium nitrate

hexahydrate ( $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ), samarium nitrate hexahydrate ( $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ), ferrous sulphate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) (Sigma-Aldrich, USA), polyethylene glycol (PEG) (Sigma-Aldrich, USA), cetyl trimethyl ammonium bromide (CTAB) (Sigma-Aldrich, USA), distilled and deionized water for preparation of solutions and washing purposes.

### 2.2. Method of synthesis

#### 2.2.1. Synthesis of $\text{Fe}_2\text{O}_3$ nanoparticles

The  $\text{Fe}_2\text{O}_3$  nanoparticles were synthesized with little modification, by using basic media of NaOH, PEG and CTAB as surfactant. 0.1 mol/L  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (2 g/50 mL), solution was prepared using deionised water. NaOH solution of 0.6 mol/L (1.2 g/50 mL) was slowly poured drop wise with continuous stirring until the pH was set to 9. Meanwhile drop wise addition of 1% PEG solution (aqueous) along with 0.1% CTAB solution, to confirm the preparation of iron oxide nanoparticles [16]. The constant stirring at 100°C was ensured for 6 h. Nanoparticles formed were washed thoroughly with distilled water many times in order to remove extra base.

#### 2.2.2. Synthesis of carbon nitride ( $g\text{-C}_3\text{N}_4$ )

The preparation of graphitic carbon nitride was carried out by using thermal exfoliation method. First, about 20 g of urea was put in alumina crucible, covered with lid and then placed in muffle furnace with heating at 550°C for 4.5 h. The graphitic carbon nitride was obtained in the form of yellowish white amorphous flakes, which was first cooled at room temperature followed by grinding using pistol and mortar [17].

#### 2.2.3. Synthesis of $\text{Sm}_2\text{O}_3$ and $\text{Nd}_2\text{O}_3$ nanoparticles

Neodymium oxide and samarium oxide nanoparticles were separately prepared by using simple sonication method. 1.5 g of neodymium nitrate and samarium nitrate were separately dissolved in 20 mL of distilled water with constant stirring, followed by addition of 30% liquid ammonia. Then sonication was carried out for 35 min to obtain pale coloured samarium hydroxide precipitates and violet coloured neodymium hydroxide precipitates respectively [18,19]. Washing of obtained precipitates was done many times using ethanol and distilled water. The products obtained were annealed at 300°C for 1 h to get  $\text{M}_2\text{O}_3$  nanoparticles where M = Nd, Sm.

#### 2.2.4. Synthesis of $\text{Fe}_2\text{O}_3/g\text{-C}_3\text{N}_4/\text{CNTs}/\text{Nd}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3/g\text{-C}_3\text{N}_4/\text{CNTs}/\text{Sm}_2\text{O}_3$

Two steps were taken for preparation of  $\text{Fe}_2\text{O}_3/g\text{-C}_3\text{N}_4$  and  $\text{CNTs}/\text{M}_2\text{O}_3$  (M = Nd, Sm). Firstly, iron oxide nanoparticles and graphitic carbon nitride were mixed together using simple dispersion and sonication methods. Mixing and sonication was continued for 30 min till homogeneity of mixture was ensured [20]. In the second-step, ultra-sonication was adopted for the formation of  $\text{CNTs}/\text{Nd}_2\text{O}_3$  and  $\text{CNTs}/\text{Sm}_2\text{O}_3$  one by one. 0.8 g of  $\text{Nd}_2\text{O}_3$  and

Sm<sub>2</sub>O<sub>3</sub> nanoparticles were dispersed separately in double distilled water followed by addition of 1.5 mL CNTs (solution) with constant sonication for 1.5 h [21].

Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> in solution form was then mixed with CNTs/Nd<sub>2</sub>O<sub>3</sub> and CNTs/Sm<sub>2</sub>O<sub>3</sub> separately, followed by sonication for almost 3 h. The products formed were dried by placing in drying oven maintained at 90°C until complete drying of solvent was ensured to get powdered materials. The step by step synthesis process is shown in Fig. 1.

2.2.5. Characterization

X-ray diffraction (XRD) of prepared samples were done by using PANalytical X'Pert Pro MPD Netherland, with Cu K $\alpha$  radiation having scanning rate 0.005, 30 mA and 35 kV at room temperature (The Islamia University Bahawalpur). The FTIR of all prepared samples was characterized through Alpha Bruker ATR with OPUS/Mentor software (400–4,000cm<sup>-1</sup>) (The Islamia University Bahawalpur). UV-Visible spectra of prepared samples were obtained using Agilent Carry 60 UV/Visible spectrophotometer (The Government Sadiq Women University Bahawalpur) and scanning electron microscopy (SEM)/

energy-dispersive X-ray spectroscopy (EDX) images were obtained using VEGA TESCAN SEM instrument and JEOL JCM-6000 Plus electron microscope (Institute of space Technology Islamabad).

3. Results and discussion

3.1. Fourier-transform infrared spectroscopy

Fourier-transform infrared spectroscopy (FTIR) spectrums of Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>/CNTs/Nd<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>/CNTs/Sm<sub>2</sub>O<sub>3</sub> have been shown in Fig. 2a and b. Some common bands are available in both of the synthesized materials owing to presence of graphitic carbon nitride, iron oxide and CNTs as same precursors. Elucidation of FTIR peaks of neodymium based materials represents band of 423 cm<sup>-1</sup> due to vibrational mode of Nd–O group, 668 cm<sup>-1</sup> band arises due to –OH group attached metal of Nd–OH [22]. The wide peak at 870 cm<sup>-1</sup> is because of iron oxide presence within composite [23], while other bands at 2,373 cm<sup>-1</sup> represents C=N bond, 2,943 cm<sup>-1</sup> for C–H stretching vibrations, band at 3,467 cm<sup>-1</sup> is for OH stretching due to adsorbed water molecules and stretching vibrations of

Table 1a  
Photocatalytic degradation of RhB using Fe<sub>2</sub>O<sub>3</sub>/C<sub>3</sub>N<sub>4</sub>/CNTs/Nd<sub>2</sub>O<sub>3</sub> NC

Sr #	Time 't' (min)	Initial absorbance A <sub>0</sub>	Absorbance at 't' time A <sub>t</sub>	% D
1.	0	1.95	1.95	0
2.	5	1.95	1.73	11.28
3.	10	1.95	1.62	16.92
4.	15	1.95	1.56	20
5.	20	1.95	1.43	26.7
6.	25	1.95	1.25	35.9
7.	30	1.95	1.07	45.12
8.	35	1.95	0.90	53.8
9.	40	1.95	0.73	62.6
10.	45	1.95	0.61	68.71
11.	50	1.95	0.48	75.38

Table 1b  
Photocatalytic degradation of RhB using Fe<sub>2</sub>O<sub>3</sub>/C<sub>3</sub>N<sub>4</sub>/CNTs/Sm<sub>2</sub>O<sub>3</sub> NC

Sr #	Time 't' (min)	Initial absorbance A <sub>0</sub>	Absorbance at 't' time A <sub>t</sub>	% D
1.	0	1.95	1.95	0
2.	5	1.95	1.70	12.82
3.	10	1.95	1.51	22.56
4.	15	1.95	1.37	29.74
5.	20	1.95	1.23	36.92
6.	25	1.95	1.11	43.07
7.	30	1.95	0.95	51.28
8.	35	1.95	0.81	58.46
9.	40	1.95	0.68	65.12
10.	45	1.95	0.53	72.82
11.		1.95	0.27	86.15

Table 1c  
Photocatalytic degradation of CR using  $\text{Fe}_2\text{O}_3/\text{C}_3\text{N}_4/\text{CNTs}/\text{Nd}_2\text{O}_3$  NC

Sr #	Time 't' (min)	Initial absorbance $A_0$	Absorbance at 't' time $A_t$	% D
1.	0	1.87	1.87	0.0
2.	5	1.87	1.73	7.5
3.	10	1.87	1.57	16.04
4.	15	1.87	1.49	20.32
5.	20	1.87	1.40	25.13
6.	25	1.87	1.29	31.01
7.	30	1.87	1.19	36.36
8.	35	1.87	1.10	41.17
9.	40	1.87	0.96	48.66
10.	45	1.87	0.87	53.47
11.	50	1.87	0.69	63.10

Table 1d  
Photocatalytic degradation of CR using  $\text{Fe}_2\text{O}_3/\text{C}_3\text{N}_4/\text{CNTs}/\text{Sm}_2\text{O}_3$  NC

Sr #	Time 't' (min)	Initial absorbance $A_0$	Absorbance at 't' time $A_t$	% D
1.	0	1.87	1.87	0
2.	5	1.87	1.60	14.43
3.	10	1.87	1.47	21.39
4.	15	1.87	1.26	32.62
5.	20	1.87	0.95	49.19
6.	25	1.87	0.87	53.47
7.	30	1.87	0.79	57.75
8.	35	1.87	0.71	62.03
9.	40	1.87	0.58	68.98
10.	45	1.87	0.44	76.47
11.	50	1.87	0.38	80.21

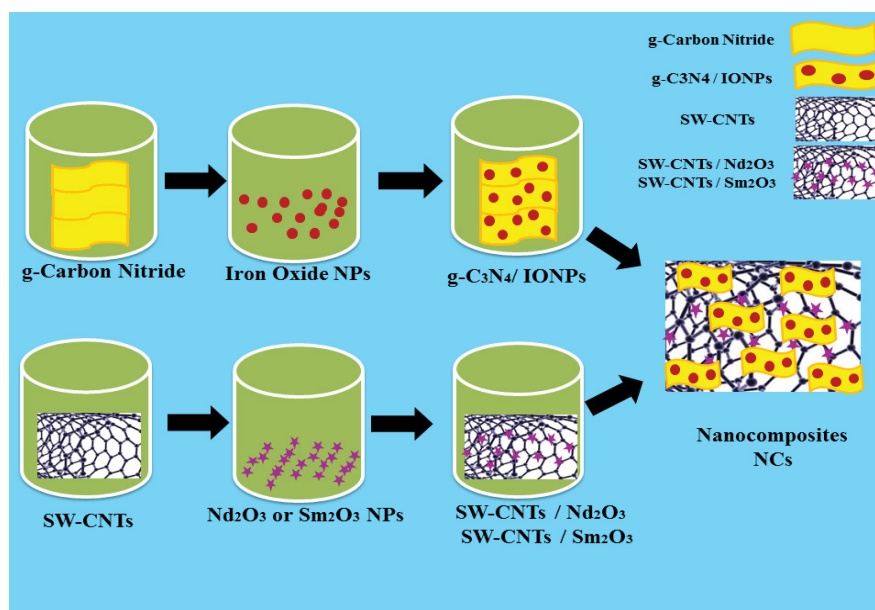


Fig. 1. Pictorial illustration for the synthesis of (i)  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Nd}_2\text{O}_3$  NCs and (ii)  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Sm}_2\text{O}_3$  NCs.

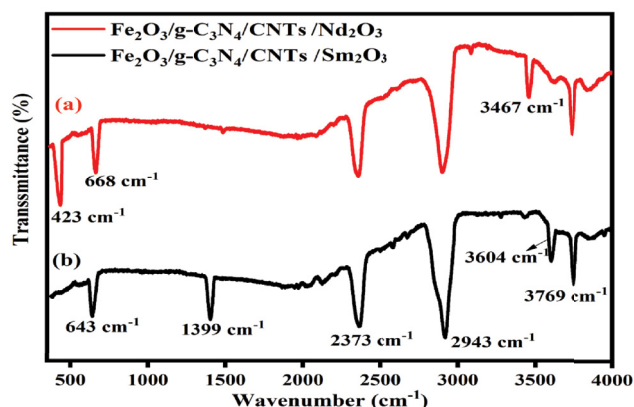


Fig. 2. FTIR of (a)  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Nd}_2\text{O}_3$  NC and (b)  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Sm}_2\text{O}_3$  NC.

$\text{NH}_2$  groups available in  $\text{g-C}_3\text{N}_4$  framework showing band at  $3769\text{ cm}^{-1}$  respectively [24]. However, the FTIR spectra for  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Sm}_2\text{O}_3$  composite shows some major peaks of  $643\text{ cm}^{-1}$  due to  $\text{Sm-O}$  functional group present [25], while the stretching mode of  $\text{C-N}$  heterocycles has been shown with band at  $1399\text{ cm}^{-1}$  respectively. The peaks of  $870$ ;  $2373$ ;  $2943$  and  $3769\text{ cm}^{-1}$  are same as peaks available in  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Nd}_2\text{O}_3$  which correspond to iron oxide,  $\text{C=N}$  bond, stretching vibrations of  $\text{C-H}$  groups and stretching vibrations of  $\text{NH}_2$  groups respectively. The FTIR peak of  $3604\text{ cm}^{-1}$  is correlated to stretching vibrations of amino groups present on carbon nitride material.

### 3.2. X-ray diffraction

XRD pattern of  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Nd}_2\text{O}_3$  is shown in Fig. 3a. It depicts peaks of respective precursors used for synthesizing the composite as; XRD peaks with  $2\theta$  values of  $19.5^\circ$  and  $26.1^\circ$  with indexed values of (113) and (002) confirm the presence of carbon nanotubes [26], while peaks at  $27.7^\circ$ ,  $57.1^\circ$  and  $62.9^\circ$  with hkl values of (002), (428) and (203) correlate  $\text{g-C}_3\text{N}_4$  within composite [27]. Whereas, peaks with diffraction angle of  $33.4^\circ$  and  $35.5^\circ$  indexed as (207) and (119) are related to  $\text{Fe}_2\text{O}_3$  nanoparticles [16]. Neodymium oxide ( $\text{Nd}_2\text{O}_3$ ) shows the XRD peaks of  $30.1^\circ$ ,  $47.2^\circ$  and  $53.8^\circ$  with hkl values of (101), (110) and (103) respectively [28].

The diffraction pattern of  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Sm}_2\text{O}_3$  in Fig. 3b can be elucidated as common peaks of CNTs at  $19.5^\circ$  (113) and  $23.4^\circ$  (002), whereas common peaks of  $\text{Fe}_2\text{O}_3$  at  $33.4^\circ$  (207)  $35.5^\circ$  (119) and for  $\text{g-C}_3\text{N}_4$  with peaks of  $27.7^\circ$  (002),  $57.1^\circ$  (428) and  $62.9^\circ$  (203) are also in accordance with that of neodymium based material. While samarium oxide ( $\text{Sm}_2\text{O}_3$ ) shows diffraction pattern with peaks at  $38.1^\circ$ ,  $46.4^\circ$  and  $53.9^\circ$  along with (332), (521) and (541) hkl values respectively [28,29]. Thus the XRD patterns confirm successful synthesis, showing all precursors with definite diffraction patterns.

### 3.3. SEM and EDX analyses

The SEM micrographs for neodymium and samarium based nanocomposite are of Fig. 4a and b. The silky

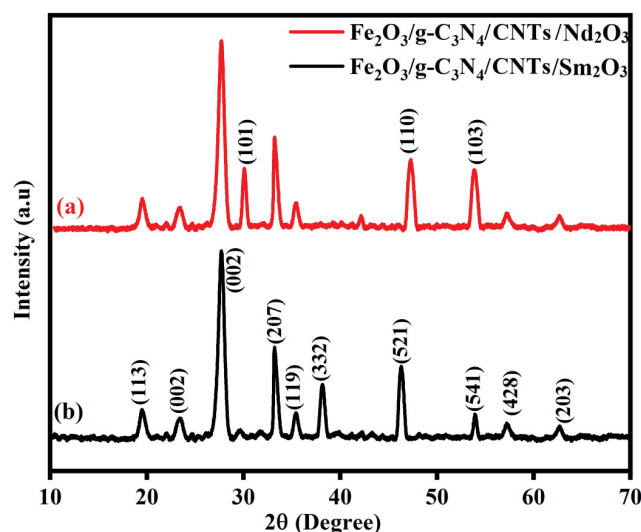


Fig. 3. XRD of (a)  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Nd}_2\text{O}_3$  NC and (b)  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Sm}_2\text{O}_3$  NC.

nanostructures and a layered, flaky sheet like surface morphology are shown by images of  $1$  and  $2\text{ }\mu\text{m}$  scale chosen, which indicate that the graphitic carbon nitride planes are stacking with nanoparticles interlinked by CNTs. The pores are visualized as the repeated tri-s-triazine units of carbon nitride which can be identified as flakes material easily [30,31]. In closer capture, samarium nanoparticles are not observed owing to their small size and well dispersed. Moreover, neodymium nanoparticles, although possesses large sized particles which are incorporated inside the flakes of graphitic carbon nitride and separate particles are not visible in SEM results.

EDX spectra of both  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Nd}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Sm}_2\text{O}_3$  nanocomposites have been shown in Fig. 5 in which all the nominal components of desired elements are confirmed.  $10\text{ }\mu\text{m}$  scales has been used for spotting the EDX sample as evident from Fig. 5.

### 3.4. Optical studies

The optical studies were completed by using the UV absorbance peaks and tauc plot were plotted as evident in Fig. 6. In this regard,  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Nd}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Sm}_2\text{O}_3$  NCs were dispersed separately in absolute ethanol with ultra-sonication for 10 min.

The UV absorbance peaks with tauc plot for the calculations of band gap regarding  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Nd}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Sm}_2\text{O}_3$  NCs can be used for the charge transfer mechanism fruitful for the explanation of photocatalytic efficiency.

The band gap energy values have been calculated using Tauc equation as [32]:

$$\alpha h\nu = A(h\nu - E_{\text{obg}})^n \quad (1)$$

The band gap calculated for neodymium incorporated nanocomposite was  $3.5$  and  $4.0\text{ eV}$  for samarium based nanocomposite respectively.

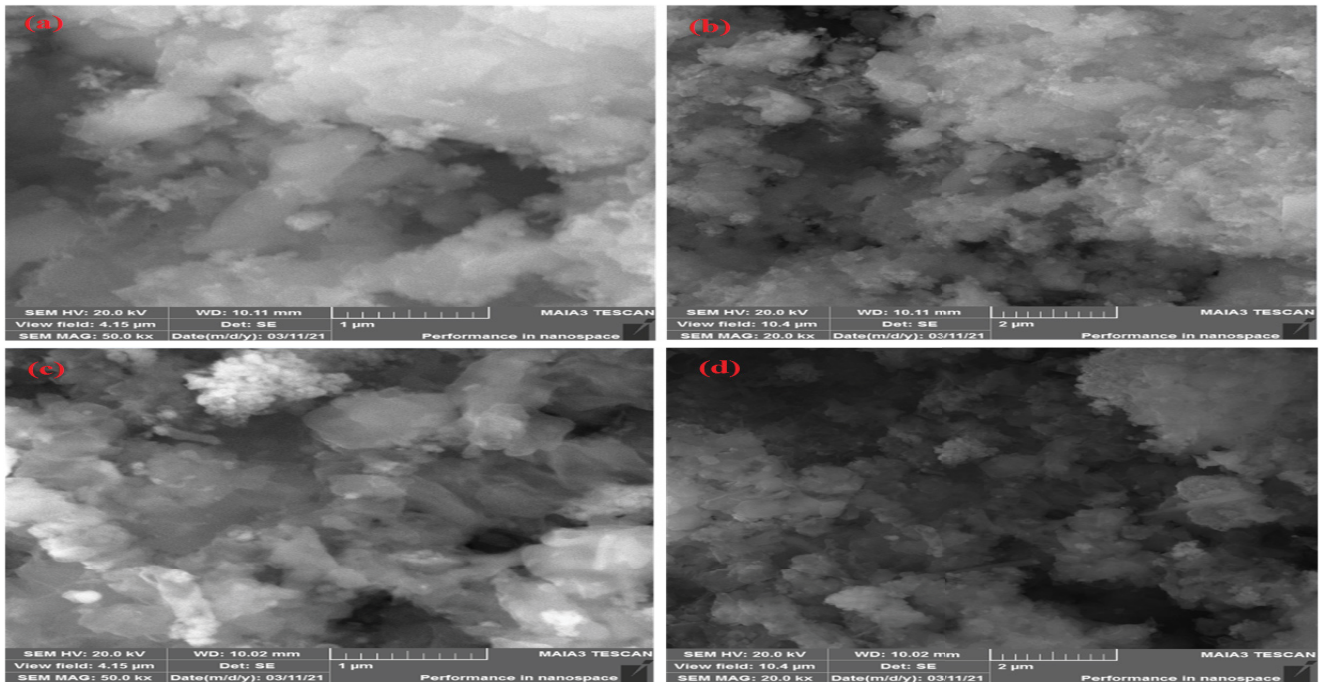


Fig. 4. SEM images of (a, b)  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Nd}_2\text{O}_3$  and (c, d)  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Sm}_2\text{O}_3$  NCs.

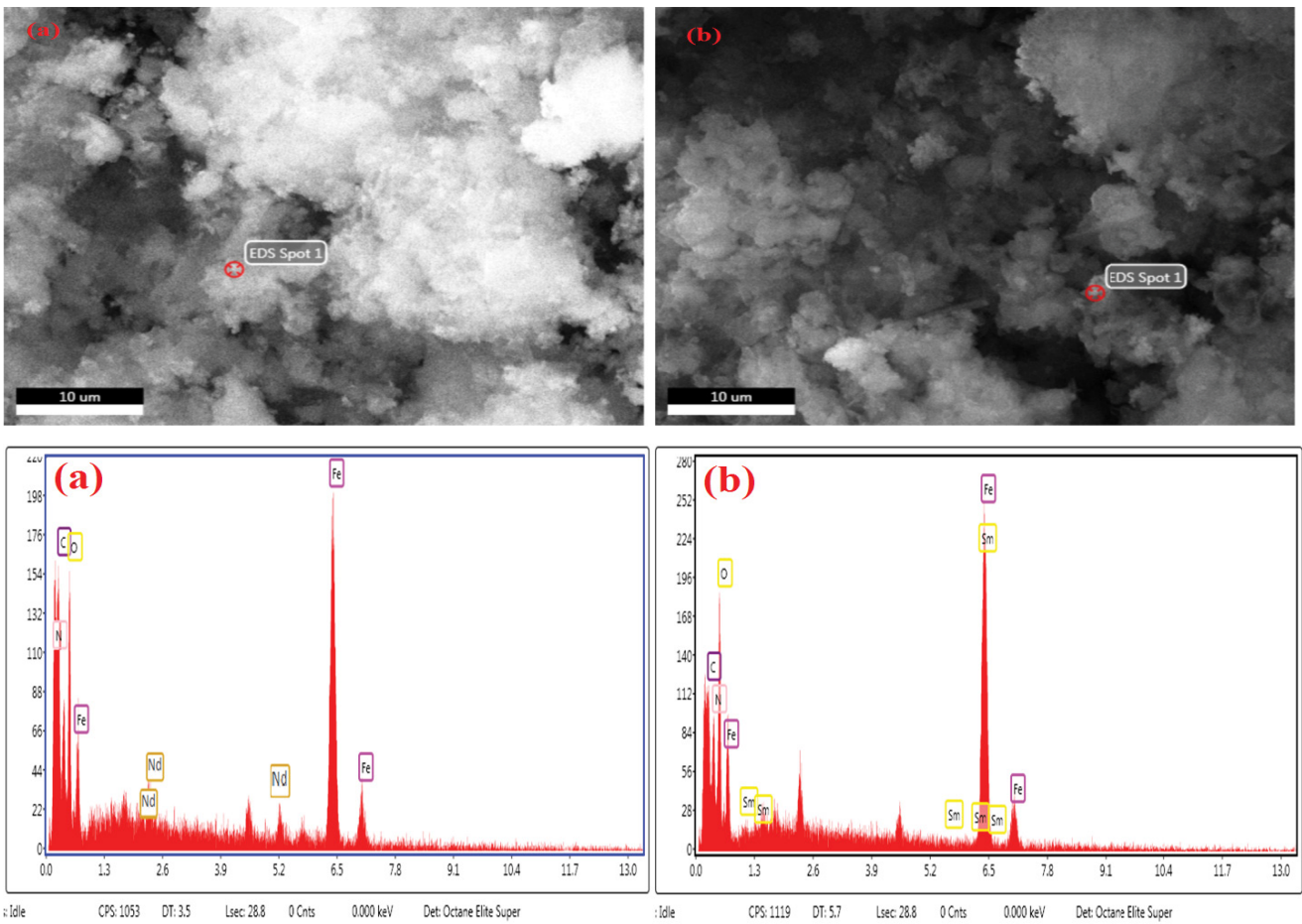


Fig. 5. EDX of (a)  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Nd}_2\text{O}_3$  and (b)  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Sm}_2\text{O}_3$  NCs.

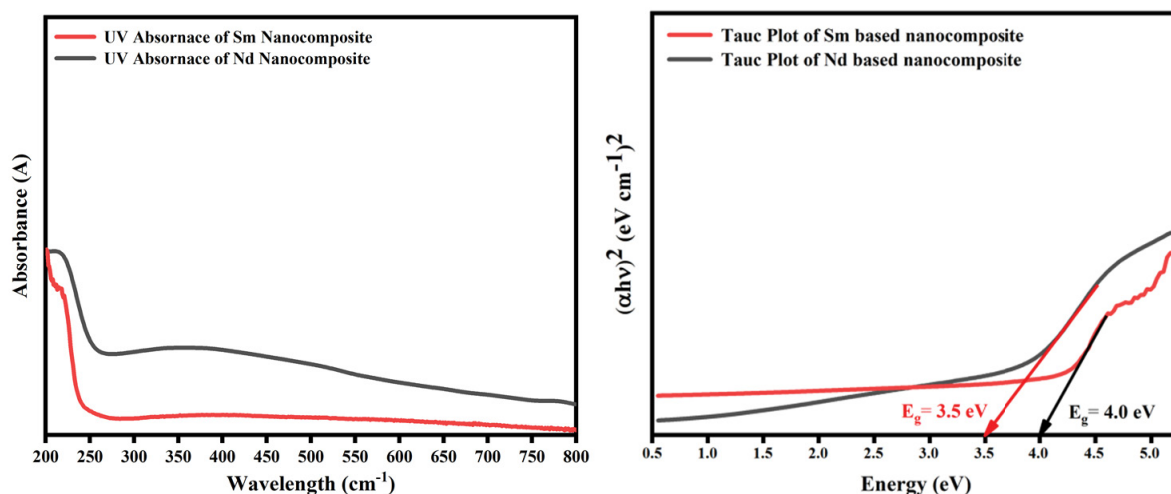


Fig. 6. (a) UV peaks of  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Nd}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Sm}_2\text{O}_3$  NCs. (b) Tauc plots of  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Nd}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Sm}_2\text{O}_3$  NCs.

### 3.5. Photocatalytic degradation of organic dyes

In industry, organic dyes are being used for staining purposes. These days can cause serious environmental problems due to their harmful and cancer causing nature. In this study, two different dyes, Rhodamine B (RhB) which is the member of cationic dye family, 25 ppm of 100 mL was taken, while Congo red (CR) which is the member of anionic dye family, 100 mL of 25 ppm have been utilized as pollutants [33,34]. The photocatalytic degradation of both dyes was observed by using samarium and neodymium based nanocomposites. Results explained in Figs. 7 and 8, show that  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Sm}_2\text{O}_3$  NCs in comparison to  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Nd}_2\text{O}_3$  NCs shows higher photocatalytic activity. Due to electron-hole recombination, least degradation activity is observed in neodymium based composite. Whereas the photocatalytic activity exhibited by  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Sm}_2\text{O}_3$  nanocomposite was high due to the availability of unoccupied 4f energy levels being used by photo electrons thus reduced the recombination pattern of electrons and holes [35,36].

For the deterioration of RhB dye (Fig. 7), the de-ethylation process or cleavage of combined structures results in degradation of dye. The peak position after absorption depicts that the dye remains constant throughout whereas, the absorption intensity decreases with time. Two peaks are shown by the absorption spectrum of Congo red (Fig. 8). One of the bands is at 265 nm that is conjugated with the p-p\* transition of aromatic ring structure, while the second band at 432 nm correlates with the n-p transition by lone pair electron which is presented in the nitrogen atom of chromophoric structure present [37,38]. During the reaction, peaks intensities are decreased which indicate that the benzene ring structures were decomposed in Congo red.

The equation used for calculating the percentage degradation of dyes used is [39]. Attained results for degradation of RhB by using neodymium and samarium based nanocomposites are given in Table 1a and 1b while for CR degradation by using neodymium and samarium based nanocomposites are given in Table 1c and 1d.

$$\% D = \frac{(A_t - A_o)}{A_o} \times 100 \quad (2)$$

### 3.6. Ion trapping experiments

Various scavengers have been tested for the confirmation of various radicals involved for the degradation of Rhodamine B and Congo red dyes [40]. In ion trapping experiment, 2-propyl alcohol for hydroxyl ions, silver nitrate ( $\text{AgNO}_3$ ) for electron capture, Ascorbic acid (Vit.C) for superoxide radicals and EDTA for holes trapping have been adapted and added in the photocatalytic reaction solution as scavengers [36,41].

From the results evident in Fig. 9, it is cleared that the concentration of dye has been considerably decreased from 86.1% to 11.8% in the presence of ascorbic acid, involved in trapping superoxide ions, confirming the main agent for degradation of dye used.

### 3.7. Control test for photolysis

Control test was performed to check the effect of photolysis using different pHs [42]. The findings of this test were, neutral and acidic pHs show minimum/no effect of photolysis due to unavailability of hydroxyl ions within the medium, whereas, when the pH shifted towards basic medium, photolysis shows its dominant effect on dye. In current work, the pH for attachment of precursors was set to 3 and the dye solution was of neutral. Therefore, the evidence of photolysis interference during the process of catalytic removal of dyes has been shown in Fig. 10.

### 3.8. Band structure and proposed mechanism for photocatalytic degradation of dyes

Photocatalysts dye mixtures were irradiated by using visible light emitted from electric bulb placed in closed cabin for dark reaction of 30 min in order to ensure adsorption desorption equilibrium. Fig. 11 shows pictorial illustration of mechanism used for photocatalytic degradation of dyes. Electrons are allowed to excite from

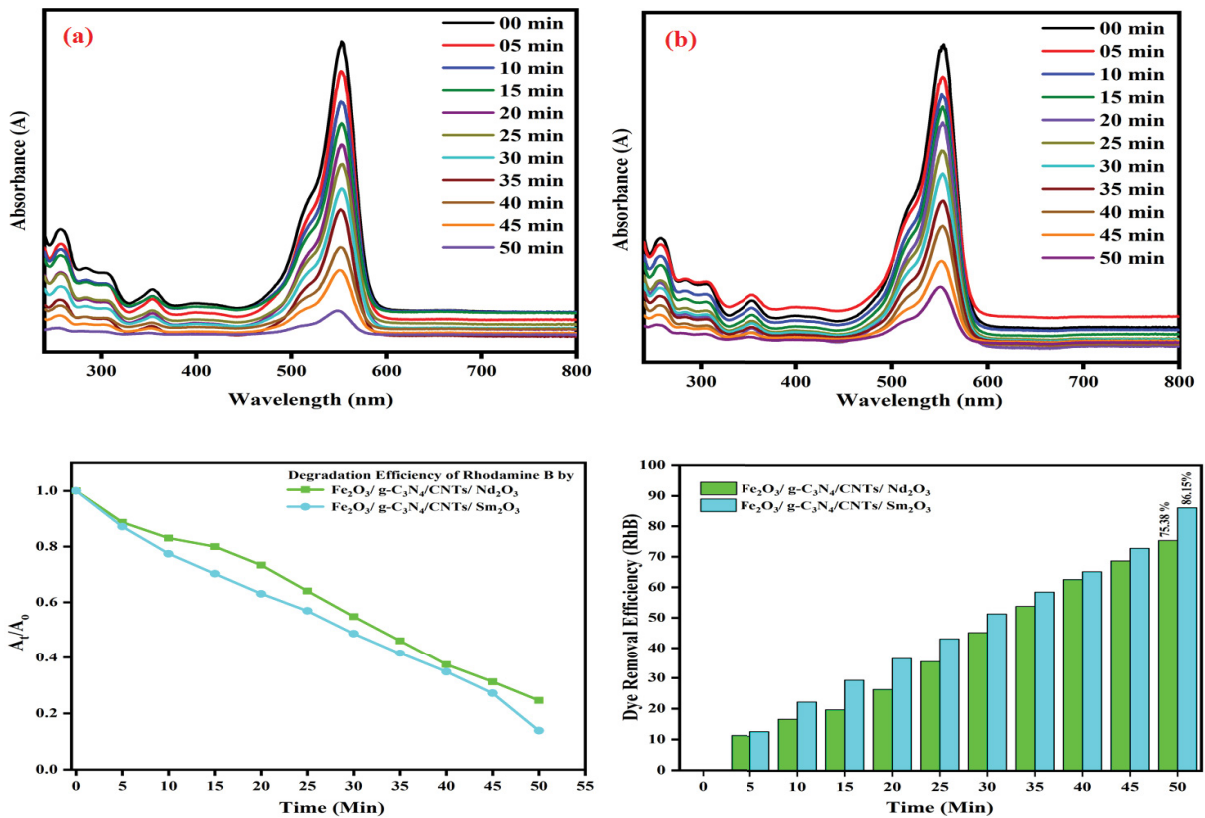


Fig. 7. Photocatalytic degradation of Rhodamine B using (a)  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Nd}_2\text{O}_3$  NCs and (b)  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Sm}_2\text{O}_3$  NCs.

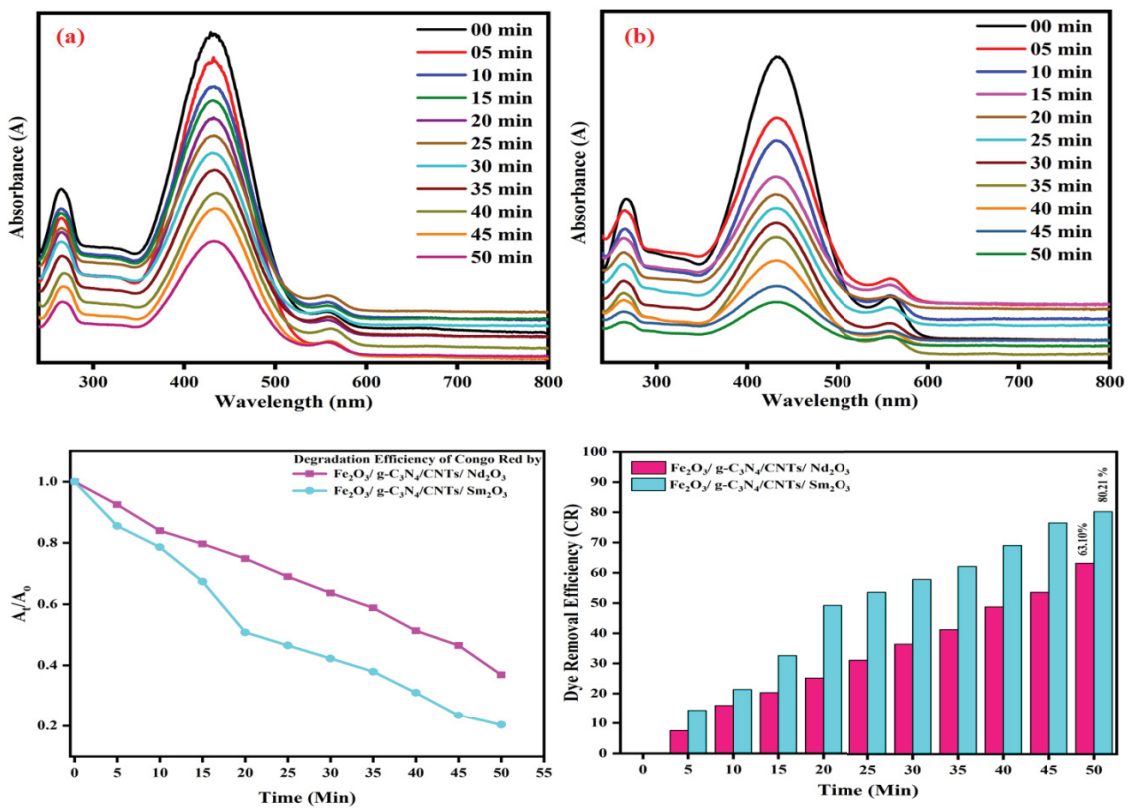


Fig. 8. Photocatalytic degradation of Congo red dyes using (a)  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Nd}_2\text{O}_3$  NCs and (b)  $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{CNTs}/\text{Sm}_2\text{O}_3$  NCs.



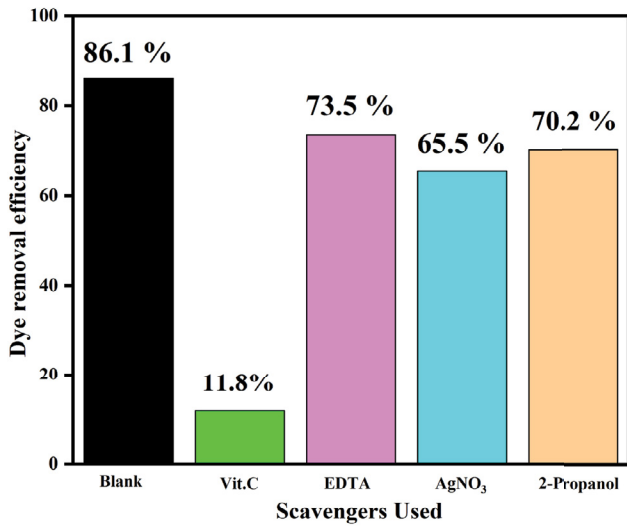


Fig. 9. Removal of RhB dye in the presence of various scavengers.

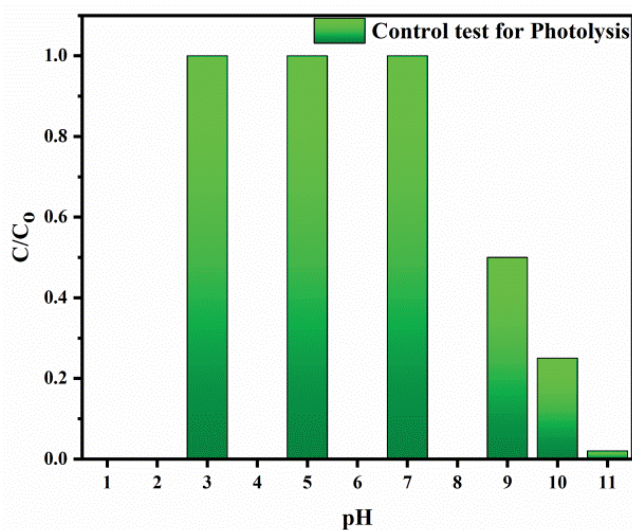


Fig. 10. Control test for photolysis using different pHs.

valance band (VB) to conduction band (CB) when sample is irradiated by light source, as a result; generated electrons and holes cause the degradation of dyes used [39]. It is observed that quantum efficiency is increased due to slow recombination rate of electrons and holes. Reduction of metals is due to the availability of electrons. When oxygen concentration is low within the medium, there is a possibility to store and release oxygen within system. The oxidation state of metals is converted from +2 to +3 states by using oxygen contents, radicals like super oxides also form. Hydroxyl radicals are produced when hydroxyl ions react with photogenerated holes. They can also be formed by the reaction of photogenerated electrons with protons and dissolved oxygen contents [43].

The mechanism involved for degradation of dye using light is shown in equations as:

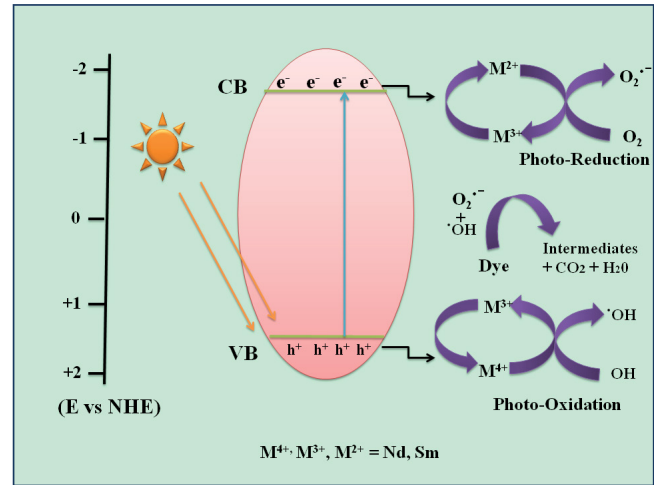


Fig. 11. Pictorial illustration of mechanism used for photocatalytic degradation of dyes.



Table 2 depicts the comparison of degradation performance of different photocatalysts using different dyes, time consumed and % removal of dyes as efficiency along with references.

#### 4. Conclusions

The graphitic carbon nitride based neodymium and samarium nanocomposites incorporated with CNTs were prepared using thermal exfoliation, co-precipitation and ultra-sonication methods respectively. SEM and EDX results confirmed the flaked morphological of as-synthesized nanocomposites of Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>/CNTs/Nd<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>/CNTs/Sm<sub>2</sub>O<sub>3</sub> respectively. The UV-Visible studies confirmed the shift of absorption band towards longer wavelength thus confirming the shortened band gap of g-C<sub>3</sub>N<sub>4</sub> as main precursor for photocatalytic applications. The results with degradation efficiency of 75.3% using RhB and 63.1% using Congo red has been calculated for Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>/CNTs/Nd<sub>2</sub>O<sub>3</sub> nanocomposite while 86.15% for RhB and 80.2% for Congo red dye has been recorded using Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>/CNTs/Sm<sub>2</sub>O<sub>3</sub> respectively. The scavenger's test confirmed that superoxide as main agent for degrading the dyes. The

Table 2

Comparison of degradation efficiency of different catalysts using Congo red and Rhodamine B dyes

Photocatalyst used	Quantity (mg)	Dyes used	Removal (%)	Time used (min)	References
Fe <sub>2</sub> O <sub>3</sub> /g-C <sub>3</sub> N <sub>4</sub>	01	RhB (Rhodamine B)	90	120	[44]
TiO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	10	RhB (Rhodamine B)	80	300	[45]
ZnO/MWCNTs	20	MO (Methyl orange)	80.2	60	[46]
Nd-TiO <sub>2</sub> -GO	20	IC (Indigo carmine)	92	180	[47]
Fe <sub>2</sub> O <sub>3</sub> /C <sub>3</sub> N <sub>4</sub> /CNTs/Sm <sub>2</sub> O <sub>3</sub>	05	RhB (Rhodamine B)	86.1	50	Present Work
		CR (Congo red)	80.2	50	

efficient removal of RhB and CR dyes using samarium based nanocomposite is higher as compared to that of neodymium based nanocomposite, thus confirming the better choice of photocatalysts as comparative study between neodymium based and samarium based nanocomposites.

### Acknowledgements

The authors are highly thankful to Islamia University of Bahawalpur (IUB) and Higher Education commission (HEC) of Pakistan for financial support.

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