Efficient photocatalytic degradation of aniline blue under solar irradiation by ternary cobalt ferrite / graphitic carbon nitride / bentonite nanocomposite.

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Abstract

The current research describes the synthesis, characterization, and application of $\text{CoFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ /Bentonite as a novel nanocomposite for the efficient degradation of aniline blue under solar irradiation. Powder XRD, TIR, SEM, TEM, VSM, and UV-DRS were used to describe the formation and morphology of the composite. The composite has been used as a heterogeneous photo catalyst to degrade aniline blue in the presence of H_2O_2 . In the presence of H_2O_2 in solar radiation, it was possible to degrade 88.5 % of 10 ppm aniline blue solution just in 50 minutes using 50 mg of the composite. The improvement in photodegradation rate in the existence of H_2O_2 was attributed to the advanced oxidation process (AOP) mechanism of Photo Fenton involving the production of reactive hydroxyl and perhydroxyl radicals. The degradation was found to follow 1st order kinetics with high regression coefficient with elevated rate constant.

1. Introduction

Aniline Blue (AB) is an acidic dye that belongs to the triphenylmethane class of dye [Egzar et al. 2013]. This dye is readily soluble [Lorenc-Grabowska and Gryglewicz 2007.] in water and is extensively used in different textile industries for dyeing of nylon, wool, silk, and cotton for which its presence in the industrial effluents may contribute aquatic environmental contamination [Eykholt and Davenport 1998]. Besides aniline blue is exceptionally steady for which its occupancy time in the aquatic environment is extremely high [Pare et al. 2008.]. This dye is also identified as china blue, Marine blue and soluble blue 3M. Aniline Blue has a characteristic of two benzene rings attached to the central carbon atom in addition to a p - quinoid group which acts as the chromophore along with $-\text{NH}_2$ and $-\text{NR}_2$ groups as auxochromes [Sirés et al. 2008]. Usually, aniline blue is considered as the xenobiotic compounds, recalcitrant molecules, and noxious substances to microorganisms, animals, and plants. Due to the poor competence of conventional supervision, this dye sustains more in industrial wastewaters and dirt [Azmi et al.1998, Culp and Beland1996].

Effluents from the textile industry containing different toxic organic dyes pose a serious threat to our aquatic environments [Daneshvar et al. 2003, Ledakowicz and Gonera1999]. These dyes have a very complex structure and generate carcinogenicity in the course of hydrolysis, oxidation, and other chemical reactions [Ooi et al. 2012, Hayati and Mahmoodi2012, Man et al. 2012]. Different conventional techniques such as biological treatment, reverse osmosis, and activated carbon adsorption are in force to eliminate such toxicity from the aquatic environment. However in modern research advanced oxidation process (AOPs) which account for photocatalysis [Rauf and Ashraf 2009, Liu et al. 2011] and Fenton's processes [Alnuaimi et al. 2007, Bouasla et al. 2010] are considered as the most encouraging method for organic dye degradation from the aquatic environment. The advanced oxidation process utilizes the in situ generations of hydroxyl and superoxide radicals as an oxidizing agent which initiate the sequence of a chemical reaction and smash down the complex molecules in less toxic components [Rauf and Ashraf 2012]. Photocatalyst having band gap in the range of 1.1–3.0 eV makes use of visible light to degrade

organic dyes competently [Vijayaraghavan et al. 2016]. Spinel metal ferrites with distinctive structural features and two or more cations along with imperfect oxygen sub lattice along with a narrow band gap play a significant role in the photodegradation [Dom et al. 2011]. Metal ferrites have recently received a lot of attention for their use as visible light photocatalysts for the degradation of organic dyes in water. One more benefit of using ferrites is their magnetic nature. Since iron (III) oxides are especially much magnetic materials [Machala et al. 2011], and hence ferrites are used alone as photocatalysts in the motive that they can be easily detached from the reaction medium easily [Ao et al. 2008]. The Pbs quantum dots decorated ZnO/TiO₂ photocatalyst exhibit a superior aniline blue degradation efficiency and photocatalytic activity [Lee et al. 2018]. In UV/solar radiation, 3d series transition metal ions doped in TiO₂ show enhanced photodegradation potential of aniline blue. [Devi et al. 2010]. Different semiconducting nanomaterials like ZnO, ZnS and SnO₂ has been investigated for efficient degradation of aniline blue in visible light [Egzar et al. 2013]. Even though literature assessment supports some efficient mode of degradation of aniline blue by different nano materials but the application of metal ferrite based ternary composite is still unexplored in this category of effort. Considering this aspect, the present paper discusses the novel ternary cobalt ferrite-based nanocomposite with narrow band gap of 1.59 eV for efficient degradation of aniline blue in visible light radiation. The physical and optical properties were documented by FTIR, powdered XRD, VSM, SEM, TEM and UV-vis-DRS techniques.

2. Experimental

2.1. Materials

Merck supplies iron (III) nitrate nanohydrate [Fe(NO₃)₃·9H₂O], cobalt nitrate hexahydrate [Co(NO₃)₃·6H₂O], urea, including sodium hydroxide (NaOH). Sigma-Aldrich provides hydrogen peroxide (6 %), bentonite, and aniline blue. Without any further purification, all chemicals were utilised for synthesis. Cinnamon is collected from local market.

2.2 Preparation of Cinnamon Extract Assisted Cobalt Ferrite.

Cobalt ferrite (CoFe₂O₄) nanoparticles were synthesized via self combustion using aqueous extract of cinnamon followed by calcinations in muffle furnace [Deraz2010, Kooti et al. 2013]. 5mM ferric nitrate [Fe (NO₃)₃·9H₂O] and 2.5mM cobalt nitrate [Co (NO₃)₂·6H₂O] were added slowly in the aqueous cinnamon extract. This mixture (pH=2) is heated at 80° C to get a gel like substance. The reddish-brown gel like substance was again heated on a heater at 250°C to decompose completely by self combustion. The ample powder so obtained is finally calcined at 600°C for 3 hours to get fine crystals of Cobalt ferrites.

2.3. Preparation of Graphitic Carbon Nitride.

Graphitic carbon nitride (g-C₃N₄) was prepared by heat treatment of urea under ambient pressure in a Muffle Furnace (Isotemp Programmable Muffle Furnace 650-750 Series, Fisher Scientific) for 3 hours at

600° C to conclude the reaction. The resulting yellowish powder was washed with distilled water to eliminate any remaining matter adsorbed on it and lastly dried up at 80 ° C.

2.4. Fabrication of Ternary Composite.

Two stages have been used to develop the ternary nanocomposite. First, a binary composite of nickel ferrite and graphitic nitride was developed, and this binary composite was then converted into a ternary composite by introducing bentonite. In a distinctive procedure 100 mg of cobalt ferrite and 80 mg of graphitic carbon nitride mixed homogeneously by using mortar- pestle for 30 minutes. The solid mixture is calcined at 400⁰ C for 2 hours. To achieve uniform dispersion, the binary mixture was dissolved in distilled water and sonicated for 30 minutes. Centrifugation was used to separate the solid binary mixture. In another experiment, 50 mg of bentonite was dissolved in 50 mL deionized water and magnetically stirred. The solid binary composite was introduced to this solution and stirred for 12 hours. After that, centrifugation has been used to extract the ternary composite.

2.5. Study of Photocatalytic Degradation of Aniline Blue (AB)

Photocatalytic activity of the as synthesized CoFe₂O₄/ g-C₃N₄/bentonite ternary composite was assessed by degrading aniline blue (AB) under solar irradiation. In a typical experiment, 10mg, 30 mg and 50 mg of composite was introduced into 60 mL of 10 ppm aniline blue solution with 1 mL of 10% hydrogen peroxide (H₂O₂) and stirred in absence of light for 30 min to reach adsorption-desorption equilibrium. Under constant stirring, the mixture was exposed to solar radiation. The degradation of the dye was monitored periodically with the help of spectrophotometer (Shimazu UV-1900i) by withdrawing 4 mL of the mixture and centrifuging immediately (5 min, 3000 rpm). The absorbance was recorded over a wavelength range of 200 to 800 nm. The eq. (1) has been used to evaluate the catalytic degradation efficiency.

See formula 1 in the supplementary files.

Where, A₀ is the absorbance of AB before degradation and A is the absorbance of AB after degradation.

3. Results And Discussion

3.1. FTIR Analysis

Careful observation on the FTIR spectra of cobalt ferrite fig. 1(a) shows intense peaks at 459 cm⁻¹ and 615 cm⁻¹ corresponding to intrinsic stretching vibrations of Fe-O at the tetrahedral site and Co-O at the octahedral site. Co²⁺ ions prefer to be in the octahedral region, whereas Fe³⁺ ions prefer to be in both the octahedral and tetrahedral sites. Further observations show strong absorptions at 1104 cm⁻¹ is the same as phenolic hydroxyl group of flavonoides type of compound in the cinnamon extract [De et al. 2018]. The standard stretching modes of CN heterocycles were assigned to the different characteristic bands in the FTIR spectra of g-C₃N₄ in the range 1200 to 1700 cm⁻¹. [fig. 1(b)] is in good agreement with

the literature [Shi et al. 2015]. The FTIR spectra of the ternary composite fig. 1(c) assign all the characteristic band of individual components present in it. The sharp peaks in the range 460- 532 cm⁻¹ are due to M-O bond in the tetrahedral and octahedral sites. Distinct peak on 811 cm⁻¹ signifies bending vibration of heptazine of g-C₃N₄. Separate peak at 1030 cm⁻¹ same as to the presence of bentonite in the composite. Three peaks in the range 1430- 1620 correspond to heptazine derived repeating unit of g-C₃N₄. The broad band in the range 3188- 3370 cm⁻¹ is due to partial condensation and absorption of water molecule.

3.2. XRD Analysis

The XRD blueprint of CoFe₂O₄, g-C₃N₄ and CoFe₂O₄/g-C₃N₄/Bentonite are presented in the figure 2 (a, b and c). In fig. 2(a) the characteristic peaks at an angle 2θ = 18.99, 32.13 and 35.58 corresponds to the plane (111), (220) and (311) for the CoFe₂O₄ sample precisely corresponding with the JCPDS card No. 770426. Further the creation of the g-C₃N₄ was justified by the presence of the peaks at 2θ angles 12.99 and 27.54 corresponding to (100) and (002) planes (fig.2 b). Intense peaks of the XDR pattern of the composite fig. 2(c) indicate high crystalline nature of the substance. The position of the peaks of the components including bentonite at an angle 2θ = 20.64, 26.52, and 54.00 corresponds to (110), (210) and (144) planes as reported in literature [Hebbar et al. 2018] is well matched, which confirms the composite formation. The average crystallite diameter (Dc) of CoFe₂O₄ particles and CoFe₂O₄/g-C₃N₄/bentonite nanocomposite was deliberate to be 26.62 nm and 30.92 nm respectively by the Debye–Scherrer formula [Bunaciu et al. 2015]. The increase in the value of crystallite size of the composite compare to cobalt ferrite confirms the encapsulation of the ferrite core by graphitic carbon nitride and bentonite.

3.3. VSM Analysis

Vibrating sample magnetometers were used to implement magnetic studies upon this synthesized cobalt ferrite nanoparticles and ternary composites. Magnetic parameters such as remanent magnetization (Mr), saturation magnetization (Ms) and coercivity (Hc) are shown in table.1.

Table.1: VSM parameters of Cobalt ferrite and the ternary composite.

Sample		Magnetic Parameters	
Ms (emu/g)	Hc (Oe)	Mr(emu/g)	
CoFe ₂ O ₄	4.9348	1048.3	1.1576
CoFe ₂ O ₄ /g-C ₃ N ₄ /Bentonite	0.8618	126.05	58.12

The hysteresis loop (Fig. 3) obtained indicates the ferromagnetic behaviors of the cobalt ferrite nanoparticles with saturation magnetization value 4.9348 emu / g. The abrupt drop in the saturation

magnetization value of the ternary composite is due to incorporation of nonmagnetic graphitic carbon nitride and bentonite in the composite.

3.4. SEM Analysis

SEM micrographs of cobalt ferrite, graphitic carbon nitride, bentonite and the ternary nanocomposite are shown in the fig.4. The micrograph of the composite (F) shows that the semiconducting graphitic carbon nitride and bentonite segments are covered over cobalt ferrite consistently. The spherical encapsulated shape of the particle confirms the composite formation within the size range of 50 micro meters.

3.5. TEM Analysis

The phase compositions of the ternary composite were studied using transmission electron microscopy. Fig.5 depicts a TEM representation of the composite. TEM picture of ternary composite fig.5 (A, B, C, D) indicates that the bentonite and graphitic carbon nitride encapsulated composite particles are almost nearly spherical and the average sizes of particles were found to be 49.29 nm. The crystalline nature of the nanocomposite was confirmed SAED analysis fig.5 (F). Leading edge of lattice 0.410 nm relates to the [211] plane of bentonite, 0.272 nm is equivalent to [100] plane of g-C₃N₄ and 0.411 nm to the [111] plane of cobalt ferrite. The ternary nature of the composite is verified by the three important planes in this composite obtained from HR-TEM (fig.5 E).

3.6. UV-DRS Analysis.

The plot of reflectance versus wavelength of the component material and composite confirms that the absorption of light will takes place in the solar radiation's visible spectrum. In addition, the measured band gap in the material and in the composite as obtained from the Tauc's plot reveals that the composite can efficiently degrade the dye in the solar radiation.

3.7. Investigation of aniline blue (AB) degradation by nanocomposite

The photocatalytic performance of the ternary composite was assessed by degrading aniline blue (AB) in presence of 10% H₂O₂ in the acidic medium under solar irradiation. The time-dependent aniline blue degradation with different composite amounts is shown in the figs.7a, 7b and 7c.

When 10 mg of composite is used along with 1 ml of 10 percent H₂O₂ 50 % degradation of AB is achieved in 50 min. As soon as 30 mg and 50 mg composites are used concurrently in the same condition, the degradation percentage rises to 77.5 % and 88.5 %.

The kinetics of AB degradation can be formulated as;

$$\ln (C_0/C) = kt$$

where ' C_0 ' is the initial concentration of AB and ' C ' is the concentration of AB after certain time ' t ' with rate constant ' k ' of the reaction. Since Beer-Lambert's law states that both absorbance and concentration are directly proportional, the concentration should be used to replace the absorbance. Plots of $\ln C_0/C$ versus time (t) at 600 nm for three different composite quantities revealed that they were all linear as shown in the figures 8(a, b and c).

From this linear plot the calculated rate constants are found to be 0.0132, 0.0323 and 0.0443 respectively. In the kinetics plots, the regression correlation coefficient (R^2) variables are found to be 0.9198, 0.9840 and 0.9849 respectively. These values suggest that the reaction rate seems to be very moderate in the presence of H_2O_2 . Figure 9 (a, b, and c) demonstrates that C/C_0 decreases exponentially with time, suggesting that the degradation follows 1st order kinetics.

3.8. A plausible mechanistic approach to the degradation of Aniline Blue (AB) under solar irradiation in presence of H_2O_2 .

Hydrogen peroxide assisted photodegradation of AB in solar radiation by Cobalt ferrite composite having $g-C_3N_4$ as one of the components may takes place through Photo Fenton mechanism of advanced oxidation process (AOP). Here Fe (II) of cobalt ferrite and H_2O_2 efficiently generate hydroxyl radical which degrade the dye successfully. Moreover, the inclusion of $g-C_3N_4$ in the composite significantly reduces the composite's band gap and increases the composite's potential for charge transfer and also facilitates the generation of electron-hole pairs, resulting in hydroxyl radical generation [Mushtaqet al. 2020, Zhanget al. 2017, Rubioet al. 2015 and Sun et al. 2015]. The reactions behind the degradation of aniline blue by Photo Fenton process can be depicted as follows[Das and Dhar 2020]and is shown in the figure10. **Please see reactions in the supplementary files.**

3.9. Comparison with other Composite/ Materials for aniline blue degradation.

Heterojunction nanocomposite dependent on cobalt ferrite has still not been thoroughly investigated, particularly in the area of toxic aniline blue degradation in aqueous solution. Some reported works are tabulated as under.

Table. 2 Correlation of efficiency of synthesized composite with some previously documented materials designed for photocatalytic degradation of aniline blue.

Sl. No	Composite /Material	Dose	Time	Efficiency	Reference
1.	PbS/ZnO/ TiO ₂	-	300 min	82%	[Lee et al.2018]
2.	Mn ²⁺ dopped polycrystalline titania	150 mg	140 min	100 %	[Devi et al. 2010]
3.	ZnO	10 mg	30 min	75%	[Egzar et al. 2013]
4	Cobaltl Ferrite/ g-C ₃ N ₄ / Bentonite	50 mg	50 min	88.5%	This Work

4. Conclusion

In a stepwise protocol, a novel type of ternary nanocomposite CoFe₂O₄/g-C₃N₄/Bentonite was productively fabricated. The composite was thoroughly examined by powder FTIR, XRD, VSM, SEM, TEM and UV-DRS studies. The composite's photo degradation ability to degrade aniline blue in the existence of H₂O₂ in solar radiation is well documented through spectrochemical observations. The composite can degrade aniline blue up to the extent of 88.5% in 50 minutes. The cobalt ferrite-based nanocomposite for such a degradation strategy is not endorsed by any such literature. In conclusion, the current finding can be said to be novel and widely recognized at the industrial scale to mitigate aquatic contamination from a hazardous dye such as aniline blue. This finding expands further scope to extrapolate the current work on environmental contamination mitigation in the future.

Declarations

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Figures

Figure 1

FTIR of Cobalt ferrite (a), Graphitic Carbon Nitride (b), and Ternary Composite (c).

Figure 2

XRD pattern of Cobalt ferrite (a), g-C₃N₄ (b) and Ternary Composite (b).

Figure 3

Hysteresis curves obtained from VSM analysis Cobalt ferrite (a) and Ternary Composite (b).

Figure 4

SEM image of Cobalt ferrite (A, B), graphitic carbon nitride (C, D), bentonite (E) and ternary nanocomposite (F).

Figure 5

TEM image (A, B, C, D), HR-TEM (E) and SAED pattern (F) of the ternary nanocomposite.

Figure 6

UV-DRS absorbance spectrum of CoFe₂O₄, graphitic nitride, bentonite and the ternary composite (wavelength reflectance and Tauc's plot)

Figure 7

Absorbance alteration of the degradation of aniline blue (10 ppm) for (a) 10mg, (b) 30 mg and (c) 50mg composite respectively in presence of 1 ml of 10% H₂O₂

Figure 8

Plots of $\ln C_0 / C$ against irradiation time for (a) 10mg (b) 30 mg (c) 50mg composite

Figure 9

Plots of C/C_0 against irradiation time for (a) 10mg (b) 30 mg (c) 50mg composite.

Figure 10

Plausible mechanism of degradation of AB

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