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Research Article

SYNTHESIS, CHARACTERIZATION OF ND DOPED SILICA NANOCOMPOSITES AND ITS PHOTOCATALYTIC ACTIVITY

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ABSTRACT

In this work, Nd/SiO_2 nanocomposites were prepared with different loading of neodymium oxide on silica by using sol-gel method. The sol-gel method represents an attractive alternative because of its relatively low processing temperature and patterning of the nanostructures with controlled size. The synthesized materials were characterized by using High resolution Transmission Electron Microscopy (HR-TEM) showed the formation of nanostructure. Energy Dispersive X-Ray Analysis (EDX) and Scanning Electron Microscopy (SEM), X-ray powder diffraction (XRD) confirmed the presence neodymium silicon oxide phase (Nd9.35 Si6 O26) with nano size 15.4 nm. Synthesized nanocomposites were studied for photocatalytic activity by methylene blue and showed higher activity for 4wt.% Nd/SiO_2.

Keywords: Nanocomposites, Neodymium oxide, sol gel, HR-TEM, Photocatalytic activity.

1. INTRODUCTION

A nanocomposite material is a material made from two or more constituent materials with significantly different properties when combined with different metal oxides. The different morphologies for nanocomposite materials are vast, including mixed metal oxides, core-shell nanoparticles, colloidal crystals and macro-scale spheres [1]. The composite materials with nanostructures have obtained more attention in recent times because of their fascinating properties and different applications in vast areas.

Rare earth oxides have been used in research areas such as optical, ceramic, solar cells, nano-electronics, semiconductor, sensors and catalytic applications due to their unique and interesting properties. Neodymium oxide is one of the important rare earth materials because of their suitability [2]. There is very limited research on study of Nd_2O_3-SiO_2 nanocomposites [3]. In literature there are few supports other than SiO_2, such as TiO_2, $NaYF_4$ for sensitizer application [4], $BiFeO_3$ to enhance ferroelectric properties [5], and LaF_3 for optical studies [6]. Neodymium oxide (Nd_2O_3) has a wealth of effective features, which result in its uses in UV absorbent, colored glass, protective coatings and catalysts [7, 8].

Neodymium-doped silica nanocomposites form important class of nanomaterials on account of their manifold applications especially in photocatalysis. As per the literature, it was observed that low decomposition temperature formed nano sized rare earth metal oxides [9].

Liu et al. [10] reported two step synthetic method for samarium and neodymium oxide nanoparticles. This method included reaction of metal precursor to fabricate nanoparticles followed by oxidation treatment form rare earth metal oxides.

Currently, La-NPs are successfully implemented in bioassays, drug delivery, imaging of cells, photo-degradation of dyes and other catalytic activities. Lanthanide nanoparticles are those that contain lanthanide elements such as Ce, Ho, Sm, Gd, Nd, Erand Eu [11].

In the present study nano-composites were synthesized with silica and neodymium by sol-gel method which is reported in literature [12]. Very few reported literature and importance of Nd (III) made us to synthesize Nd/SiO_2 with various loadings of Nd_2O_3 like 2, 3 and 4 wt.%. Further we report here about their structure elucidation with the help of XRD, EDX, HR-TEM and also photo-degradation of different dyes with UV light irradiation were carried out and it showed photosensitive catalyst, reduced methylene blue dye in short time.

2. MATERIAL AND METHODS

Tetraethylortho silicates as a silica source was purchased from Sigma-Aldrich and all other chemicals ethanol, aqueous ammonia, hydrazine, sodium hydroxide, neodymium chloride were HPLC grade and used as received without further purification.

2.1. Preparation of SiO_2 particles

Five (5) ml of TEOS (Tetraethyl orthosilicate) was sonicated with ethanol for 10 min. Aqueous ammonia (25% solution) and ethanol with 1:1 ratio were added to the above mixture. Sonication was continued at 25°C for an hour to get a white turbid suspension. 10 ml of this suspension was removed to be used in the next preparation.

2.2. Preparation of Nd/SiO_2 nanoparticles using liquid silica

Nd/SiO_2 nanoparticles were prepared by a new modified sol- gel method as given in literature. At first 10 ml of the liquid silica prepared by the above method was sonicated for 30 min. and to that 2% $NdCl_3$ in ethanol solution was added slowly with continuous stirring. 35 ml of 0.5 M hydrazine and 80 ml of 1 M sodium hydroxide were added drop by drop to the previous mixture under reflux for 90 min to complete the sol-gel process. Thereafter, the product suspension was filtered and washed with pure ethanol. Finally, the sample was dried in an oven at 100°C for 24 h and calcined at 500°C and 600°C. Similarly other compositions of Nd/SiO_2 were prepared.

2.3. Characterization

The morphologies of all samples were examined using a scanning electronmicroscopy (SEM) (Nova NanoSEM NPEP303) and High Resolution transmission electron microscopy (HR-TEM) (make; FEI, model, Tecnai G2, F30, accelerating potential 300kv). The elemental compositions were analyzed by SEM associated energy-dispersed X-ray microanalysis (EDX) operated with the beam energy of 15 kV. Powder X-ray diffraction analysis of the samples was carried out using Rigaku, Miniflex G-600 diffractometer.

2.4. Photocatalytic property of Nd/SiO_2 nano-composites

The photocatalytic performance of Nd/SiO_2 composites was evaluated by the photocatalytic degradation of organic dye methylene blue under ultra violet light. The experiments were conducted with 0.5g of Nd/SiO_2 composite dispersed in 50 mL of methylene blue aqueous solution (100 mgL^{-1}). In order to establish the adsorption-desorption equilibrium between the catalyst and substrate, the solution was pre-stirred in dark for about 30 min. Then, the solutions were exposed to a visible light source to irradiate the suspension under stirring. 5mL of the suspension was collected from the reactor at different irradiation time intervals. The catalytic performance of the composites was analyzed quantitatively for the absorption peak at 664 nm of methylene blue.

3. RESULTS AND DISCUSSION

3.1. XRD analysis

The structural properties of the synthesized material of various amount of (2, 3 and 4 wt %) Nd (III)doped on SiO_2 were investigated by X- ray diffraction studies over the 2θ values in the range of 10-80°. The powdered samples calcined at 500°C (4 h) showed slight crystalline nature. As per the literature, in case of neodymium, if it was calcined above 500°C, then it showed crystalline nature [5]. But in our case, the samples were calcined at 500°C, still samples of Nd/SiO_2 showed crystalline nature. XRD pattern of 2wt%, 3wt% and 4wt% showed their spectra in Fig.1a.

In order to achieve more crystallinity, the calcination temperature was increased up to 600°C and the samples were resulted into more crystallinity. This change in crystallinity was observed by studying XRD. The diffraction peaks were observed at 21.74° (200), 27.75°(102), 28.79°(210), 31.59°(211), 33.65°(202), 48.66°(213). All these peaks showed neodymium silicon oxide phase (Nd9.35 Si6 O26) (ICDD, PDF2 DB card no. 01-083-9034). The crystallite size is from 15.4 nm to 34.3 nm was calculated from the Debye Scherrer equation ($D=0.9\lambda/\beta \cos\theta$), where D is the crystal size, λ is the wavelength of X-ray, θ is the Braggs angle in radians, and β is the full width at half maximum of the peak in radians.

It may be due to at high calcination temperature, the actvation energy increases which help to merge individual nanostructures together and therefore cross grain-boundary diffusion dominates over parameters such as surface and volume diffusion process and therefore crystallinity increases [3].

3.2. EDX-SEM

The chemical composition of resulting Nd/SiO_2 composite has been analyzed by EDX and shown in Fig.

2. In this pattern, Si, O, and Nd peaks were clearly seen which confirmed the composition of the composites.

The surface morphology of the Nd/SiO_2 nano-composites was investigated by SEM microscopy. Fig.3 showed the SEM images of Nd/SiO_2nanocomposites, the results indicated that distorted spherical sized particles with agglomeration. Agglomeration may be due to the more amount of silica present in the sample.

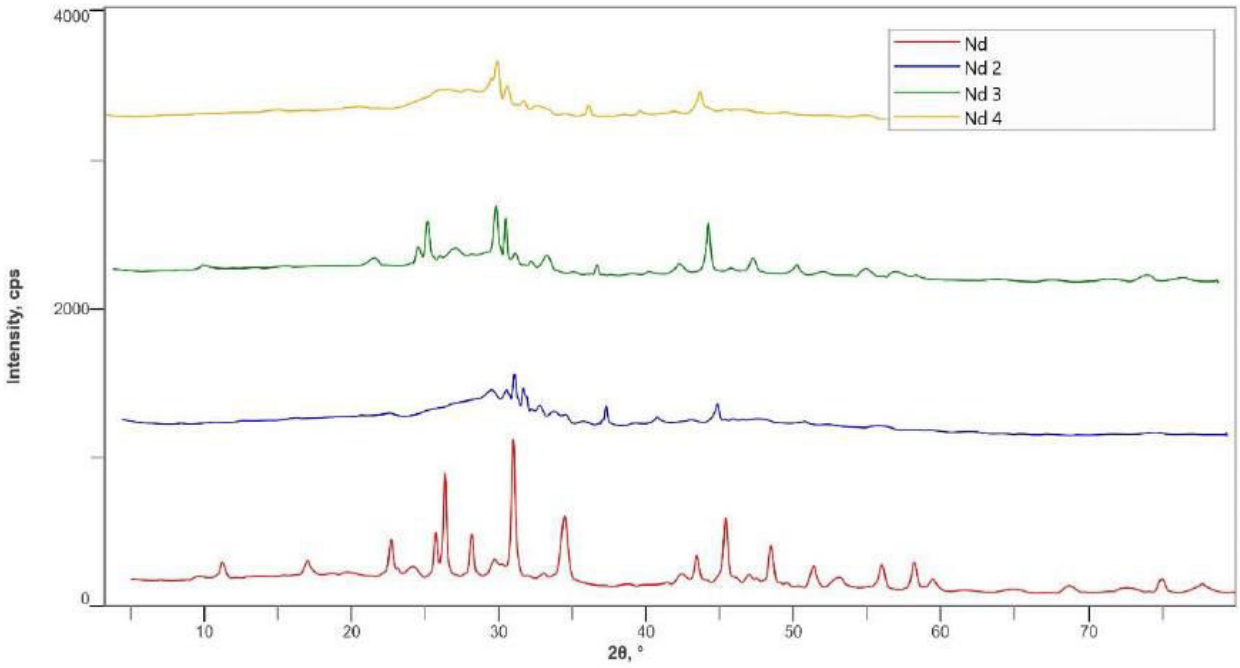


Fig. 1a: X-ray diffraction pattern of Nd/SiO_2 Composite calcined at 500°CA) Plane Nd B) 2wt.% Nd/SiO_2 C) 3wt.% Nd/SiO_2 D) 4wt.% Nd/SiO_2

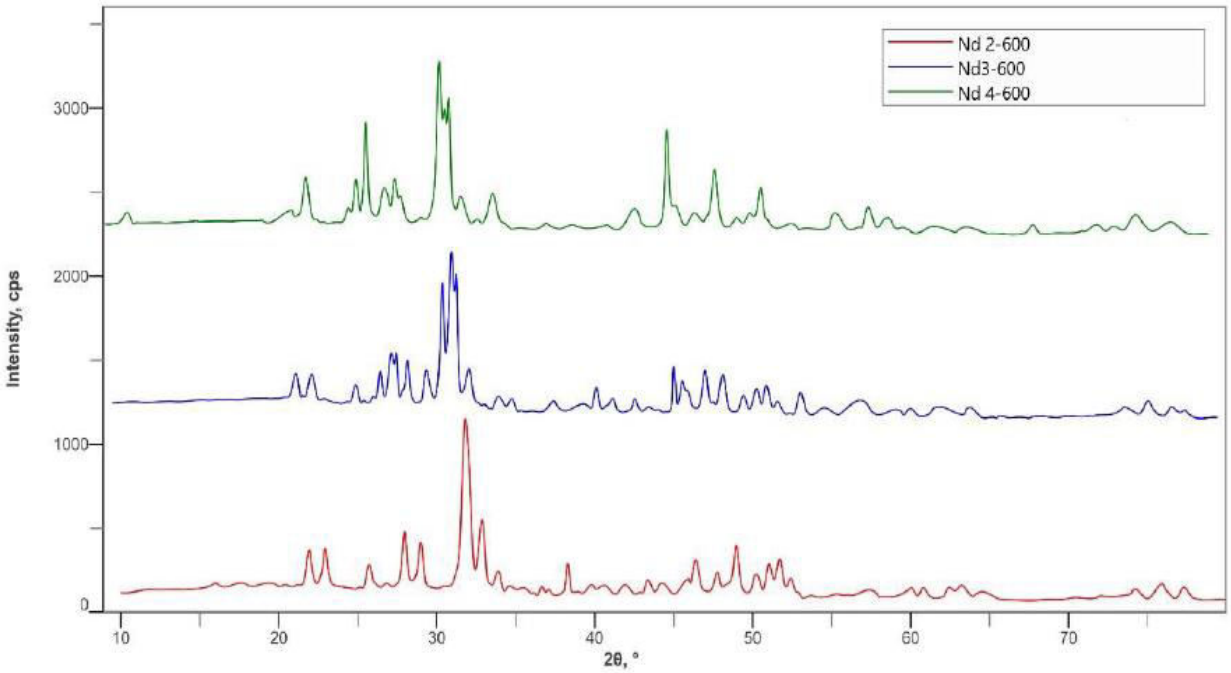


Fig. 1b: X-ray diffraction pattern of Nd/SiO_2 Composite calcined at 600°CA) 2wt.% Nd/SiO_2 B) 3wt.% Nd/SiO_2 C) 4wt.% Nd/SiO_2

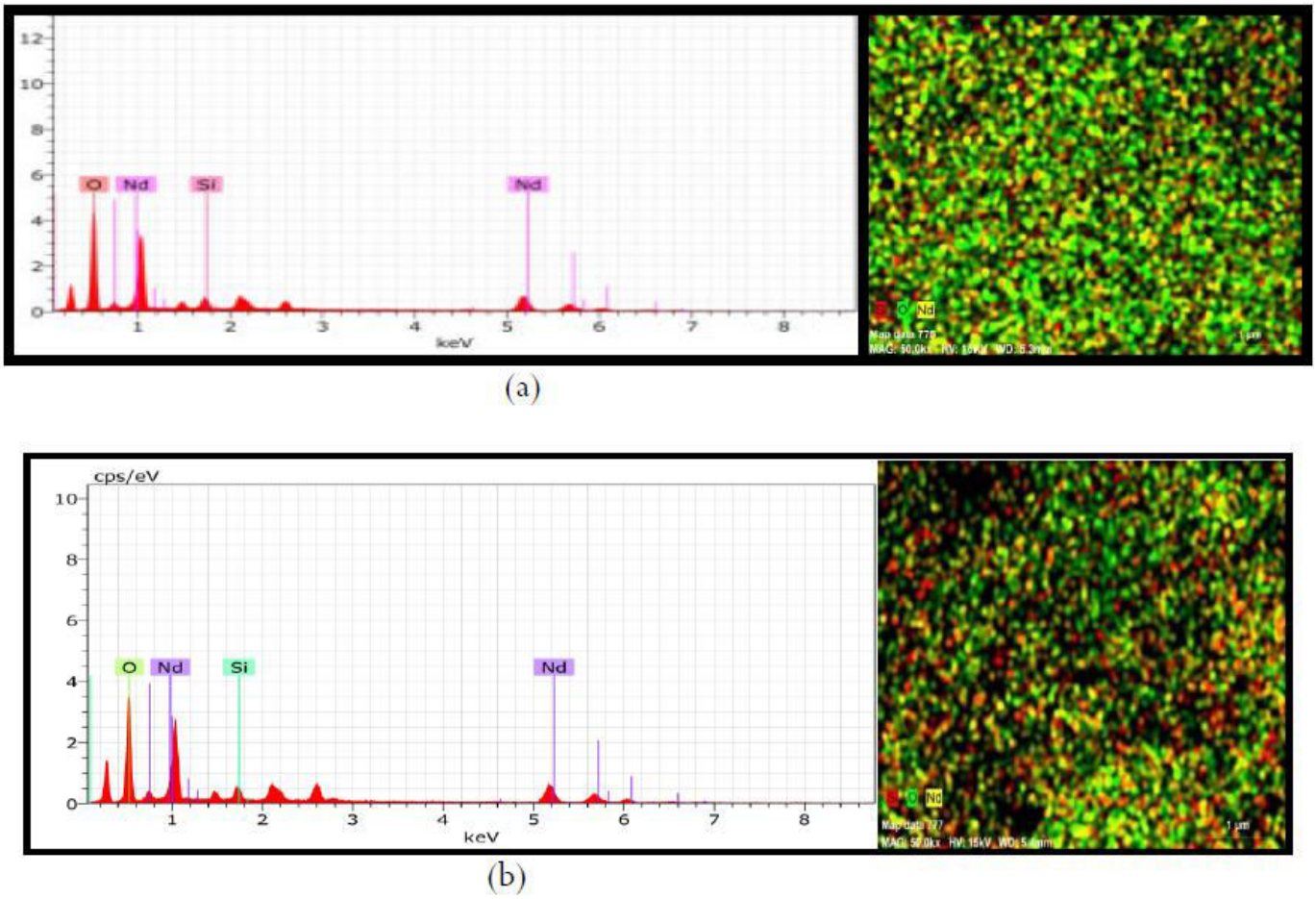
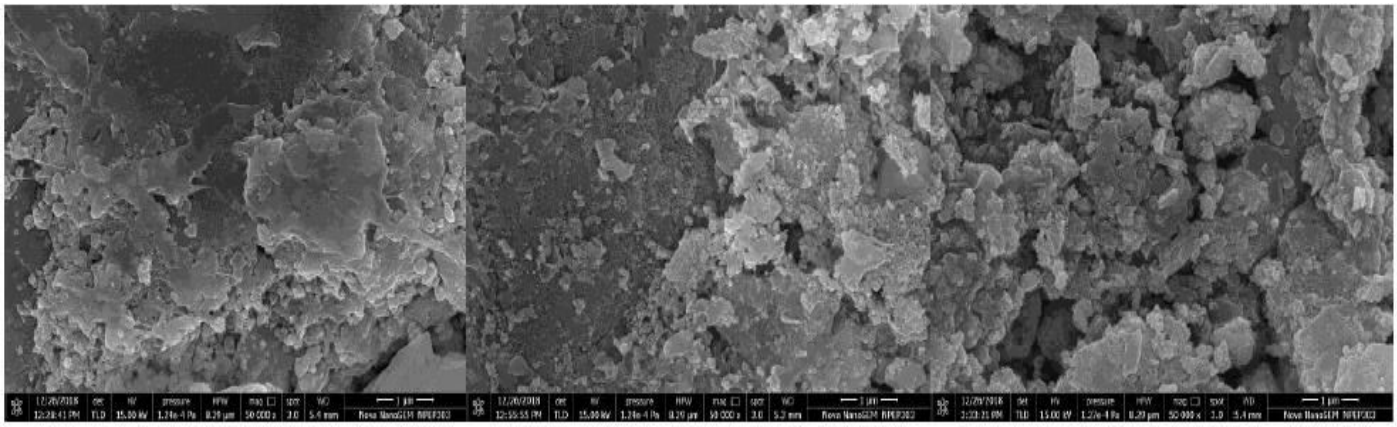


Fig. 2: EDX spectrum of a) 2wt.% Nd/SiO_2 b) 4wt.% Nd/ SiO_2composites



(a) (b) (c)

Fig. 3: FE SEM Images of a) 2% Nd/ SiO_2nanocomposite b) 3% Nd/ SiO_2 nanocomposite c) 4% Nd/ SiO_2 nanocomposite

3.3. HR-TEM study

The Nd/SiO_2nanocomposites were examined with the use of HR-TEM to confirm nano size of the particle and surface morphology. It was observed that the surface of SiO_2 was covered with Nd (III)thin layer. Although the large amount of aggregation was observed. The size calculated from HR-TEM was well matched with XRD. Therefore it confirmed the formation of nanocomposite.

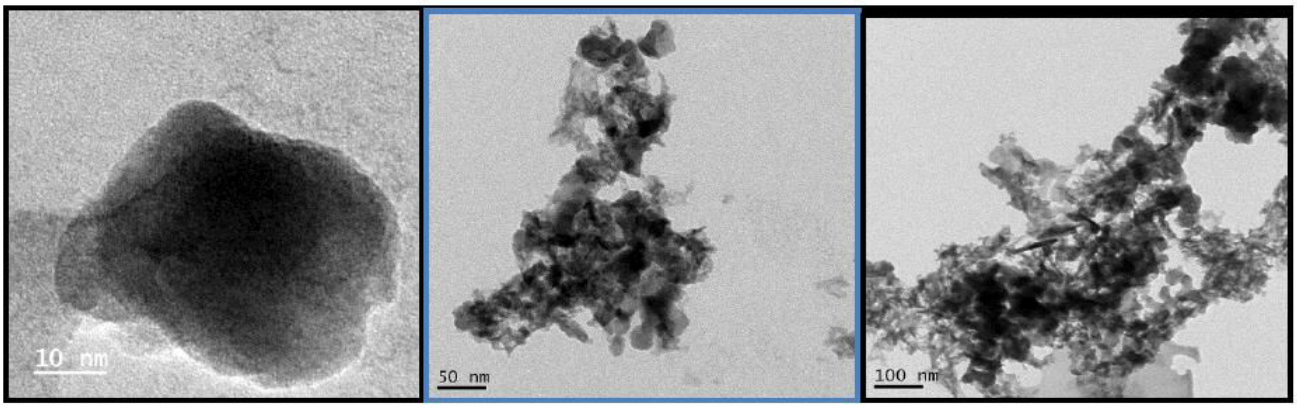


Fig. 4: HR-TEM images of 3% Nd/SiO_2composites.

3.4. Photocatalytic degradation analysis of Nd/ SiO_2composites

The general photocatalysis process and the involved photochemical reactions which are reported by literature is given following [13]:

Nd_2O_3 + Light energy (hυ) ⟶ $Nd_2O_3 + e^- + h^+$

$h^+ + H_2O \longrightarrow H^+ + OH•$

$h^+ + OH^- \longrightarrow OH•$

$e^- + O_2 \rightarrow O_2^-$

$2e^- + O_2 + 2H \longrightarrow H2O2$

And $e^- + H_2O_2 \rightarrow OH• + OH^-$

When the light with energy falls on the surface of the photocatalyst, the valence band (VB) electron jumps to the conduction band (CB) leaving a hole or positively charged void. The catalyst would be more efficient if these positively charged holes and negatively charged electrons take longer time before recombination. When the catalyst is in aqueous medium and exposed by light it generates H^+ and OH•. The photo generated electrons then react with trapped O_2 and H^+ to produce H_2O_2 that further promote OH^- ion and OH• free radical. Therefore highly reactive radical species created which helps in delaying the recombination of holes and electrons charge carriers and provides extra time to interact with the pollutant dyes OH• [14, 15]. The photocatalytic activities of the Nd/SiO_2composites have been investigated by the degradation of methylene blue (MB) under visible light.

The methylene blue contaminant photodegradation efficiency has been determined as follow:

Degradation Efficiency = $Ao - \frac{At}{Ao} \times 100$

Where A0 and At are the absorbance quantity of methylene blue contaminant solution at zero minute and a time‘t’ respectively.

The photodegradation results of neodymium doped SiO_2nanocomposites are presented in Fig. 5. As can be seen in Fig. 5, the degradation efficiencies are 60, 62 and 70% for 2%, 3% and 4% Nd/SiO_2 nanocomposites respectively.

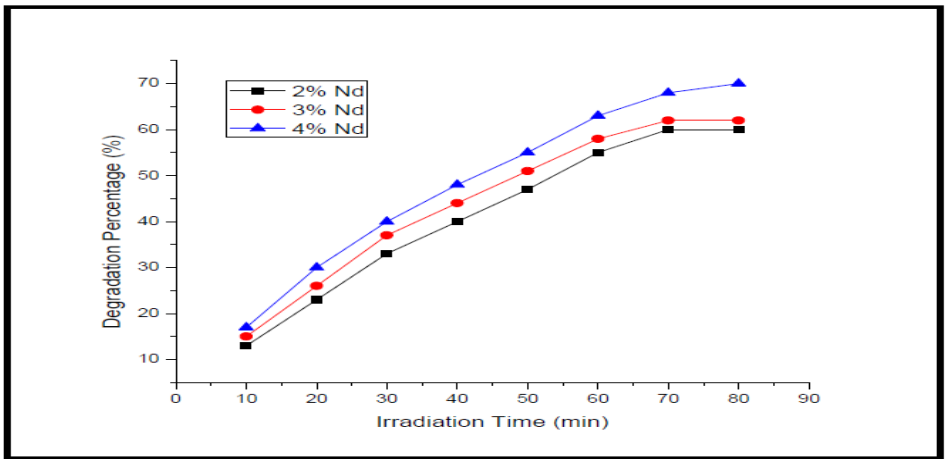


Fig. 5: Photodegradation of Nd/SiO_2

These results clearly showed that 4% Nd/SiO_2 was optimum concentration which has depleted concentration of dye by 70% within 80 min. It means 4% doped Nd showed highest photocatalytic activity.

4. CONCLUSIONS

In this study, we have demonstrated a relatively mild and facile route for the formation of Nd/SiO_2 nano-composites. Their nanostructure, chemical composition, and visible light driven photocatalytic performances were investigated. The results of XRD, FESEM, and HRTEM showed that the formation of nanocomposites with size 34.3nm and neodymium oxide silicate phase with crystalline nature. All the Crystalline samples were screened and indicated photocatalytic activity but 4wt% Nd/SiO_2 showed higher photocatalytic activity.

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