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A COMPARATIVE STUDY ON CHARACTERIZATION AND PHOTOCATALYTIC ACTIVITIES OF PbS AND Co DOPED PbS NANOPARTICLES

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Nanocrystalline particles of lead sulphide and cobalt doped lead sulphide were prepared by a hydrothermal method. The crystalline nature and particle size of the samples were characterized by powder X-ray diffraction analysis (XRD). The thermal stability of nanocrystals was studied by thermo gravimetric analysis (TGA). The morphology of prepared nanocrystals was studied by scanning electron microscope (SEM) and the presence of Co^{2+} in the sample was confirmed by energy dispersive X-ray analysis (EDX). The formation of the lead sulphide and cobalt doped lead sulphide nanoparticles was analyzed using FTIR analysis. The optical absorption of the synthesized samples was studied using UV absorption spectral analysis. The photoluminescence properties were studied using PL spectral analysis. The degradation of methyl blue (MB) in aqueous medium was studied by using lead sulphide nanoparticles. The cobalt doped lead sulphide works as an efficient photocatalyst for degradation of methyl blue dye.

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Keywords: Nanocrystalline PbS, PL, XRD, SEM, EDX, Dye degradation

1. Introduction

Lead sulphide is an important semiconductor due to its optical and electronic properties and it is used in many fields as an advanced material such as IR detectors [1], solar batteries [2], advanced optoelectronic devices [3], photonic materials [4] and Pb^{2+} ion selective sensors [5]. Metal sulphide semiconductors with nanometer size dimensions have been the focus of many researchers due to the quantum semiconductors [6]. Lead sulphide nanoparticles are an important direct band gap semiconductor material with small band gap [7]. It has high dielectric constant [7] and very high carrier mobility [8]. Lead sulphide nanoparticles can also show multiple exciton generation (MEG), in which the impact of a single photon produces two or more excitons [9, 10]. Lead sulphide band gap can be extended to the visible region by forming nanocrystals. Consequently, lead sulphide nanocrystals and nanowires are potentially useful in electroluminescent devices such as light-emitting diodes. The absorption edge of lead sulphide nanocrystals exhibits a large blue shift [11], when one shrinks the crystalline size to the nanometer size regime. The semiconductor nanoparticles also have photochemical properties [12]. Therefore, a great deal of research efforts has been devoted to the method development for the synthesis of lead sulphide nanoparticles doped with cobalt ion. Among these, the most common routes involve the use of strong matrix [13]. Some attempts have been reported to produce organic monolayer protected semiconductor nanoparticles [14-16]. The discharge of large quantity of colored water from industries posse's serious environmental problems. The colorization of water due to the presence of dyes may have an inhibitory effect on the process of photosynthesis and thus may

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affect the aquatic ecosystem. The colored molecules absorbs visible light, decreasing the amount of light available for photosynthesis. Due to high concentration of organics in the effluents and the higher stability of modern synthetic dyes, the conventional biological treatment methods are ineffective for the complete colour removal and degradation of organics and dyes [17]. So, attempt was made to prepare materials that have absorption's extending towards visible range and thereby allowing the use of the main part of solar spectrum. To develop more efficient ecofriendly photocatalyst, there is an urgent need to develop photocatalytic systems, which are able to operate effectively under visible light irradiation. The use of naturally available visible light has recently drawn much attention.

In the present work, lead sulphide nanocrystalline particles were synthesized by hydrothermal method. The synthesized samples were subjected to characterizations such as powder X-ray diffraction analysis, SEM, EDX, TGA, FTIR, UV and PL analysis. Further an efficient approach has been developed for degradation of methyl blue dye.

2. Experimental

2.1 Synthesis of PbS and Co^{2+} doped PbS nanoparticles

The pure AR grade lead nitrate and sodium sulphide were dissolved in distilled water. In this solution Triton X-100 and sodium hydroxide solution was slowly added and solution was stirred for 2 hrs. The solution was filtered and nanocrystalline lead sulphide material was dried in heating oven at 110^0C. The lead sulphide nanocrystal was further calcinized at 400^0C for 2 hrs. The mixture of synthesized lead sulphide nanocrystals and cobalt nitrate with sodium hydroxide was stirred in a Teflon bottle and heated at 120^0C using heating oven for 20 hrs. The solution was filtered, dried and the Co^{2+} doped lead sulphide nanocrystals obtained was further heated for 2 hrs at 110^0C.

2.2 Photocatalytic degradation of Methyl blue dye

In photocatalytic degradation, methyl blue dye (50 ml) and the catalyst (PbS or Co^{2+} doped PbS nanoparticles) were taken in a beaker and exposed to sunlight. The dye solution was mixed properly with a magnetic stirrer during the reaction process. Dye solutions of about 2-3 ml were taken out at regular interval and their absorbance was recorded at 610 nm using spectrophotometer (UV- Vis Ultra Spec CL-540). The control experiments were also conducted under visible light without catalyst to measure any possible direct photo catalysis of this dye.

3. Results and discussion

3.1 FT-IR Analysis

The FTIR spectra of lead sulphide and Co^{2+} doped lead sulphide nanoparticles are shown in Figs 1. From the spectrum, the broad band at 3600 to 2000 cm^{-1} is assigned to O-H bending vibration of the sample. This proves the moisture absorbing capacity of the sample. The frequencies due to hetero polar diatomic molecules of lead sulphide are confirmed by the peak at 608, 1061 and 1399 cm^{-1}. In the FTIR spectrum of Co^{2+} doped lead sulphide, the overlapped peaks at 598 and 1076 cm^{-1} confirm the vibrational frequencies of hetero polar diatomic molecular vibration of Co-Pb, Co-S and Pb-S functional groups.

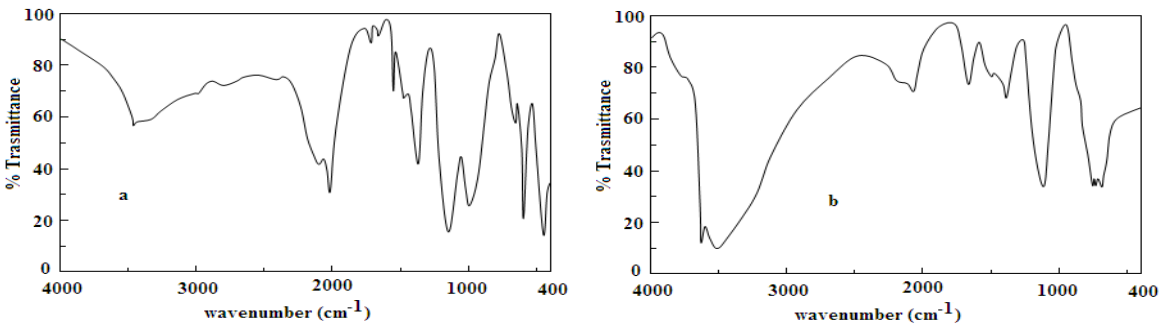


Fig. 1. IR spectra of a) PbS nanoparticles, b) Co^{2+} doped PbS nanoparticles

3.2 UV-DRS Analysis

The UV-DRS spectrum of lead sulphide and Co^{2+} doped lead sulphide samples are shown in Figs 2. The bands at 260, 300 and 360 nm are observed for the lead sulphide nanoparticles. Compared with bulk lead sulphide the blue shift is observed for the lead sulphide nanomaterial. The spectrum of Co^{2+} doped lead sulphide shows a band at 370 nm. This is due to incorporation of the dopant which shows broad band at UV region and variation in the band gap shows the presence of dopant in the synthesized lead sulphide nanoparticles. The spectra illustrate soft extended absorption edge (~360 nm) of synthesized PbS nanoparticles, which corresponds to 3.44 eV. The UV-VIS absorption edge for cobalt doped PbS nanoparticles about 370 nm, which corresponds to 3.35 eV.

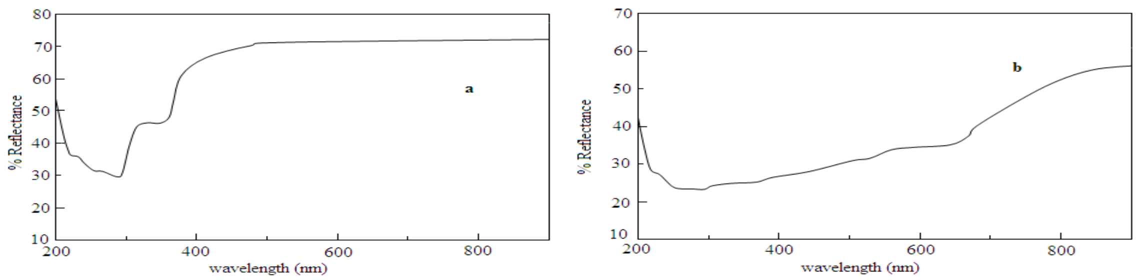


Fig. 2. UV- DRS spectra of a) PbS nanoparticles, b) Co^{2+} doped PbS nanoparticles.

3.3 UV-Visible Absorption Analysis

The UV-visible absorption spectra of the synthesized lead sulphide and Co^{2+} doped lead sulphide nanoparticles are shown in Figs 3.The position of absorption edge is shifted to lower wavelength indicating great influence of small size of lead sulphide nanoparticles. In addition to these two well-defined absorption bands at 260 nm and 550 nm are also observed in the spectra. The Co^{2+}doped lead sulphide nanoparticles shift in UV cut off wavelength at 295 nm. This is attributed due to incorporation of the dopant and shows broad absorption at UV region.

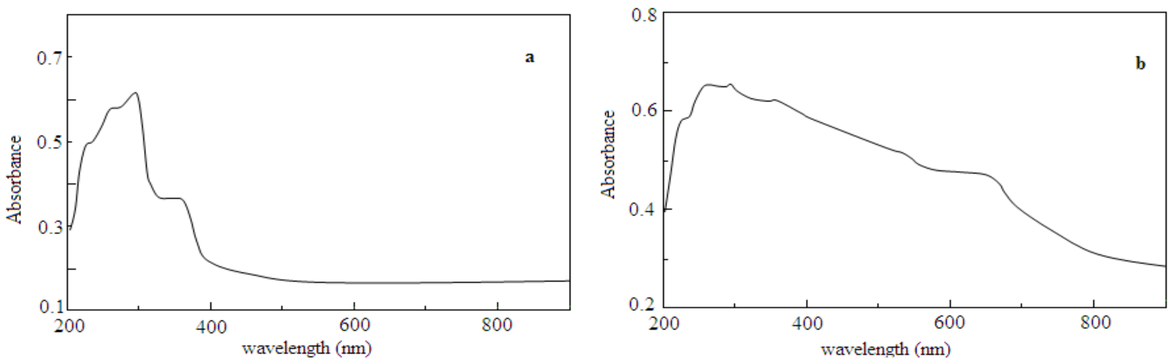


Fig.3. UV- Absorbance spectra of a) PbS nanoparticles, b) Co^{2+} doped PbS nanoparticles

3.4 PL Analysis

The optical properties of synthesized lead sulphide nanoparticles were characterized by photoluminescence (PL) measurement. The PL spectrum of lead sulphide nanoparticles is shown in Fig 4. The spectrum shows emission band within ultraviolet range (310-550 nm). This bands shifts from 360 nm to 376 nm, and is attributed due to nanosized particles.

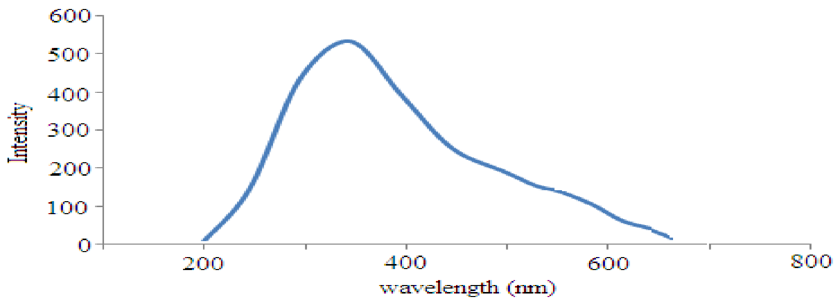


Fig. 4: PL spectra of PbS nanoparticles

3.5 X- Ray Diffraction Analysis

Powder X-ray diffraction pattern of synthesized samples was recorded using Philips - 1710 diffractometer instrument with a scan speed of 2^0/min in the range of $20\text{-}80^0$ using monochromatic wavelength of 1.54 A^0 (CuKα). The XRD pattern of lead sulphide and Co^{2+} doped lead sulphide nanoparticles are shown in Figs 5. The XRD pattern of lead sulphide nanoparticles have fundamental peaks due to diffraction of lead sulphide on the plane (111), (200), (220), (311), (222), (400) and (420) which is in good agreement with the reported value [18]. In XRD pattern of Co^{2+} doped lead sulphide nanoparticles, the fundamental peaks were incorporated with the synthesized lead sulphide sample. This confirms the presence of dopant in the lead sulphide nanoparticles. The XRD pattern of synthesized lead sulphide nanoparticles shows only single phase system. In case of Co^{2+} doped lead sulphide nanoparticles, the spectrum consists of incorporation of Co^{2+} diffraction peaks, which changes the single phase into multiphase system. The particle size (d) was calculated using Debye-Scherrer equation.

$$d = 0.9\,\lambda / \beta \cos\theta \qquad (1)$$

From the XRD data it is found that synthesized lead sulphide nanoparticles having a minimum particle size of 31 nm and Co^{2+} doped lead sulphide nanoparticles have a minimum particle size 30 nm. The broadening of XRD peaks observed for the present sample indicates that the sample synthesized in the present study is nano structured. The XRD pattern is an agreement with the cubic structure of lead sulphide sample (JCPDS Card No. 78-1057) with a space group Fm3m (225).

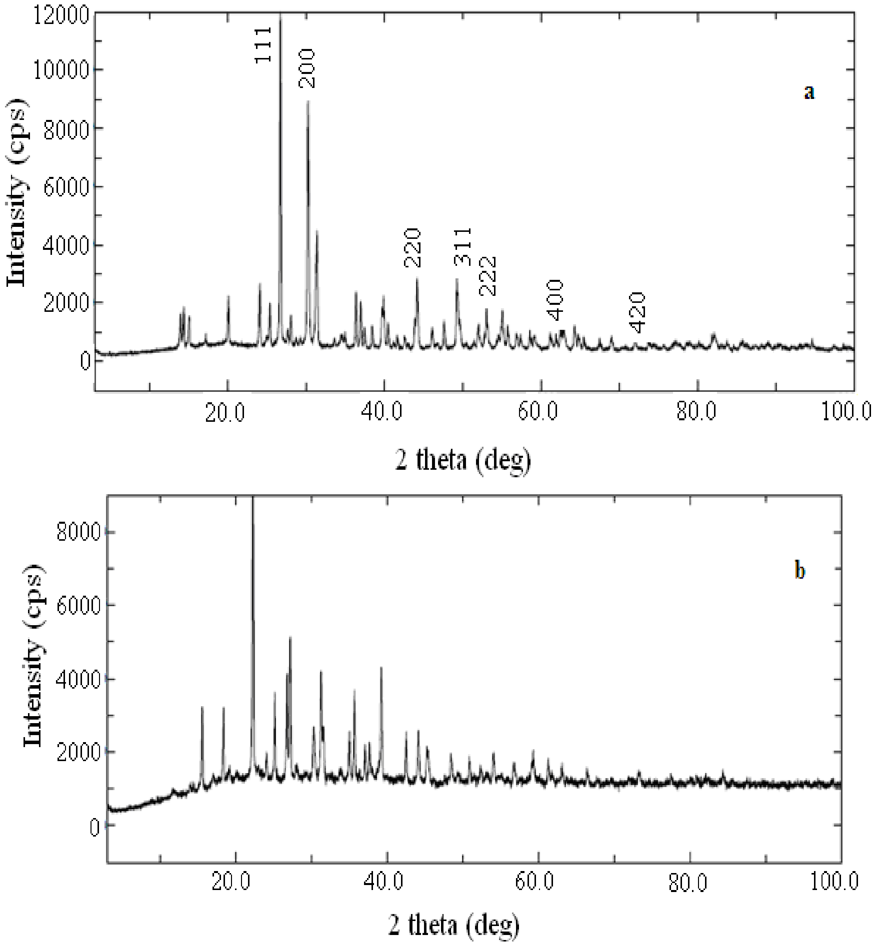


Fig. 5. XRD pattern of a) PbS particles, b) Co^{2+} doped PbS nanoparticles

3.6 SEM Analysis

The morphology of the lead sulphide nanoparticles is decided by SEM images. The SEM image of lead sulphide and Co^{2+} doped lead sulphide nanoparticles were shown in Figs 6. From the image it is observed that the synthesized lead sulphide sample has minimum particle size between 30-40 nm and the materials are porous. The nanosized lead sulphide particles form globular aggregates of micro dimensions. These aggregates are of uniform particle dimension (shape and size). Cobalt doped lead sulphide shows rod shaped morphology and some of the particles are agglomerated.

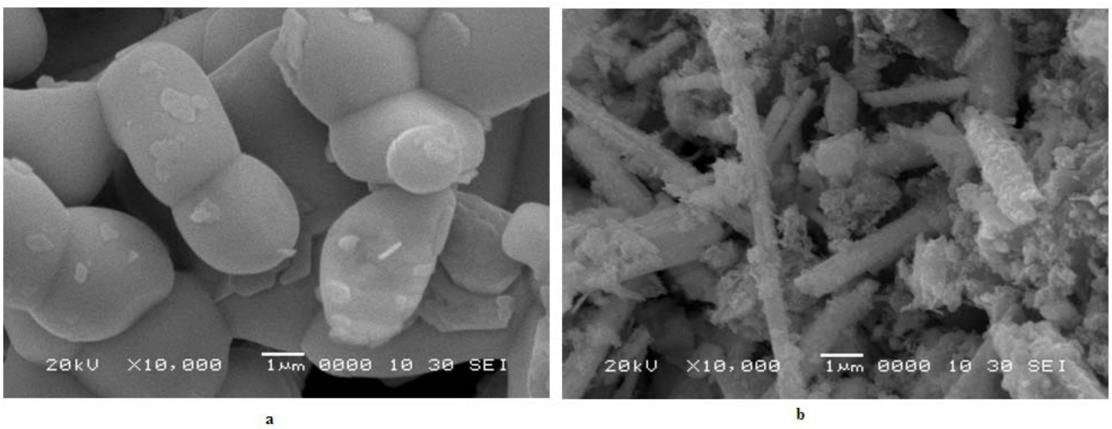
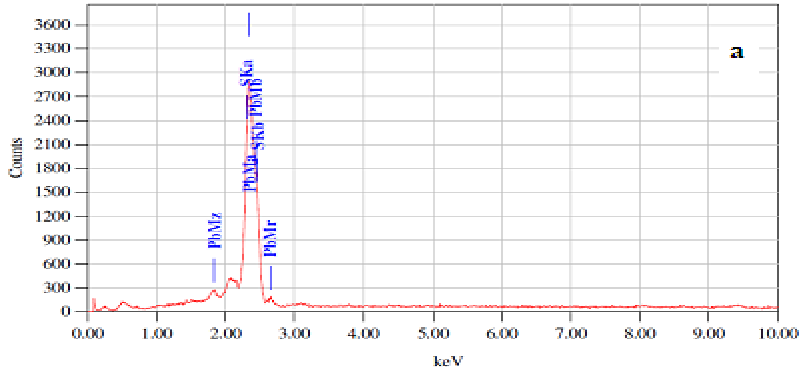


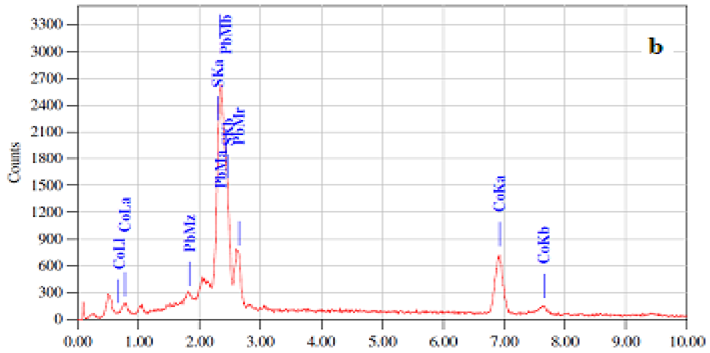
Fig. 6: SEM images of a) PbS nanoparticles, b) Co^{2+} doped PbS nanoparticles

3.7 EDAX Analysis

The elemental analysis of lead sulphide and Co^{2+} doped lead sulphide nanoparticles is reported by EDAX and represented by Figs 7. The EDAX spectrum of lead sulphide shows the presence of Pb and S metal. The EDAX spectrum of Co^{2+} doped lead sulphide shows the inclusion of Co^{2+} into lead sulphide nonmaterial and peak confirms the presence of Co, Pb and S metal into the sample.



Element	(KeV)	Mass %	At %	Cation
S	2.307	6.00	29.00	6.7037
Pb	2.342	94.00	70.80	88.3138
Total		100.00		



Element	(KeV)	Mass %	At %	Cation
S	2.307	4.29	18.21	4.7794
Co	6.924	8.48	23.50	8.8296
Pb	2.342	87.23	58.29	81.9410
Total		100.00		

Fig. 7. EDAX of a) PbS nanoparticles, b) Co^{2+} doped PbS nanoparticles

3.7 TGA Analysis

The stability of the lead sulphide nanoparticles was studied by using thermal gravimetric analysis (TGA). The TGA spectrum of lead sulphide nanoparticles is shown in Fig 8. TGA spectrum shows that up to 400^0C the loss in weight to the removal of water molecules and hydrated compounds associated with the lead sulphide nonmaterial.

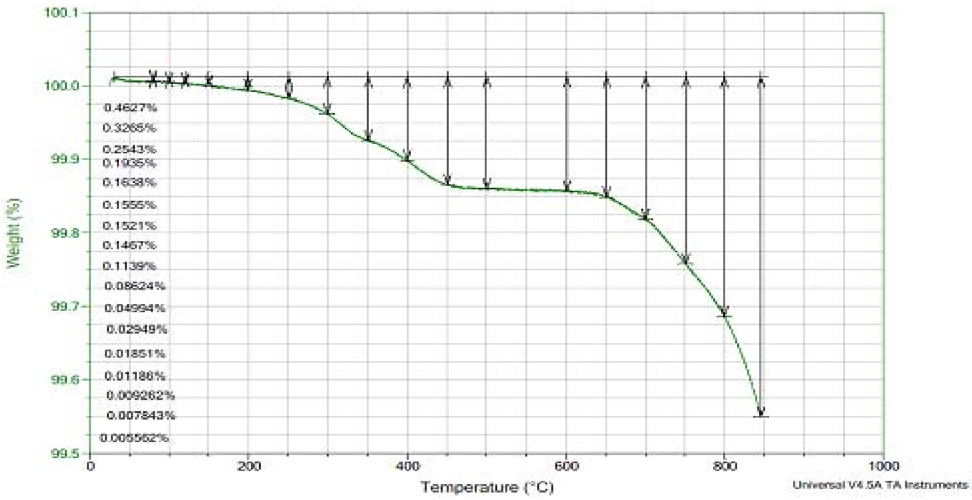


Fig. 8. TGA spectrum of PbS nanoparticles

The spectrum shows that lead sulphide nanoparticles are stable within 400-600^{0}C temperature region. The lead sulphide nanoparticles decomposed above the temperature 600^{0}C and shows large loss in weight.

3.8 Photocatalytic degradation of Methyl blue dye

The photo degradation of methyl blue is shown in Figs 9. The active surface of lead sulphide and Co^{2+} doped lead sulphide nanoparticles are responsible for the degradation process. The lead sulphide and Co^{2+} doped lead sulphide nanoparticles produce hydroxyl free radical in aqueous medium which degradates the methyl blue dye. The rate of degradation is more with Co^{2+} doped lead sulphide nanoparticles, because the large active sites of lead sulphide are available for the degradation. The lead sulphide and Co^{2+} doped lead sulphide nanoparticles are also reused after washing and drying at 100-110^{0}C. The reused nanoparticles have an efficient photoactivity after three turns also. Therefore it reduces the cost of photodegradation process. The lead sulphide and Co^{2+} doped lead sulphide nanoparticles works more effectively in a presence of visible light.

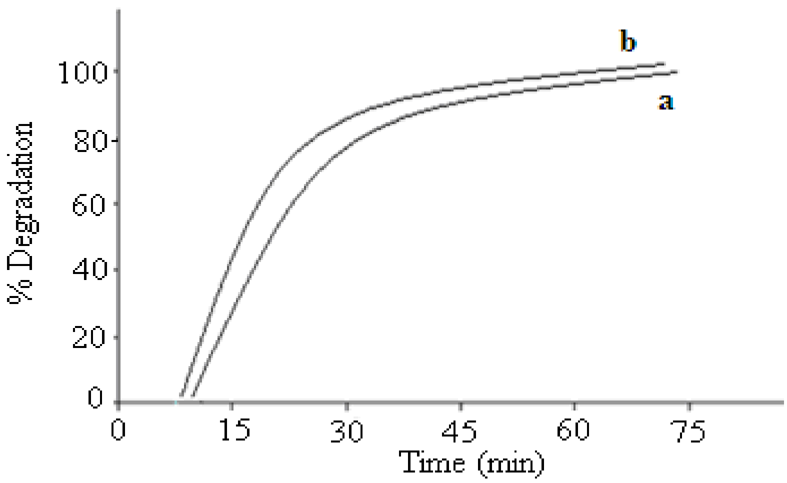


Fig. 9. Photocatalytic degradation of Methyl blue dye with a) PbS nanoparticles, b) Co doped PbS nanoparticles

4. Conclusions

Lead sulphide and Co^{2+} doped lead sulphide semiconducting nanoparticles were successfully synthesized by hydrothermal method. The yield, grain size and other characteristics observed indicate that the method followed in the present study can be considered as suitable. The lead sulphide nanoparticles have cubic structure with particle size 31 nm. Encapsulation of cobalt ion in lead sulphide nanoparticles enhances the photocatalytic activity of lead sulphide nanoparticles. The result shows that the synthesized lead sulphide nanoparticle degradates the methyl blue dye in the presence of sunlight.

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