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Enhanced Photocatalytic Activity of Two Dimensional Graphitic carbon nitride: C_3N_4@Co_3O_4 Core shell nanocomposite for Discriminatory Organic transformation of CF dye under Hg-vapor reactor

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Abstract

In the present investigation the material Co_3O_4 nanoparticles were prepared by co-precipitation method, while graphitic carbon nitride (g-C_3N_4) was prepared by direct heating of melamine. The nanocompositeg-C_3N_4- Co_3O_4 were prepared by stoichiometric mixing and direct heating in porcelain boat followed by calcination. The prepared nanomaterials were characterized by various techniques. These both materials were characterized by XRD to get structural parameters and to confirm the average particle size of prepared nanomaterial. The scanning electron microscopy(SEM) was carried out to get surface characteristics of prepared materials. The energy dispersive spectroscopy was conducted to get elemental composition prepared material Co_3O_4 and g-C_3N_4- Co_3O_4. The transmission electron microscopy (TEM) was conducted to get lattice information of prepared

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material. While magnetic properties of both the material were investigated by means of vibrating sample magnetometer (VSM), since cobalt oxide is a ferromagnetic material. The surface area was confirmed from Brunauer-Emmett-Teller (BET) study. The g-C_3N_4- Co_3O_4 nanocomposite has found enhanced surface area of 78.48 m^2/g in comparison to the sole Co_3O_4 nanomaterial (55.23 m^2/g). Both these prepared materials were utilized in photocatlytic degradation of Carbol Fuchsin (CF) dye. The various parameters related to optimization of photocatlytic degradation of dyes were investigated in detail. The carbon nitride mediated cobalt oxide material is found to be very effective for degradation of CF dye and almost 97% of dye was successfully decomposed by the g-C_3N_4- Co_3O_4 nanocomposite. The reusability test confirms that the prepared g-C_3N_4- Co_3O_4 nanocomposite is very efficient in degradation of CF dye in multiple cycles with 110 minutes of contact time.

Introduction

Nanotechnology has been successfully utilized in several applications in technical fields. Nanotechnology is associated with countless solutions to the engineering, science and technology. There are many applications of material science such as photocatalysis,[1,2] waste treatment,[3] gas sensors,[4] biosensors, SOFC, electrochemical cells, solar cells, organic conversions, organic LED, adsorption studies, H_2 production etc.[5-9] Presently mankind is associated numerous problems. Most of the problems are solve with the use nanomaterials as catalysts. The major problems today we are facing are associated with pollution, more specifically air and water pollution. The water problems are originated from industrial, anthropological activities and waste effluents discharged tough water stream. Several organic, polymer and chemical industries producing several drugs and products, the waste after producing these chemicals are unnecessarily discharged through the rivers and nearby costal region which initiates the basis of pollution. Although several researchers have developed some efficient systems through engineering work to defeat these water pollution related problems, but still we are not completely successful to overcome these environmental challenges. Formerly, the metal oxides were utilized as catalysts very effectively in various applications of science streams. With the movement of time the sole metal oxide are modified by researchers with the ease of doping and other modification methods. There are plenty of fabricated materials by transition metal doping to metal oxides, non-transition elements doped to metal oxides. In last decades the nanocomposite materials such as CNS doped metal oxide,[10-11] graphene doped metal oxides, CNT mediated materials, graphitic carbon nitride doped metal oxides, boron nitride metal oxide nanocomposite are very popular materials in various applications of catalysis. Now days there is vast trend of nanocomposite mediated with carbon nitride over metal oxide applied in photocatalysis or adsorptive removal of dyes or effluent treatment.[12-14]

Carbon nitride is now days a new class of material in association with metal oxides to be applied in photocatalysis and useful catalysis related applications. Carbon nitride has a good thermal stability made up from the elements C, H, N in two dimensional (2D) frameworks. The C_3N_4 is exists in planar polymeric form with planar structure having structural similarities with graphite molecule. The g-C_3N_4 is metal free polymer with the band gap energy of 2.8 eV. Due to its good thermal stability with metal oxides it is being used in most of the catalytical applications. Most importantly the methods of preparation of g- C_3N_4 arevery cheap and cost effective. Among the popular methods of preparation of g-C_3N_4, the heating of melamine, thermal reaction between cyanuric chloride and sodamine, in situ chemical vapor deposition (CVD) etc.[15-18] Although, there are many inherent properties of g-C_3N_4 but as per the photocatlytic applications it has several draw backs such as rapid recombination of charge carriers, not efficient in light utilization from visible range and average electrical conductivity. Thus, there is a great need to modify this material to get access in photocatlytic route.[19-20]

Most of the researchers worked to overcome this problem and get successful to utilize this material in photocatalysis. As per the reports from, Hassani *et.al*, Vadivel *et.al*, and kumar *et.al*, the magnetic graphitic carbon nitride i.e graphitic carbon nitride along with magnetic material such as CO_3O_4, Fe_3O_4 or $NiFe_2O_4$ etc. found to be excellent photocatlyst to remove several organic pollutant dyes.As per the reports the magnetic graphitic carbon nitride is able to overcome recombination of electron hole pair, enhancements in visible light strength required for absorption, etc. There is some modern trend to modify the g-C_3N_4 such as chemical doping, physical doping, and morphology command etc. out of that chemical and physical doping of g-C_3N_4 over the metal oxide to prepare nanocomposite to enhance many physical, chemical properties of g-C_3N_4 is a good practice now days. In physical and chemical methods of modification with graphitic carbon nitride there is use of semiconducting material such as $NiFe_2O_4$, $NiFe_2O_4$, ZrO_2, TiO_2, ZnO, CuO etc. are more common semiconducting material are being utilized to prepare carbon nitride–metal oxide nanocomposite.[21-30]

The present research deals with low cost and efficient synthesis of carbon nitride mediated magnetic cobalt oxide nanocomposite. The prepared nanocatalyst was successfully utilized for photocatlytic degradation of Carbol Fuchsin dye. The prepared catalysts were optimized for various parameters such as effect of catalyst dose, effect of pH, effect of initial dye concentration and contact time. The prepares carbon nitride mediated cobalt oxide nanocomposite was successful in degradation of CF dye with reaction conditions 20 ppm dye, 0.8 g catalyst dose and 7.5 pH. The nanocomposite is found to be very successful, almost 97% of CF dye.

Materials and Methods

All the chemicals utilized in the present research are of AR grade, purchased from merk limited, Mumbai and used without further purification. Chemicals used are cobalt acetate tetra hydrate, Melamine powder, NH_3, deionized water.

Synthesis of Undoped Cobalt Oxide (Co_3O_4) Nanoparticles by Co-Precipitation Method

0.02 moles of Cobalt acetate tetra hydrate and 0.03 moles of urea were dissolved in 50 ml of deionized water in separate beakers. After the complete dissolutions both these solutions were mixed together, the pink colored sol was obtained. The mixed solution cobalt precursor and urea were kept over magnetic stirrer for 30 minutes to get homogenous mixed solution. The stirred solution was then transferred to round bottom flask (RB) , then the RB was fitted to the water condenser , the whole solution was allowed to refluxed for 12 hours. After the constant heating the pink colored solution was turned to indistinct blue color with solid residue, the solution containing residue was allowed to cool at room temperature and then filtered out. The residue was washed with hot water and ethanol to free from impurities. The dried residue was shifted to silica crucible and incinerated in muffle furnace for 5-6 hours at 650^0C. At the end black colored cobalt oxide nanoparticles were recovered from muffle furnace for further use and characterization.[31-32]

Fabrication of Graphitic Carbon Nitride (g-C_3N_4)

The graphitic carbon nitride (g-C_3N_4) was fabricated by utilizing melamine ($C_3N_6H_6$) as a resource. The direct heating strategy was employed for synthesis of graphitic carbon nitride from melamine. Initially, 5 gram of melamine was kept in silica crucible and transferred to muffle furnace at 550^0C for nearly 130 minutes. After this time, the sample melamine was converted to graphitic carbon nitride with the elimination of ammonia gas molecules. The sample was kept at room temperature for 30 minutes, after cooling the (g-C_3N_4) material was grinded further in mortar pestle for 40 minutes to get well homogenized graphitic carbon nitride sample for further use.[33-34]

Synthesis of g-C_3N_4@Co_3O_4 nanocomposite

The graphitic carbon nitride-cobalt oxide nanocomposite was prepared by mixing 1 g of g-C_3N_4 with 1 g of Co_3O_4 nanoparticles. Initially, both these materials graphitic carbon nitride and cobalt oxide were grinded in mortar pestle for nearly 30 minutes. After homogeneous mixing, the mixture was transferred to porcelain boat and heated with constant heating rate of 15^0C min^{-1} in oxygen atmosphere up to 600^0C for nearly 3 hours. The dark gray color graphitic carbon nitride-cobalt oxide nanocomposite was obtained on next day for further use and characterization.[35-36]

Results and Discussion

XRD Analysis

The prepared material g-C_3N_4/Co_3O_4 nanocomposite was characterized by x-ray diffraction technique to confirm structural and chemical characteristics of the prepared nanocomposite. The Braggs scanning angle for the XRD instrument was varying from 10-90^0. While, the copper Kα metal was used as a source to produce x-ray beams. The XRD pattern for fabricated g-C_3N_4/Co_3O_4 nanocomposite is as depicted in figure 1 from which crystalline nature and average nanoparticle size of the prepared material was confirm. From XRD pattern the Braggs reflection patterns can be assign to the formation of graphitic carbon nitride mediated cobalt oxide nanocomposite. From the XRD data the 2θ signals of diffracted peaks for g-C_3N_4/Co_3O_4 are 32.45, 37.89, 45.10, 61.20, 65.13 for the reflection of (220), (311), (400), (511), (440) planes. While two additional peaks obtained in the XRD spectrum are 13.100 and 27.5 0 with (100) and (002) planes are attributed to the characteristics interlayer planar ring two dimensional structure for g-C_3N_4 material (JCPDS 87-1526). The x-ray diffraction data as mention above with typical two theta values and corresponding hkl planes confirms the formation of cubic crystal lattice of for g-C_3N_4/Co_3O_4 nanocomposite material.The average crystallite size calculated by using of Debye-Scherer's formula. [D = Kλ/β COS θ]. where D is average particle size, K is constant (0.9 to 1), β is full-width half maxima (FWHM) of a diffracted peak, θ is the angle of diffraction. The average particle size calculated for g-C_3N_4/Co_3O_4 was found to be 23.44 nm.[37] The match scan data of g-C_3N_4/Co_3O_4 shows the formation of g-C_3N_4/Co_3O_4 nanocompositewith JCPDS number 43-1003.

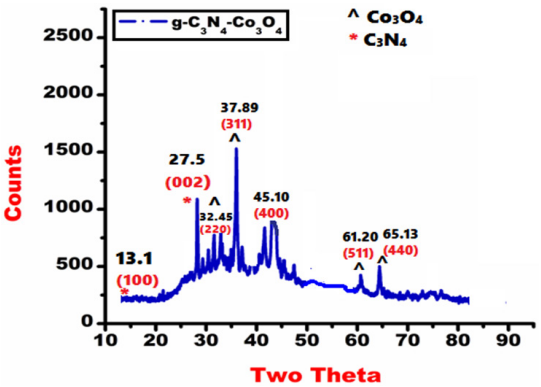

Fig.1: XRD pattern of C_3N_4-Co_3O_4 nanocomposite

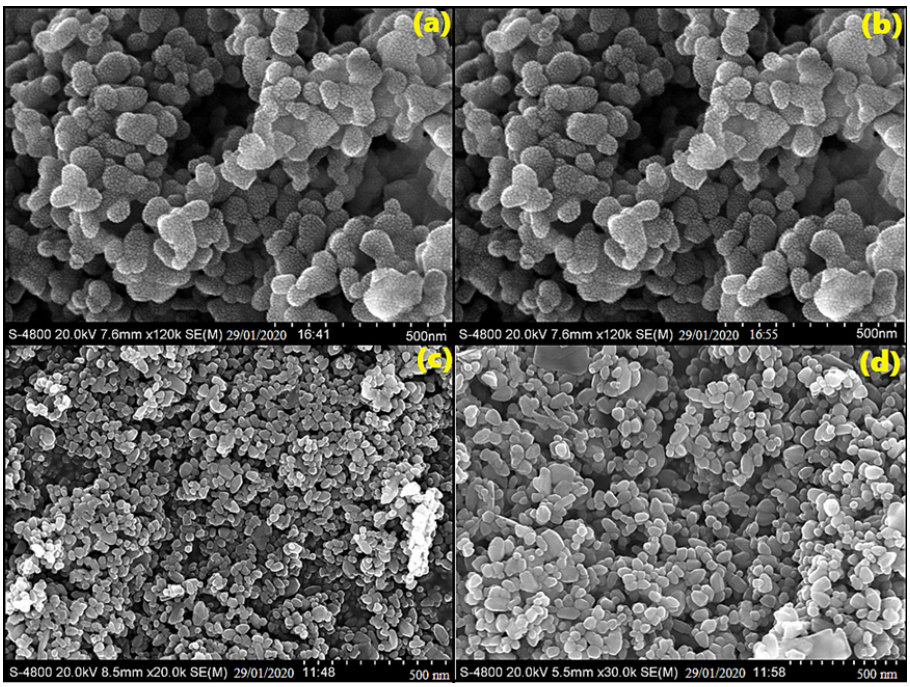

Fig. 2: (a,b) FE-SEM Images of Co_3O_4 nanoparticles (c,d) FE-SEM Images C_3N_4-Co_3O_4 nanocomposite

Scanning Electron Microscopy (SEM) Study

The Figure 2 a-d showing the scanning electron micrographs for the prepared cobalt oxide and carbon nitride mediated cobalt oxide nanocomposite. The surface texture, appearance of nanoparticles and porosity of the prepared materials can be easily seen from the images as given below. The different size nanoparticles of cobalt oxide and carbon nitride mixed cobalt oxide with homogeneous surface can be seen for both these materials. The SEM images also showing good porous appearance of the prepared material as well as over the surface lattice smaller intestinal spaces or voids can be seen for both the materials.The voids sometimes act as adsorbate to occlude several smaller molecules via chemisorption or physisorption mechanism. Since, photocatalysis is a surface phenomenon hence voids, porosity and surface area over the material lattice are the key points for the mechanism. Both the prepared materials showing close agglomeration of various dimensions nanoparticles all over the surface lattice.[38-40]

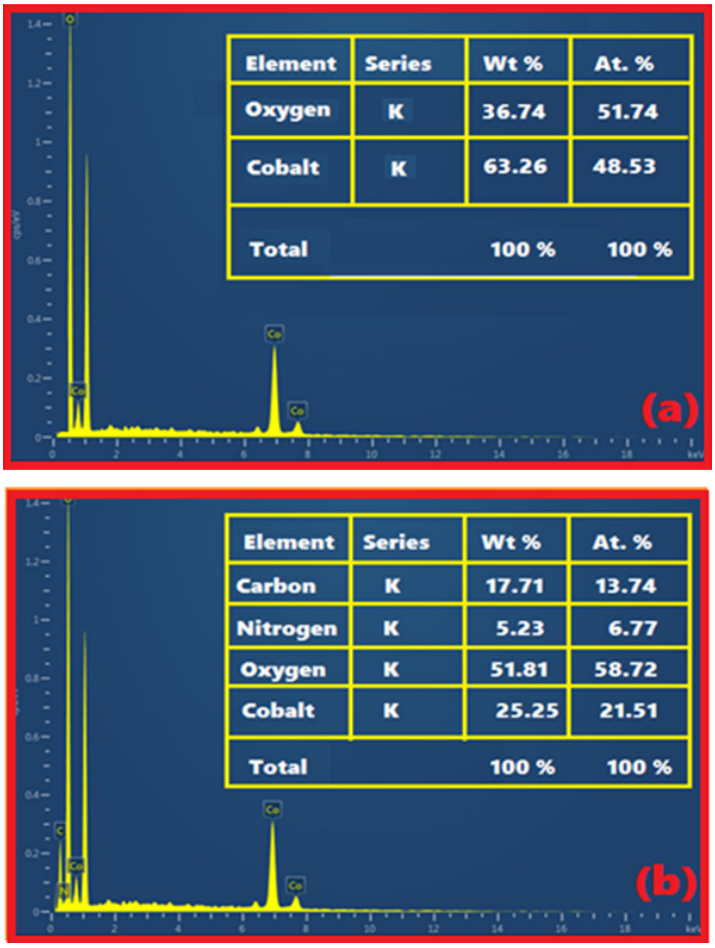

Fig.3: (a) Energy dispersive spectrum for Co_3O_4 nanoparticles, (b) energy dispersive spectrum for C_3N_4-Co_3O_4 nanocomposite

Energy Dispersive Spectroscopy (EDS) Study

The elemental composition of undoped cobalt oxide and graphitic carbon nitride modified C_3N_4-Co_3O_4 nanocomposite was confirmed by using energy dispersive spectroscopy study. The spectrum for sole cobalt oxide nanoparticles is as depicted in figure in which the embedded table is showing the elemental composition of each individual element in fabricated cobalt oxide material. The spectrum shows sharp resolution of elemental oxygen at 1KeV, while the elemental cobalt is found to be resoluted at approximately 7 KeV. While EDS

spectrum for graphitic carbon nitride mediated cobalt oxide is as depicted in figure 3-b. The spectrum depicts resolution of elemental cobalt at 7 KeV. The additional sharp lines for elemental carbon and nitrogen from carbon nitride can be observed within the range of 1KeV. The EDS results obtained for both the materials is in good agreement with the reported research data.[41]

High Resolution Transmission Electron Microscopy (HR-TEM)

The crystal lattice morphology of the prepared cobalt oxide and carbon nitride mediated cobalt oxide nanocomposite was investigated by using high resolution transmission electron microscopy. The HR-TEM images of both the fabricated material is as depicted ii figure 4 a-d. According to the literature study the crystal lattice for cobalt oxide belongs to the cubic lattice .The TEM data obtained for both these materials is also showing the approximate cubic lattice images for these prepared materials. The TEM depicts the close agglomeration of varied size nanoparticles ranging from 20 to 100 nm. From the TEM data for both the fabricated materials showing good agreement with X-ray diffraction data as per as the nanoparticle size is concern.[42]

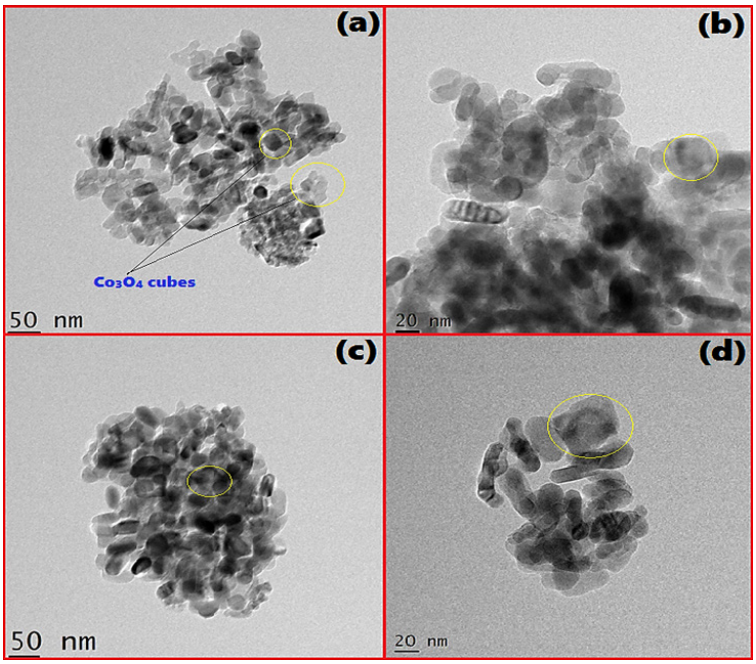

Fig.4: (a,b) HR-TEM Images of Co_3O_4 nanoparticles (c,d) HR-TEM images C_3N_4-Co_3O_4 nanocomposite

Magnetic Study by Vibrating Sample Magnetometer (VSM)

Since cobalt oxide is a ferromagnetic in nature hence magnetic parameters cobalt oxide and carbon nitride mediated cobalt oxide were identified with the help of vibrating sample magnetometer (VSM) technique with 1000 guass applied magnetic field model number Lakeshore VSM-7410 at normal temperature region. The magnetic saturation curves for the fabricated materials undoped Co_3O_4 nanoparticles and C_3N_4-Co_3O_4 nanocomposite is as depicted in figure 5a and 5b respectively. Both the figures of VSM for prepared materials shows the characteristics hysteresis loop, indicating the definite ferromagnetic character of fabricated materials. From figure 5a it can observe that the extent of saturation magnetization for undoped Co_3O_4 material is found to be 188.12 emu/g, while figure 5b shows extent of saturation magnetization for C_3N_4-Co_3O_4 material it was 89.56emu/g. Cobalt oxide being inherently magnetic in nature the magnetic saturation is found to be very high in comparison to the carbon nitride-cobalt oxide nanocomposite.[43-44] The declined in magnetic saturation in case of

C_3N_4-Co_3O_4 material may be attributed to the presence of existence of smaller concentration of carbon nitride ring structures making weak magnetic domains for cobalt oxide material. The magnetic characteristics such as Retentivity (Mr), Coercivity (Hc) , sensitivity and magnetization saturation (Ms) is as depicted in table 1.

Table 1: Magnetic parameters of Co_3O_4 and C_3N_4- Co_3O_4 nanoparticles

S.N	Compound	Saturation Magnetization Ms (emu/g)	Sensitivity (emu)	Coercivity Hc (G)	Retentivity Mr(emu/g)
1	Co_3O_4	188.12	-5.400	1020.10	349.56
2	C_3N_4- Co_3O_4	89.56	-5.400	1248.20	82.41

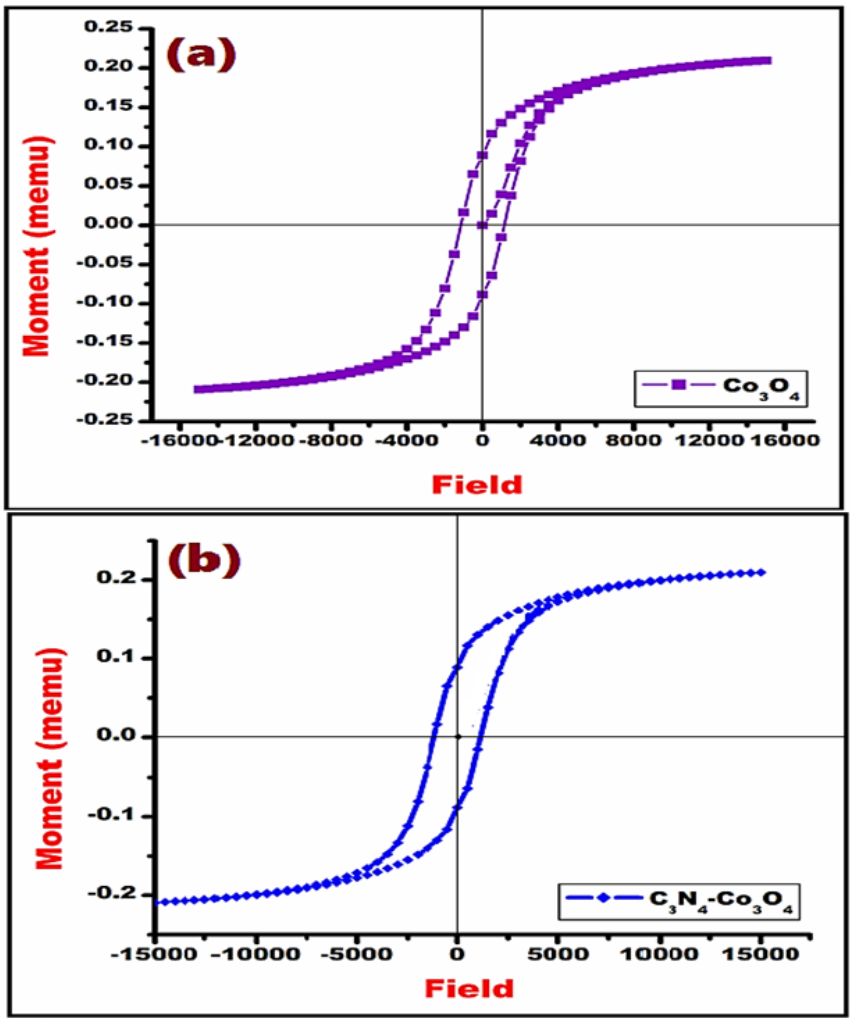

Fig. 5: (a) Magnetization curve for Co_3O_4 nanoparticles (b) Magnetization curve for C_3N_4-Co_3O_4 nanocomposite

Brunauer-Emmett-Teller (BET) study

Brunauer-Emmett-Teller nitrogen adsorption-desorption experiment was carried for the fabricated materials Co_3O_4 and C_3N_4-Co_3O_4 nanocomposite. BET curves plotted for both these materials as a function of relative (P/P_0) against the volume of gas (cc/g) is as depicted in figure 6 a-b. Since, Photocatalysis is a surface phenomenon over the catalyst hence the surface area investigation is very prime for this type of investigations. The BET analysis was carried over the prepared catalysts for the investigation of pore size, pore radius and surface area of the prepared materials. After, the analysis of BET the fundamental properties related to surface entities of the prepared catalysis is as mention in table 2. From the present analysis it was observed that the carbon nitride mediated cobalt oxide material has improved surface area (78.48 m²/g) in contrast to the sole cobalt oxide nanoparticles. According to six BDDT adsorption isotherm categories, the present adsorption is belongs to the type 4 adsorption isotherm category.[45]

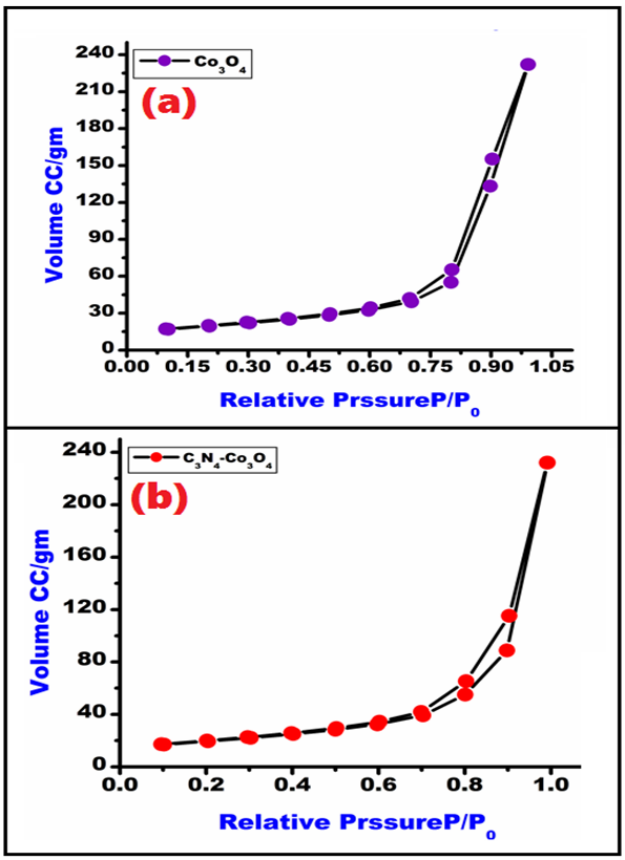

Fig. 6: Brunauer-Emmett-Teller nitrogen adsorption-desorption spectrum for (a) Co_3O_4 nanomaterial b) C_3N_4-Co_3O_4 nanocomposite

Table 2: Brunauer-Emmett-Teller pore volume, surface area, pore diameter for Co_3O_4 nanomaterial and C_3N_4-Co_3O_4 nanocomposite

Fabricated Material	Surface Area (m^2/g)	Pore volume (cc/g)	Pore radius (Å)	Correlation Coefficient (R_2)
Co_3O_4	55.23	0.258	75.70	0.99
C_3N_4-Co_3O_4	78.48	0.361	78.47	0.99

Photocatalytic Activity

Both the prepared catalysts viz. Co_3O_4 nanomaterial and C_3N_4-Co_3O_4 nanocomposite were studied for photocatlytic application over the Carbol Fuchsin basic dye. The photocatlytic degradation of the CF dye was investigated using photocatlytic reactor equipped with Mercury vapor lamp (200 watts). Additionally, the photocatlytic reactor consists of magnetic stirrer, chiller for circulation of solvent system, control panel units for function controlling like catalyst loading, temperature, and dye concentration etc. The various concentrations of selected dye were prepared in ppm level (mg L^{-1}) for degradation study. The complete changes in dye concentrations were examined with the aid of double beam spectrophotometer (Systronics-model number 118), while the pH of the catalyst system and reaction components was measured with the assists of digital pH meter (make Lab-India) fitted with glass electrode. General mechanism of CF dye for both fabricated material and general properties of CF dye are depicted in figure 7.

The deradation efficiency of the catalys for selected dye concentration was computed using equation 2

$$\% D \text{ (degradation)} = (C_0-C_t)/C_0 *100 \quad ...(2)$$

C_0 is initial concentration of dye and C_t is concentration of dye at time t

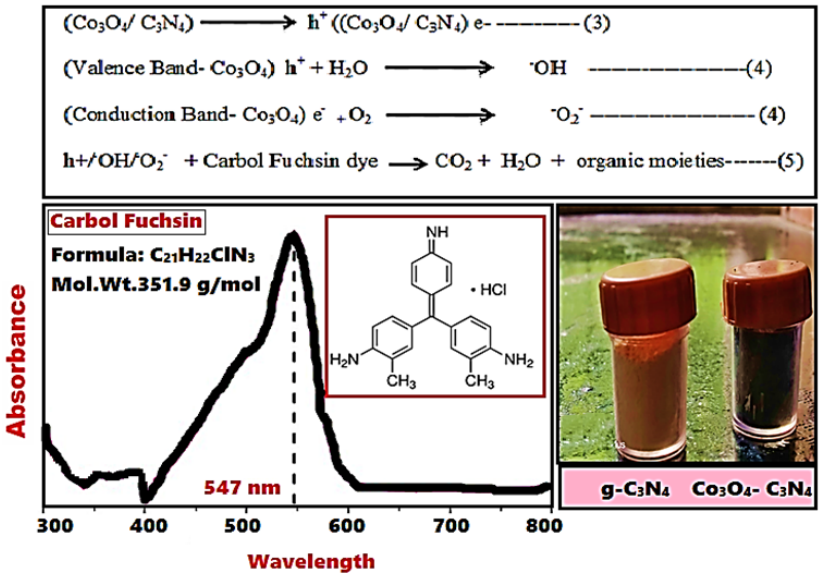

Fig. 7: General mechanisms of photocatalytic degradation of CF dye degradation by C_3N_4-Co_3O_4 nanocomposite, General properties for CF dye and prepared materials C_3N_4-Co_3O_4

Parameters Optimization

Parameter optimization is an crucial investigation to get overall concluding idea about the effective degradation of dye over catalyst surface. The photocatlytic degradation of dye was conducted at λ max of 551nm. After careful investigations the suitable parameters to degrade the Carbol Fuchsin were observed as, dye concentration of 20 mg/L, catalyst dose of 0.8 g L^{-1}, pH at 7.5. The overall graphical presentation for dye degradation by fabricated catalysts as depicted in figures from 8, 9, 10, 11.

Effect of Catalyst Dose

The catalyst dose optimization is a prime step in the photocatlytic degradation process. Since, catalyst is surface at which the overall photocatlytic mechanism is carried out. Here, the fabricated catalysts Co_3O_4 nanomaterial and C_3N_4-Co_3O_4 nanocomposite were utilized in various concentrations from 0.2 to 0.8 g L-1. The catalyst dose was applied from 0.2 to 0.8 g/L for both prepared catalysts at 20 ppm Carbol Fuchsin dye concentration in batch experiment study. In every enhancement of catalyst dose from 0.4 to 0.8 g/L catalyst dose at 20 ppm dye concentration, the

percent degradation for sole cobalt oxide catalyst was observed to be increase from 53. 18 % to 92.74 % respectively for 0.4 to 0.8 g/L catalyst dose. While in case of carbon nitride mediated cobalt oxide the same batch study was conducted at 20 ppm dye concentration. The percent degradation was observed to be 59.12 % to 97.88 % for 0.4-0.8 8 g/L catalyst dose. The behavior of increase in % degradation due to increment of catalyst dose may be attributed to the increase in more number of active sites over catalysts surface due do increase in catalysts concentration. In case of carbon nitride the highest degradation rate at Carbol Fuchsin dye was observed this may be due to enhanced surface area, declined band gap results into more rapid transfer to electrons from valence band to the conduction band of cobalt oxide catalyst. As the electron jumps from valence to the conduction band of catalysts, creates electron hole pair. The positive holes interact with aqua molecules to OH^- radicals, while negatively charged electrons come in contact with oxygen moieties to form superoxide radicals. The overall species form at valence band and conduction band responsible for faster degradation of dye. The comparative graph for catalysts dose of Co_3O_4 nanomaterial and C_3N_4-Co_3O_4 nanocomposite is as represented in figure 8a-b.

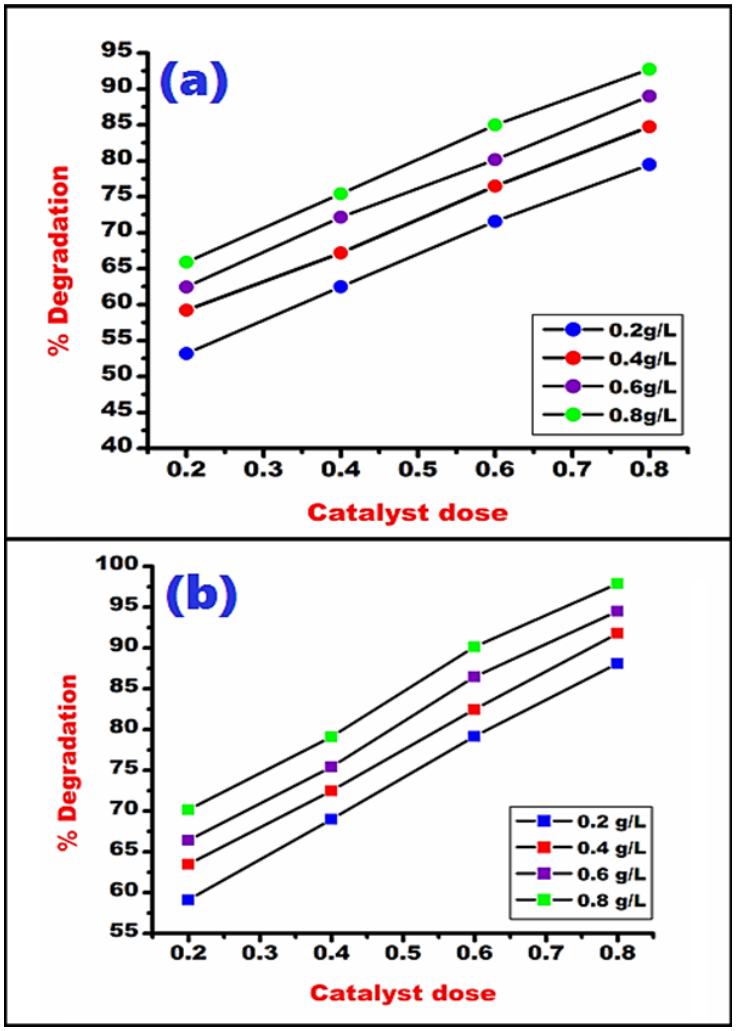

Fig. 8: (a) Effect of catalyst dose 0.2-0.8 g/L (Co_3O_4) at Carbol Fuchsin dye for 20 ppm concentration, (b) Effect of catalyst dose 0.2-0.8 g/L (C_3N_4-Co_3O_4) at Carbol Fuchsin dye for 20 ppm concentration

pH Study

Catalysis is surface dependent and pH dependent process. Hence, pH optimizing is an essential process for effective catalysis. For photocatalysis mechanism over both the prepared catalysts, pH was optimized from 1- 12 ranges i.e. from acidic to basic range. Before pH optimization the catalysts dose was fixed at 0.8 g L^{-1} and Carbol Fuchsin dye concentration was fixed at 20 mg L^{-1}. The photocatalysis for both the prepared catalyst was conducted by fixing above criteria and monitored from pH1-12. During this study it was observed that the rate of photocatalysis for both the materials was enhanced from pH1 to 7.5 or approximately pH 8. After crossing pH value 8 the rate of degradation of Carbol Fuchsin dye for both the catalysts Co_3O_4 and C_3N_4-Co_3O_4 was observed to be declined. Since, the pH_{pzc} (point zero charge or isoelectric point) calculated for both these materials was 7.5. As per the experimental facts, catalyst surface has net zero charge at pH_{pzc}, while pH>pH_{pzc} the catalyst surface is anionic in nature (OH- ions) and pH <pH_{pzc} the catalyst surface is cationic in nature (H+ ions). Hence, the CF dye being anionic in nature will be more attracted blow pH_{pzc} value that is 7.5 and hence almost 96 % of dye degradation was observed at pH_{pzc} value i.e. 7.5. After this pH_{pzc} value the % degradation for both the material was decrease. The probable reason for the decline in degradation was anionic surface after 7.5 pH and being anionic in nature there strong repulsion between dye molecule and catalyst surface charge and hence rate of photocatalysis was found to be decreased after pH PZC value.

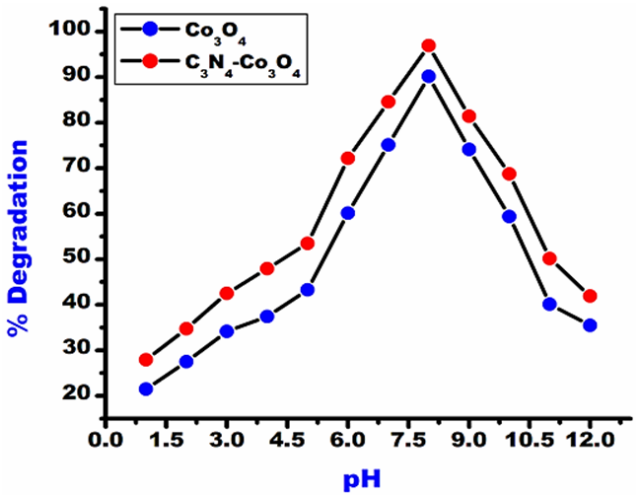

Fig. 9: (a) Effect of pH on degradation of CF dye by Co_3O_4 (b) Effect of pH on degradation of CF by C_3N_4-Co_3O_4

Catalyst Contact Time Effect

The catalyst contact time is crucial parameter in photocatalytic degradation phenomenon. Since, the required for efficient degradation for every concentration of dye is can be examined from this study. The curves of contact time between % degradation and time in minutes is as shown in figure 10 a-b for Co_3O_4 and C_3N_4-Co_3O_4 catalysts respectively. From this study it was observed that CF dye was decomposed very faster after induction period of 20 minutes of reaction and stagnant to the reaction equilibrium at the time period of 90 minutes and almost degraded in 110 minutes for each catalyst. The probable justification could be assign to this trend of degradation of CF dye by both catalysts. Since, in the starting period both the catalysts have enough number of sprightly sites which is responsible for faster CF dye degradation. With the enhancement of time, the concentration of dye increase over the catalysts surface and dye concentration is reached at the equilibrium at this stage and degrade in 90 minutes and hereafter get degraded in 110 minutes. The C_3N_4- Co_3O_4 catalyst has degradation efficiency for CF dye was 86.13% to 96.89 % for 80-20 ppm CF dye concentration. While for Co_3O_4 catalysts the rate of dye degradation was found to be 79.10 to 90.14 % over CF dye for 80-20 ppm dye concentration.

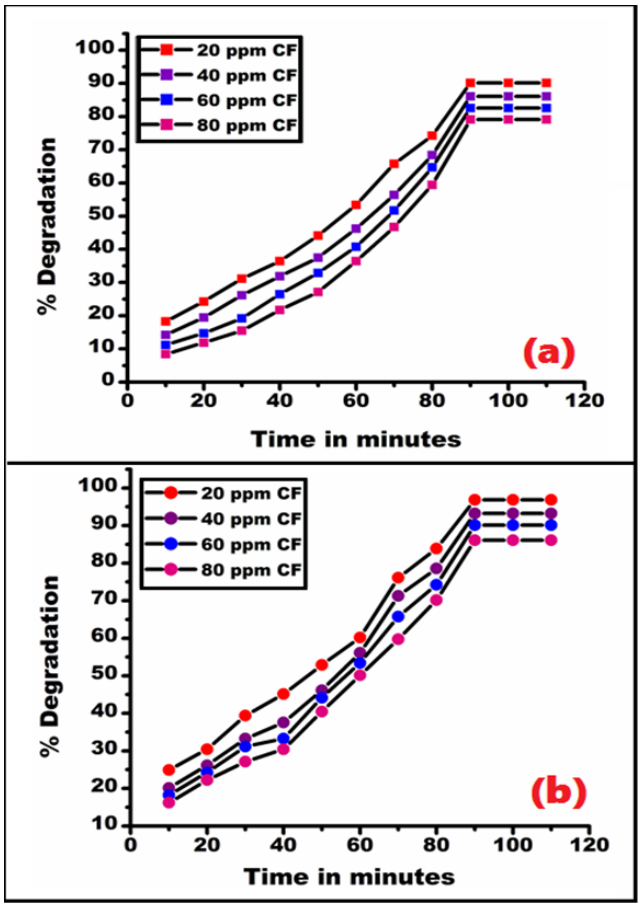

Fig. 10: (a) Effect of contact time on % degradation of CF dye for Co_3O_4 catalyst, (b) Effect of contact time on % degradation of CF dye for C_3N_4-Co_3O_4 catalyst

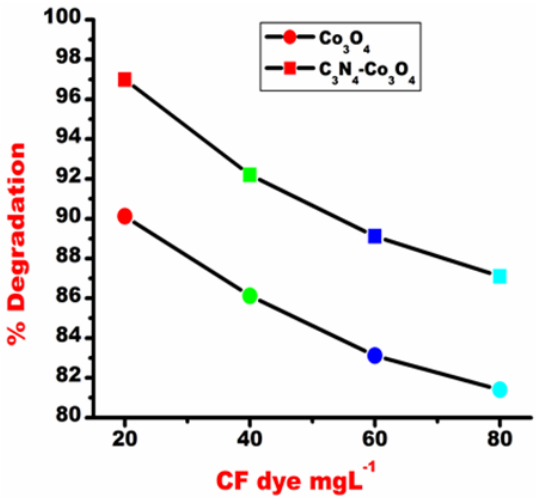

Fig. 11: Effect of initial dye concentration on % degradation of CF dye for Co_3O_4 and C_3N_4-Co_3O_4 at catalyst dose 0.8 g, pH 8.0

Effect of Initial Dye Concentration

The dye concentration optimization is very essential step in photocatlytic degradation study. The rate of photocatlytic degradation of dye is primarily depends and alter with change in dye concentration.In the present research the CF dye degradation study of carried for the concentration from 20 mgL^{-1} to 80 mg L^{-1}. The effect of dye concentration study for both the Co_3O_4 and C_3N_4-Co_3O_4 catalysts for fixed catalyst dose at various ppm CF dyes is as depicted in figure 11. It is observed from the figure trend that the rate of dye degradation is declined with enhance in dye concentration i.e. the degradation rate was decrease from 20 to 80 ppm. When the catalysts dose is kept definite the active remain constant and hence with increase in dye concentration the photocatlytic degradation efficiency was found to be declined. During the CF dye photocatalysis experiment the adsorption phenomenon between the excited CF dye

and catalysts get increase in presence of Hg vapor lamp. This quenching between the catalysts and CF dye is increased with rise in dye concentration, hence reverse trend is observed i.e. with increase in dye concentration photocatlytic degradation rate decrease.

Reusability of the Co_3O_4 and C_3N_4-Co_3O_4 Nanocomposite

For every catalyst the reusability parameter is crucial to know multiple performance and longtime stability. Due to recycling one can get the overall idea about efficient working of the prepared catalyst for frequent utilization. Both the fabricated materials were utilized for reusability test in four cycles. After every cycle the catalyst was recovered from reaction mixture by filtration process, and then it was dried and calcined in muffle furnace to make it free from adsorbed water molecules. In the first run the C_3N_4-Co_3O_4 for CF dye was found to be 96.99%, in the second run it was 95.40%, in the third run the degradation rate was found to 94.30% and in the final run 93.10 %. Similarly, for sole Co_3O_4 the photocatlytic degradation of CF in four runs was found to be 90.12%, 88.20%, 87.12%, 86.16%. The slight declined in the photocatlytic degradation of CF dye by Co_3O_4 and C_3N_4-Co_3O_4 nanocomposite is attributed to the decrease in surface active species over the catalyst surface due to more accumulation dye molecules. From the overall study it can be concluded that the carbon nitride mediated cobalt oxide nanocomposite is very efficient in degradation of CF dye in multiple use.

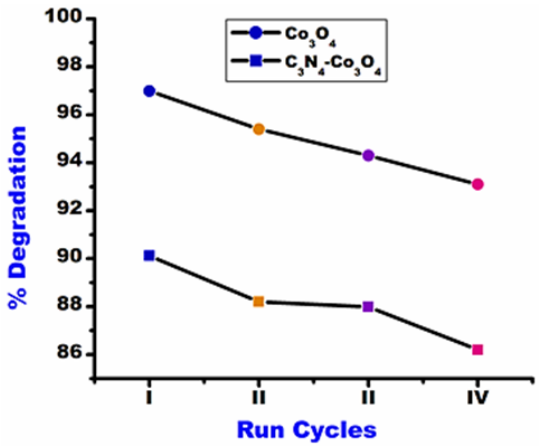

Fig. 12: Reusability performance of Co_3O_4 and C_3N_4-Co_3O_4 nanocomposite for CF dye degradation

Conclusions

The material cobalt oxide fabricated by coprecipitation method. While carbon nitride prepared by direct heating of melamine powder. The nanocomposite C_3N_4-Co_3O_4 was utilized for photocatlytic degradation of Carbol Fuchsin dye. The present work deals with the reporting the model method (laboratory method) for the degradation of water pollutant Carbol Fuchsin dye. The prepared catalyst was investigated for series of batch experiments of various dye concentration from 20-80 mg L^{-1}. The ideal batch set up for photocatlytic removal of CF dye was found to be 20 mg L^{-1}, pH 7.5, and catalyst dose of C_3N_4-Co_3O_4 0.8 g/L with contact time 110 minutes. The research demonstrates that the prepared catalyst was highly successful for complete mineralization of CF dye, which is very crucial as per as the environmental rehabilitation is concern. The reusability results for C_3N_4-Co_3O_4 catalysts shows that the fabricated nanocomposite is very efficient for degradation of CF dye for multiple usage of catalyst. This indicates long time stability, efficiency and reusability for the fabricated catalyst C_3N_4-Co_3O_4.

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Conflict of interest

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