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COMPARATIVE STUDY ON THE PHOTOCATALYTIC ACTIVITY OF ZNS NANOPARTICLES SYNTHESIZED WITH DIFFERENT CAPPING AGENTS

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Abstract

ZnS nanoparticles are prepared by coprecipitation method using various capping agents like PVP (polyvinylpyrrolidone), PVA (polyvinylalcohol) and PEG-4000 (polyethyleneglycol). These are characterized by UV-Visible spectra, X-ray diffraction (XRD) studies, Fourier Transform Infra-red spectra (FTIR) and Transmission electron microscopy (TEM). UV-Visible absorption spectra are used to find the optical band gap and the values obtained have been found to be in the range of 3.80-4.00eV. The particle size of nanoparticles calculated from XRD pattern has been in the range of 2-4 nm. It is also observed that the particle size of nanoparticle is affected by the nature of capping agent. Photo catalytic degradation of xylenol orange (XO) by the nanoparticles shows that these act as photo catalysts under sunlight irradiation. The XO dye was degraded more than 87.24, 83.42 and 73.05% in the presence of PEG-4000, PVA and PVP capped ZnS nanoparticles in 120, 150 and 180 min. respectively. The kinetics of catalyzed by synthesized ZnS nanoparticles with XO dye follows pseudo-first order kinetics with reasonable apparent rate constants.

Keywords: Coprecipitation method, Kinetic study, Photocatalytic activity, Xylenol orange, ZnS nanoparticle.

Introduction

Nanoparticles or quantum dots are defined as small particles with 1-100 nm in diameter at least in one dimension. As the diametersof the particles approach their Bohr diameter, the optical properties begin to change and quantum confinement effect begins to play a much more important role. Itbrings a great difference in physical and electronic properties of the nanometer scale particles compare to bulk materials. Among the family of semiconductors, II-VI groupsemiconductorcompounds have immense technological importance in various applied fields of science and technology. For instance, ZnS [1-2], CdS[3], ZnO [4], CdTe [5] etc., are important because of their excellent electronic and optical properties for optoelectronic applications. Among those ZnS is an important member in II-VIgroup semiconductors having a larger value of band gap energy [6]. It has two structures: a cubic form and a hexagonal form [7-8]. Transition from bulk to nanoparticles lead to the display of quantum mechanical properties and an increased dominance of surface atoms which increases the chemical reactivity of a material. Notable examples include the tunable band gap [9] and catalytic behavior [10]of nanoparticles. For nano crystals prepared by solution based chemical methods, a capping agent who adsorbs to the nano crystals surface, generally is added both to control the size of nano crystals and to prevent agglomeration of synthesized nano crystals. Polymers are chosen as good host materials because they usually exhibit long-term stability and possess flexible reprocess ability. In addition, the small size and high optical activity of ZnS nanoparticles make them interesting for optoelectronic applications operating in the ultraviolet region [11-14].

In past decade, semiconductor micro/nanoparticles have been synthesized through various ways including hydrothermal process [15], micro-emulsion method [16], sol-gel method [17], chemical coprecipitation method [18], sonochemical method [19], microwave irradiation [20] and solvothermal method [21] etc. However, these methods normally consist of two or more steps and rigorous conditions, such as high pressure or high temperature, usually are required [15-16, 22]. Fabrication of inorganic nanoparticles in solid polymer matrices has attracted considerable interest because, the combination of inorganic particles and polymers provide a simple route for the preparation of stable and processable materialshaving the promising properties of both components [23].

ZnS nanoparticles could be used as good photo catalysts due to rapid generation of the electron-hole pairs by photo-excitation and highly negative reduction potentials of excited electrons; as conduction band position of ZnS in aqueous solution is higher than that of other semiconductors such as TiO_2 and ZnO[24]. Since, a larger ratio of surface to volume of a catalyst would facilitate a better catalytic activity [25-26]; the size controlled synthesis of ZnS nanostructures to produce a larger ratio of surface to volume is of great importance. The enhanced surface to volume ratio causes increase of surface states, which change the activity of electrons and holes, affecting the chemical reaction dynamics. The size quantization increases the band gap of photo catalysts to enhance the redox potential of conduction band electrons and valence band holes [27].

In the present work, ZnS nanoparticles are prepared by coprecipitation technique and PVP, PVA and PEG-4000 are used as capping and stabilizing agents, which modify surface of nanoparticles and prevents the growth of the particle to larger size. The effect of capping agent on optical absorption spectra has been investigated. XRD, FTIR and TEM studies are made for these samples. To explore possible application of the ZnS nanoparticles, the catalytic degradation of XO is carried out under the exposure of sunlight.

Experimental

2.1. Preparation of ZnS nanoparticles

ZnS Nanoparticles were synthesized using PVP, PVAand PEG-4000 as capping agents by simple coprecipitation technique. The principle involved in this technique is the precipitation of metal ions with sulfide ions in the solution. 0.1 M aqueous solution of Zincacetate dihydrate and 0.1 M aqueous solution of Sodiumsulfide were mixed in the presence of various capping agent solutions like PVP, PVAand PEG-4000. First, solutions of 0.1 M Zinc acetatedihydrate, 0.1M Sodium sulfide and 1% by weight of capping agents were prepared in double distilled water. 15 ml of zinc acetate and 15 ml of 1% of PVP were mixed together and stirred for 30 minuteson a magnetic stirrer to get a homogeneous solution. This was followed by drop wise addition of appropriate amount of 0.1 M Sodium sulfide under vigorous stirring for 1 hour. A white colour precipitate was obtained which was separated by centrifugation and washed several times with double distilled water. The precipitate was dried in oven at 80°C for 4 hours to get powder sample. Using the same method, ZnS Nanoparticles were prepared using other capping agents also.

2.2. Characterization of ZnS nanoparticles

The absorption spectra of ZnS nanoparticles were recorded with an UV-Visible spectrophotometer (UV-3600 series, Shimadzu) in the range of 200-800 nm. X-ray diffraction (XRD) measurement of ZnS nanoparticles was carried out on X'pert Pro X-ray diffractometer (Panalytical B.V., Netherlands) operating at 40 kV and a current of 30 mA at a scan rate of 0.388 min^{-1}to determine the nano crystalline phase and structure. The FTIR spectra of the samples were recorded with Shimadzu spectrophotometer in the range of 4000-400 cm^{-1} using KBr pellet technique. The size and morphology of the nanoparticles were determined by TEM (HITACHI H-7500). For sample preparation, dilute drops of suspensions were allowed to dry slowly on carbon-coated copper grids for TEM measurements.

2.3. Degradation of Xylenol Orange ($C_{31}H_{28}N_2Na_4O_{13}S$)

Xylenol orange (3,3′-bis[N,N-bis(carboxymethyl)aminomethyl]-o-cresolsulfonephthalein) (XO), a water-soluble dye of the triphenylmethane group, was tested for the degradation by ZnS nanoparticles. The degradation of XOwas carried out in the presence of sunlight at 35°C. A 30 mg sample of ZnS Nanoparticles was dispersed in a 30 ml of double distilled water under ultrasound irradiation. Then the solution was mixed with 30 ml of 5×10^{-5}M XO (0.0038 gr./lit.) solution. The solution was stirred in dark at room temperature for one hour to make the absorption/ desorption between XO and catalysts and to reach equilibrium. Then, the solution was stirred by the magnetic stirrer under the sunlight.2 ml of the solution was withdrawn from the reaction mixture during the study of catalysis for every 30 minutes time interval to record UV-Visible absorption spectrafor the photodegradation of the XO dye.

The bleaching of XO catalyzed with ZnS Nanoparticles capped with PVP, PVA and PEG-4000 was studied under sunlight. The absorbance of XO samples at λ_{max}= 570 nm was measured by a UV-Visible spectrophotometer. The decrease of absorbance values of samples at λ_{max} of dye after irradiation at definite time intervals should be the rate of decolourization and therefore, photodegradation efficiency of the dye. The degradation efficiency was calculated as:

$\% D = 100 \times [(Ao-At)/Ao]$

Where, A_o and A_t are the initial and at time t absorbance of the sample respectively and t is the irradiation time of sample.

Results And Discussion

3.1. UV-Visible measurements

UV-Visible spectra are very much helpful in identifying the nanomaterials. The optical absorption spectra of ZnS Nanoparticles with different capping agents like PVP, PVA and PEG-4000 are shown in Fig.1. The study of optical absorption is important to understand the behavior of semiconductor nanoparticles. A fundamental property of semiconductors is the band gap – the energy separation between the filled valence band and the empty conduction band. Optical excitation of electrons across the band gap is strongly allowed, producing an abrupt increase in absorption at the wavelength corresponding to the band gap energy (E_g). This feature in the optical spectrum is known as the optical absorption edge. It is evident that, the samples exhibit a strong absorption wavelength at 312 nm for PVP capped ZnS, 321 nm for PVA capped ZnS and 327 nm for PEG-4000 capped ZnS Nanoparticles suggesting blue shift with respect to the bulk arising from quantum confinement effect of the nanoparticles. The band gap energy of the samples corresponding to the absorption edge is found to be 3.98 eV, 3.86 eV and 3.79 eV respectively. The band gap of bulk ZnS is 3.68 eV at 300 K.

The quantum confinement effect allows one to tune the emission and excitation wavelengths of nanoparticles by tuning particle size D(E).The particle size is given by the following expression [28].

$$D(E) = \frac{0.32 - 2.9\sqrt{\mathrm{Eg} - 3.49}}{3.50 - \mathrm{Eg}}$$

Where, E_g is the band gap in eV and D(E) is the diameter of the nanoparticle in nm.The obtained band gap and particle size values for different samples are shown in Table 1. From the table, it is clear that the values of optical band gap decreases with the increase in the particle size.

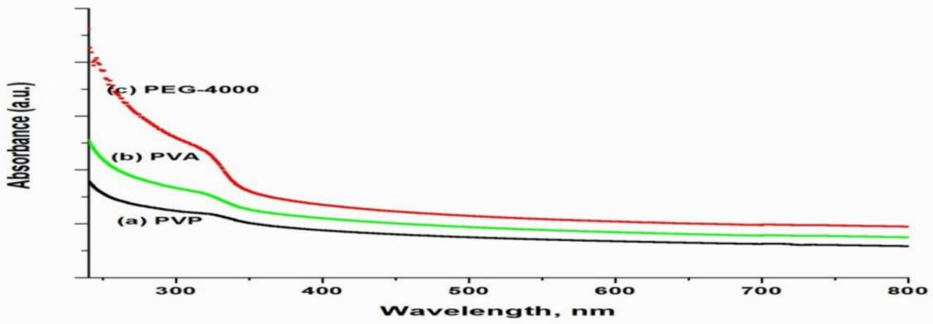

Fig. 1 UV-Visible absorption spectra ofZnS nanoparticles.

S.No	Sample	Wavelength (nm)	Band gap (eV)	Particle size (nm)
1	ZnS-PVP	312	3.98	3.5
2	ZnS-PVA	321	3.86	4.0
3	ZnS-PEG	327	3.79	4.3

Table 1. Particle size calculations from band gap energy.

3.2. X-ray diffraction measurements

Fig.2 shows the typical powder XRD patterns of prepared ZnS nanoparticles using different capping agents like PVP, PVA and PEG-4000 bycoprecipitation technique. In each of these patterns three reflections from (111), (220) and (311) planes are observed indicating the cubic zinc blende structure (cubic, β-ZnS). It is found that the change in the capping molecule do nothave any effect on the crystal structure of nanoparticles. The typical broadening of the three diffraction peaks is also observed, implying that the size of ZnS nanoparticles is very small. The broad diffraction peaks are attributed to the characteristic small particle effect [29]. The peak broadening at lower angle is more meaningful for the calculation of particle size. Therefore size of nanoparticles has been calculated using Debye-Scherrer formula using (111) reflection from the XRD pattern. Debye-Scherrer formula for particle size determination is given by [30]:

$$D = \frac{0.94\,\lambda}{\beta\ COS\Theta}$$

Where, D is the particle size, λ is the wavelength of X-rays (1.54056A^{o}), β is the full width at half
Maximum after correcting the instrument peak broadening (β expressed in radians) and θ is the Bragg's angle.

The values of particle size obtained from XRD for different capping agents are listed in Table 2. From the table, it is clear that the particle size of PVP capped ZnS nanoparticles is more when compared to PVA and less with PEG.XRD broadening could be due to other contributions like strain (ε) and stress. The lattice parameter (a) of the unit cells is calculated according to the relation [31]:

$$\frac{1}{d^2} = \frac{1}{a^2}(h^2 + k^2 + l^2)$$

Where, d is the interplaner spacing of the atomic planes as determined from the position of the peak (111), lattice parameter is estimated in the range of 5.35 – 5.43A^{0}. These values are smaller compared to the bulk value of 5.48A^{o}. As already mentioned the XRD peak broadening could also be due to the strain in addition to the crystalline size of the particles. Hence an attempt has been made to estimate the average strain of the ZnS nanoparticles using Stokes-Wilson equation:

$$Strain\ (\in) = \frac{\beta}{4\ tan\Theta}$$

The Dislocation density (δ) was also calculated from the relation [32-33]:

$$Dislocation\ Density\ (\delta) = \left(\frac{}{aD}\right)^{15\in}$$

Where, ε is average strain, $'a'$ is the lattice parameter and D is average crystal size.The average strain and the dislocation densities values are given in Table 2. The lattice parameter, strains and dislocation densities are found to decrease in the orderPEG-4000, PVA and PVP.

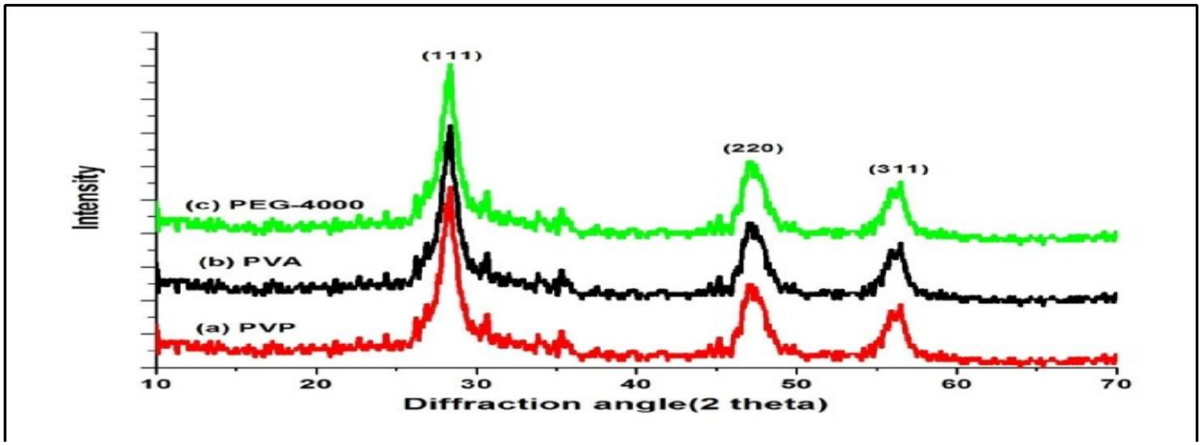

Fig. 2 XRD pattern of ZnS nanoparticles with various capping agents.

S.No	Sample	Avg.Lattice parameters (a) in A^o	Avg.Strain (ε) in A^o	Avg. Dislocation density(δ)	Avg. Particle size(nm)
1	ZnS-PVP	5.43	0.42	0.46	2.60
2	ZnS-PVA	5.38	0.56	0.91	2.45
3	ZnS-PEG	5.42	0.37	0.45	3.25

Table 2. Values of particle size, lattice parameter (a), strain (ε) and dislocation density (δ) from XRD spectra

3.3. Fourier Transform Infra-red measurements

The FTIR spectraZnS nanoparticles are recorded in the range of 4000-400 cm^{-1}and are shown in Fig.3.In the PVP capped ZnS nanoparticles, theabsorption peaks at 2933 cm^{-1}correspond to -C=O stretching, 1646 cm^{-1}, 1583cm^{-1}and 1007 cm^{-1}are attributed to -C=N stretching. This is believed to be due to the formation of co-ordinate bond between the nitrogen atom of the PVP and the Zn^{+2} ions. In the PVA capped ZnS nanoparticles,the strong absorption peaks at 1577 cm^{-1}corresponds to -C=O stretching, 1412 cm^{-1} correspond to -CH$_2$bending and the peaks at 3381 cm^{-1}and 2935cm^{-1}are also observed. In the PEG-4000 capped ZnS nanoparticles, the absorption peaks around 2882 cm^{-1}correspond to -C-H bending and 1110 cm^{-1} attributed to C-O stretching and the peaks 1577 cm^{-1}, 1441 cm^{-1} are also observed. These peaks are attributed to the formation of ZnS nanoparticles.

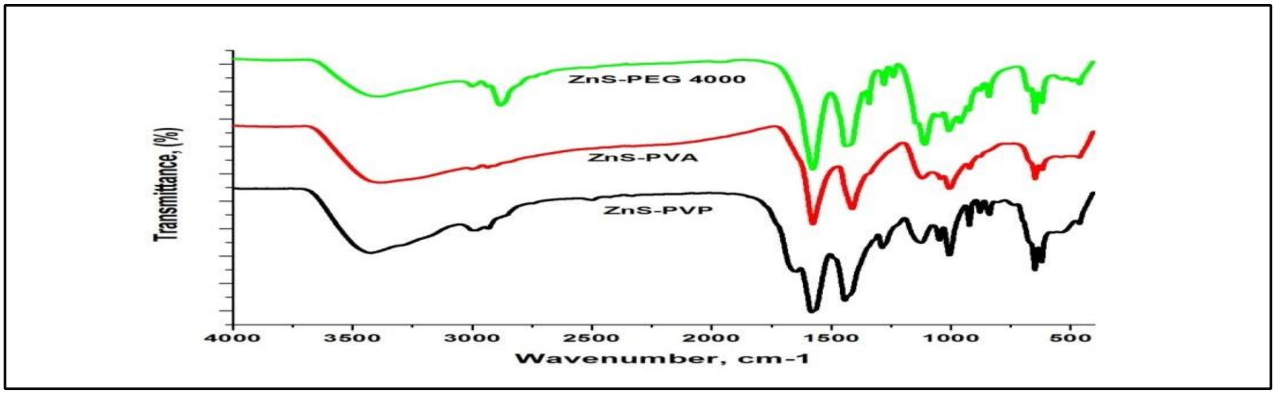

Fig. 3 FTIR spectrum of ZnS nanoparticles with various capping agents.

3.4. Transmission electron microscopy measurements

The typical morphology of the obtained ZnS nanoparticles using coprecipitation method could be intuitively determined by TEMin Fig.4.TEM images showed that sample was composed of agglomerated and isolated particles and it reveals that small particles aggregate into secondary particles because of their extremely small dimensions and high surface energy. Therefore the diameter and the size distribution of the nanoparticles are difficult to be determined precisely by simply viewing the TEM image.

Fig. 4 TEM images of ZnS nanoparticles.

3.5. Photo catalytic activity

3.5.1. The effect of ZnS nanoparticles on the photodegradation of XO dye

In Fig. 5, the XO dye without ZnS nanoparticles and presence of ZnS nanoparticles capped various capping agentsdegradation with sunlight exposure at different time intervals was observed. It can be seen from the recorded spectra that without ZnS nanoparticles the dye degraded 7.4 % only.The enhancement of percentage of XO dye degradationwasobserved 73.05% in 180 min., 83.42% in 150 min. and 87.24%in 120 min. in the presence of PVP, PVA and PEG-4000 capped ZnS nanoparticles. It clearly shows that the absorption maximum of XO dye at 570 nm gradually decreases with increasing irradiation time. No new absorption peak appears in the UV-Visible spectra during the whole process. The percentage of degradationefficiency of XO dye was plotted against the irradiation time, as shown in Fig.6. It indicates that in the presence of ZnS nanoparticles, the photo degradation of XO dye is taking place under sunlight exposure.It can be observed that XO dye degraded to maximum extent by PEG-4000 capped ZnS nanoparticles when compared to PVP and PVA capped ZnS nanoparticles. In the absence of synthesized ZnS nanoparticles, there is no significant change in the absorption maximum of XO dye. These results indicate that the decomposition of XO dye can be ascribed to the photo catalytic process of ZnS nanoparticles.The percentage of degradation efficiency of XO dye is shown in Table 3.

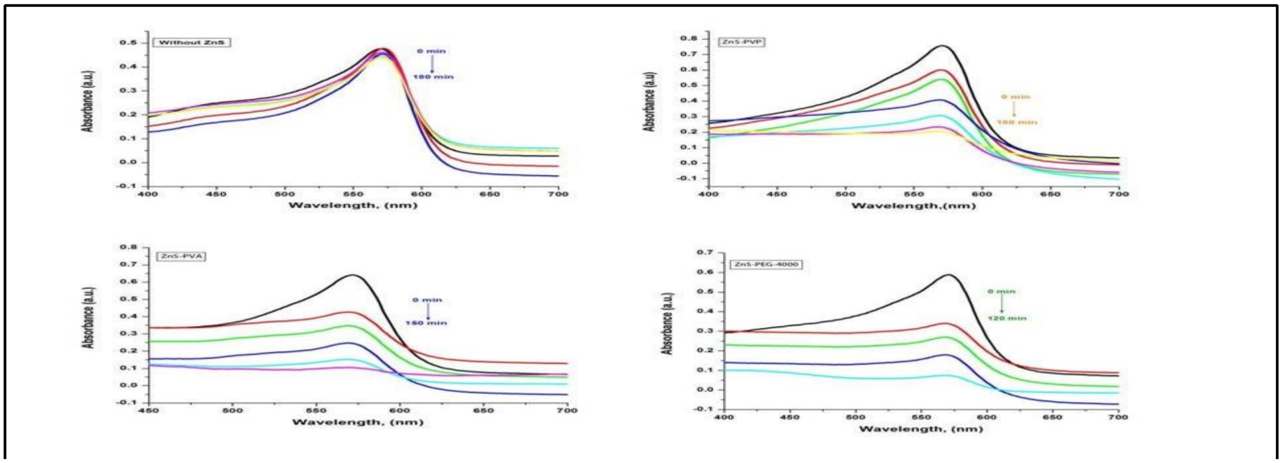

Fig. 5The absorption spectrum of 0.038gr/LXO solution only (a) and photodegradation of XO dye solution by (b) PVP, (c) PVA and (d) PEG-4000 capped ZnS nanoparticles under sunlight irradiation.

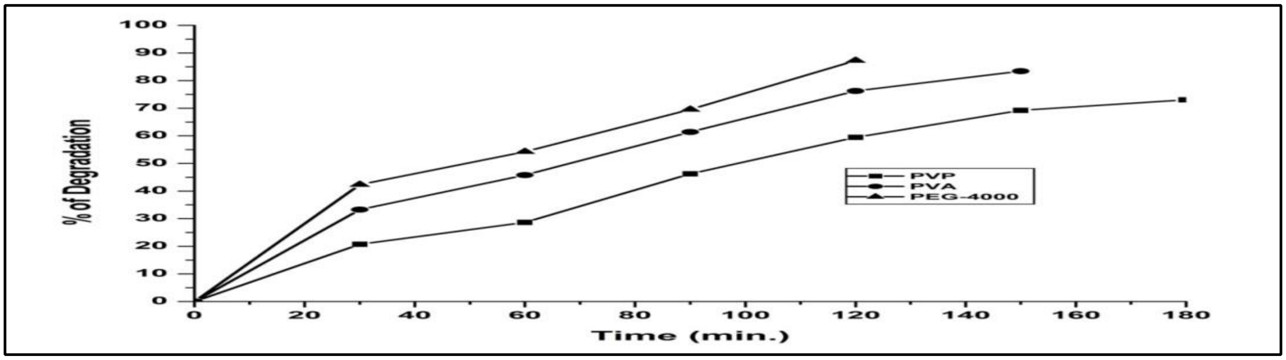

Fig. 6 The effect of XO dye degradation by various capping agents capped ZnS nanoparticles.

S.No	**Time (min)**	**% of Degradation of Dye**		
		ZnS-PVP	ZnS-PVA	ZnS-PEG-4000
1	0	0	0	0
2	30	20.74	33.28	42.34
3	60	28.66	45.78	54.25
4	90	46.23	61.40	69.55
5	120	59.44	76.25	87.24
6	150	69.22	83.42	
7	180	73.05		

Table 3.Degradation efficiency of dye in the presence of ZnS nanoparticles with various capping agents.

3.5.2. The effect of capping agents and kinetic rate constants

The kinetics of XO photo degradation catalyzed by synthesized ZnS nanoparticles was studied under sunlight. The photo catalytic degradation of various organic compounds such as dyes in the presence of a heterogeneous photo catalyst can be formally described by the Langmuir-Hinshelwood Kinetics model [34]. Rate (r) $= dC/dt = k\,KC/1+KC$

For low concentrations of dyes ($KC<<1$), neglecting KC in the denominator and integrating with respect to time t, the above equation can be simplified to the pseudo-first order kinetic model equation.

$\ln C_o/C_t = k\,Kt = K_{app}\,t$ then the equation is modified as $\ln A_o/A_t = K_{app}\,t$

Where, dC/dt is the rate of dye degradation (mg/L. min.), k is the reaction rate constant (min^{-1}), K is the adsorption co-efficient of the dye on to the photo catalyst particle (L/mg.) and K_{app}(min^{-1}) is the apparent rate constant calculated from the curves. Fig.7shows the $\ln A_o/A_t$ values plotted against time of degradation ofXO dyewith different capping agents catalyzed by ZnS nanoparticles. The apparent rate constants of degradation with different capping agents with XO dye, K_{app}were determined from the slopes of the plotsand are in accordance to the proposed pseudo-first order kinetic model. The apparent rate constants are given in Table 4, which show photo degradation of XO dye decreases from PEG-4000 to PVA and PVP.

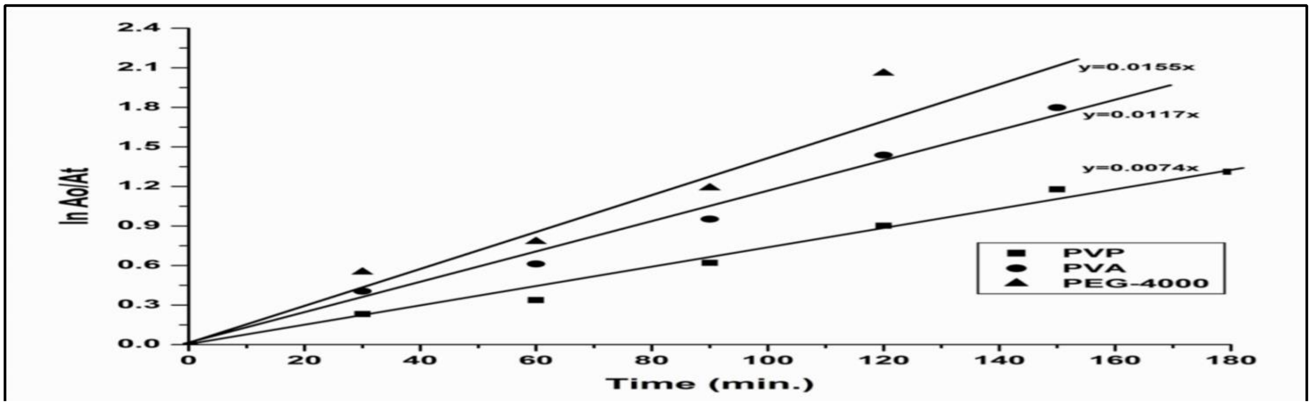

Fig. 7 Kinetic study of photo degradation of XO in the presence of ZnS nanoparticles.

Sample	Rate constants
ZnS-PVP	7.4×10^{-3} min^{-1}
ZnS-PVA	11.7×10^{-3} min^{-1}
ZnS-PEG-4000	15.5×10^{-3} min^{-1}

Table 4. Values of apparent rate constants K_{app} (min^{-1}) for the degradation of 5×10^{-5} M XO in the presence of ZnS nanoparticles synthesized using various capping agents.

Conclusion

The simple synthesis of the ZnS nanoparticles by coprecipitation method using various capping agents like PVP, PVA and PEG-4000 is reported. The UV-Visiblespectra revealed that there is a blue shift of absorption band from the bulk. FTIR spectra supported theformation of ZnS nanoparticles.In XRD spectra the particle size (2-4 nm) was calculated from the Debye-Scherrer formula. TEM analysis indicates that the ZnS nanoparticles are small in size.The photo catalytic degradation ofXO illustrates that this newly synthesized PEG-4000 capped ZnS nanoparticles could be used as a promising catalytic degradation material than PVP capped ZnS and PVA capped ZnS nanoparticles. The kinetic rate constant of degradation is higher in the presence of PEG-4000 capped ZnS nanoparticles.

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