Synthesis, Size Characterization and Photocatalytic Studies on the Oxidative Degradation of Ritrodrine, Pentazocine, Isoxsuprine and Amoxicillin By Silver Nanoparticles In Aqueous Medium At 25°C.

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Abstract—**Metal nanoparticles show enhanced physical and chemical properties when compared to the bulk materials. Particularly silver nanoparticles (AgNPs) show wonderful catalytic, optical and spectroscopic properties. We report here, the synthesis, size characterization and photocatalytic behavior of AgNPs, synthesized using poly N-vinyl pyrrollidone (PVP) as the capping agent. Temperature effect during the synthesis of AgNPs was studied. The reductant used was sodium borohydride ($NaBH_4$). Three reaction temperatures 20^oC, 30^oC, and 45^oC are maintained and silver nanoparticles recovered are size characterized using PXRD and HRTEM data. 10±1nm, 14±1 nm and 20±1nm are the sizes of AgNPs corresponding to 20°C, 30°C,and 45°C respectively. The variation in the catalytic activity of the differently sized AgNPs are investigated on the UV irradiated oxidative degradation of 4 potential drugs such as ritrodine (RTH), isoxsuprine (ISH), pentazocine (PZH) and amoxicillin (AMX) in aqueous medium at 25°C. These drugs are widely used in therapeutic applications of analgesics, antibacterials and muscle relaxants. In recent years it was deducted that environmental water resources have been loaded in exceeding levels by these drugs. Using UV irradiation (300nm) for 1hour and controlled amounts of hydrogen peroxide [H_2O_2], the kinetics of degradation of the 4 drugs in the presence of AgNPs are carried out. The pseudo first order rate coefficient values are determined based on the absorbance decrease with various time intervals, at constant Λ_{max} equals to 275 nm, 230 nm, 250 nm, and 216 nm corresponding to RTH,PZH, ISH and AMX respectively. It was found at 25°C and at constant catalyst loading 5mg for 20ml of 1mM of drug solution and with1ml of 5% by wt H_2O_2 aqueous solution. The trend in the photocatalytic degradation rate constants was found to be ISH>PZH>RTH>AMX. It was also found that, AgNPs combined with H_2O_2 with and without UV irradiation, forming reactive radicals. A plausible mechanism of oxidation and mineralization of each drug in aqueous medium was proposed.**

I. INTRODUCTION

Metallic silver and its components exhibit photo activity in the form of bulk materials and as well as in the nano size particles. Silver nanoparticles [AgNPs] are well known to show unique optical, spectroscopic, catalytic, and photo physical properties. Many reports are available on the utilization of the unique properties exhibited by AgNPs for the synthesis of organic substrate, photocatalytic degradations, in solar devices etc,. In this work the synthesis, size characterizations and photocatalytic behavior of AgNPs are investigated. Synthetic polymer like poly N-vinyl pyrollidine [PVP] which is water soluble was used as capping agent for preparing AgNPs from silver nitrate salt precursor using freshly prepared sodium borohydride aqueous solution as the reductant. The AgNPs are prepared at three different temperatures such as 20^0C, 30^0C and 45^0C, so that the reaction temperature effect on the nanoparticle sizes can be investigated. The size characterizations are carried out by using PXRD and HRTEM data. Three different temperatures are size characterized. The sizes are found to be 10±1nm, 14±1nm and 20±1nm respectively for the reaction temperatures 20^0C, 30^0C and 45^0C. The remediation of drug polluted waters require advanced oxidation process in which AgNPs with UV irradiation can be used. These methods are categorized in greener environmental methods [1-3]. The variation in the photocatalytic activity of the differently sized AgNPs are investigated on the oxidative degradation of four potential drugs in aqueous solution at 25°C. The drugs used are Isoxsuprine [ISH], Pentozocine [PZH], Ritrodrine [RTH] and Amoxcillin [AMX] and UV irradiation source. The drugs chosen popularly and widely used in the therapeutic application, analgesics anti-bacterials and muscle relaxants. The progress of the reaction was studied by measuring absorbance values at regular intervals of time. Adopting pseudo first order experimental conditions, the kinetic plots are made by using $\log(OD_0/OD_t)$ versus time data. The pseudo firsts order values are determined for the degradation of four drugs, separately by using three differently sized AgNPs. Based on the kinetic parameters the catalytic efficiency of the AgNPs are derived. The drug compositions and AgNPs size, photo degradability of the drugs are analyzed. Salient features of the investigations are discussed.

II. EXPERIMENTAL

A. Chemicals and Materials

Silver nitrate and Sodium borohydride are purchased from Aldrich Ltd Analar grade reagents. The drugs Ritrodrine, Pentazocine, Isoxsuprine and Amoxicillin are obtained from Johnson Mattthey Alfa AESAR. Triple distilled water was used for solution. Poly N-vinyl pyrollidone(PVP) was purchased from MERCK Hydrogen peroxide used belong to Qualigens, India. All chemicals are used as such without further purification.

B. Synthesis of Silver Nanoparticles

10ml of 0.1mM silver nitrate solution was taken in a round bottomed flask covered with carbon paper to avoid light. 10ml of 5 wt % PVP solution was added drop wise with constant stirring. To this solution 10ml of 0.1M sodium borohydride solution was added with vigorous stirring. The additions are complete within 30 minutes. The reaction temperature was maintained at 35^0C and continuously stirred for 4hours. Lemon yellow coloured solution resulted and small aliquots was taken and UV-SPR was measured. The SPR peak was observed at 408nm which ensures the formation of Ag-PVP nanoparticles. The bulk solution samples was used for further size characterization.

C. Size Characterisation

The morphologies and microstructure of the AgNPs were characterized using S-4800 FESEM emission scanning electron microscope. Hitachi Japan using an X-ray diffraction meter with Cu-K radiation M21X,MAC science Ltd Jap an. The HRTEM images of the catalyst show the presence of spherical structured particle with a mean size lying around11 ±1nm. Using Scherrer formula on the X-ray diffraction patterns containing maximum intensity peak the mean size of AgNP was found to be 10±1nm. The peaks at 38.00, 44.40, 64.60 and 77.50 in the XRD were attributed to metallic Ag [JCPDS file card 65-2871]. The preparation of AgNPs mentioned above was carried out at 25^0C. However, synthesis at three different temperatures such as 25^0C, 30^0C, and 45^0C are carried out separately by maintaining the temperature using double walled thermostat into which preheated and temperature maintained water was circulated. AgNPs are synthesized adopting similar procedure maintained at these three different temperatures under vigorous stirring for 5hrs.

D. Photocatalytic Studies

The photocatalytic degradation of drugs are carried out by irradiation by vertically placing 2mlof the prepared AgNPs suspensions in quartz beaker containing 20ml of 1mM drug solution at pH=7.0. A 500W xenon arc lamp[PLS-SXE] TECH. India, served as the light source to stimulate irradiation . Before beginning of the degradation the contents were kept in darkness for 30minutes to attain adsorption equilibrium of drug and photo catalyst in the solution. The progress of the degradation was determined by measuring absorbance variation with time. Schimadzu UV-visible spectrometer was used for absorbance measurements.

III. RESULTS AND DISCUSSIONS

A. Size Characterizations of Silver Nanoparticles

In figure.1 the UV-SPR spectra of silver nanoparticles synthesized at 200°C is given. The presence of SPR spectra at 408nm confirms the presence of AgNPs and the XRD pattern of solvent dried AgNPs are shown in figure.1. On comparing [JCPD file card no. 65-2871], the presence of nano crystalline silver nanoparticles are observed. Applying Scherrer formula on the FWHM of XRD pattern the mean size values are found to be 10±1nm. The TEM photographs of AgNPs synthesized at 20^0C are shown in figure-2. The mean size values of the AgNPs is found to be 11±1 nm. These values are found agreeable. The spherical morphology was found for AgNPs in TEM.

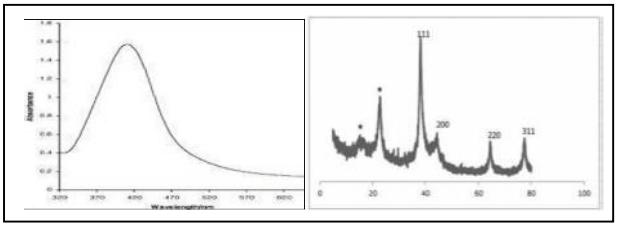

Figure 1. UV-SPR and XRD pattern of Silver nanoparticles

B. Effect of Temperature

The effect of temperature on the synthesized AgNPs can be studied from the TEM photographs of AgNPs collected from the reaction mixture maintained at 20°C, 30°C, and 45°C. The TEM photos are given in figure - 2. The mean size values are found to be 10±1nm, 14±1nm, 20±1nm corresponding to the AgNPs from reaction temperatures 20^0C, 30^0C, and 45^0C. It may be seen that increase in reaction temperature during the synthesis of AgNPs increases the mean particle sizes.

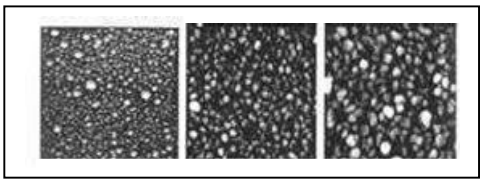

Figure 2. HRTEM photos of Silver nanoparticles resulted from reaction at 20^0C, 30^0C and 45^0C, with sizes 10±1nm, 14±1nm, and 20±1nm respectively.

C. Kinetic Studies

The photocatalyst loading amount was optimized to be 1mg/20ml of the 1mM drug solution. At regular interval of time the absorbance of the aliquots drawn out measured in a UV spectrometer. In figure-3 absorbance versus time plots for the four drugs separately carried out in the presence of UV irradiation are shown. Applying Pseudo first order kinetics expressions plots of log $[OD_0/OD_t]$ versus time are made and shown in figure-4.

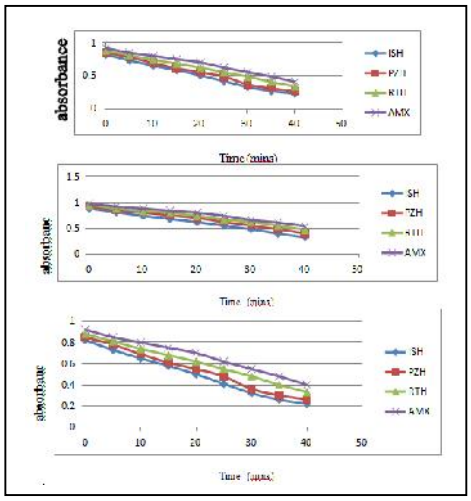

Figure 3. Absorbance versus time plots of drug degradation in the three differently sizes silver nanoparticles

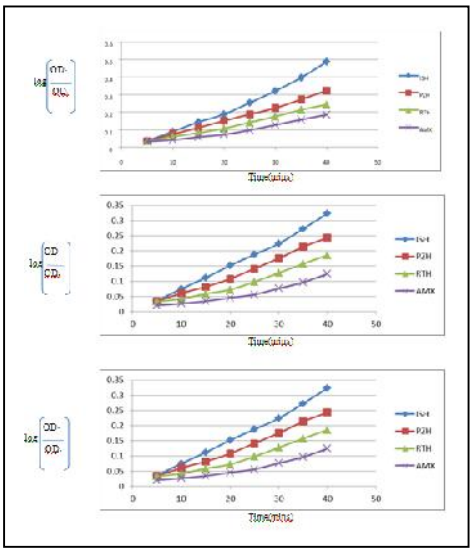

Figure 4. The kinetic plots of log (ODo/ODt) vs time for drugs degradations in three differently sized silvernanoparticles.

a-10±1nm, b -14±1nm; c-20±1nm

The rate coefficient values are determined from slope values when multiplied with 2.303. In table I the kinetic parameters for the photodegradation of the drugs in the presence of AgNPs are given. The effect of the size of the nanoparticles on their photocatalytic activity can be deduced from the rate coefficient values of the degradation of the drugs. Keeping the drug system and drug compositions constant, the rate coefficient values are found to decrease with increase in size of the nanoparticles. i.e., when the nanoparticle synthesized temperature is increased the photo catalytic activity of the nanoparticle seem to decrease, for constant catalyst loading. When the sizes of the nanoparticle are smaller, the number of the density of the particles formed are larger. The total surface area generated by the nanoparticles increases when the particle size decreases. Hence the photocatalytic activity trend for AgNPs synthesized at different temperature increases as $45^0C<30^0<20^0C$. The variation in the photodegradability in the presence of AgNPs catalyst at constant size and composition for the four drugs based on the rate coefficient values has been found to be ISH> PZH>RTH>AMX. In order to ascertain complete degradation of the drugs, effect of hydrogen peroxide addition in to the photodegradation mixture was adopted. At 25^0C and at constant catalyst loading with 1ml of 5% by wt hydrogen peroxide was incorporated. Absorbance are made for this photocatalytic mixture. The rate coefficient values are known from the slopes of the kinetic plots. It was found that in the presence of photocatalyst AgNPs, the rate coefficient values for each drug degradation in the presence of hydrogen peroxide is greater than in the absence of hydrogen peroxide. Hydrogen peroxide induces drug oxidation independently and also AgNPs combined with hydrogen peroxide produces higher extends of drug degradation. The reason attributed to this behavior may be due to the formation of reactive radicals from hydrogen peroxide by AgNPs in presence of UV irradiation.

TABLE I. OVERALL PSEUDO FIRST ORDER RATE CONSTANT VALUES FOR THE PHOTO CATALYZED DRUG DEGRADATIONS BY SILVER NANO PARTICLES AT 25°C.

DRUG SYSTEM	**AgNPs Sizes**		
	10±1nm	***14±1nm***	***20±1nm***
ISH	**$8.25 \times 10^{-4} sec^{-1}$**	**$6.25 \times 10^{-4} sec^{-1}$**	**$4.2 \times 10^{-4} sec^{-1}$**
PZH	**$5.12 \times 10^{-4} sec^{-1}$**	**$4.84 \times 10^{-4} sec^{-1}$**	**$3.63 \times 10^{-4} sec^{-1}$**
RTH	**$4.14 \times 10^{-4} sec^{-1}$**	**$3.83 \times 10^{-4} sec^{-1}$**	**$2.576 \times 10^{-4} sec^{-1}$**
AMX	**$3.15 \times 10^{-4} sec^{-1}$**	**$2.53 \times 10^{-4} sec^{-1}$**	**$1.508 \times 10^{-4} sec^{-1}$**

D. Photocatalytic Mechanism

The work function of element silver lies around 4.26eV with Schottky barrier. On photolysis, photo generated electrons are transferred between surfaces of AgNPs, through electron tunneling process. The conductive bridge of AgNPs arising due to electrons moving between inter AgNPs could be transferred to surface absorbed oxygen rapidly, thus forming activated superoxide anion radical O_2^*, OH^*,and HO_2^* in aqueous medium. Simultaneously, the remaining photogenerated holes and electrons react with water giving rise to OH^*radicals.

$$Ag + h\Upsilon \longrightarrow Ag^+ + e^- \xrightarrow[H_2O]{2O_2} {}^*OH + HO_2^* + O_2^{-*}$$

In the aqueous environment the stabilized drug molecules are easily attacked by hydroxyl (OH^*) hydroperoxide ($^*O_2H$) and superoxide anion (O_2-*) radicals, resulting in degradation of the drug molecule [5-6].

IV. CONCLUSION

The AgNPs are synthesized in different sizes adopting various reaction temperatures with PVP as the stabilising agent. Upon size characterization by XRD and TEM measurements the sizes of AgNPs synthesized from 20^0C, 30^0C, and 45^0C are 10±1nm, 14±1nm, and 20±1nm respectively. Potential and popularly used drugs such as ISH, PZH, RTH, and AMX are photo catalytically degraded using 1mg/20ml of catalyst loading separately for the different sized catalyst and for the four drugs. Absorbance variation with time measurements are used to evaluate rate coefficient values. The trend observed in the photo degradability is ISH>PZH>RTH>AMX. The photocatalytic activity variations among the three AgNPs synthesized are found to be 20°C>30°C>45°C. The sizes of AgNPs increased with increased in reaction temperature due to agglomeration of the particles. Smaller the size of the AgNPs greater is the total surface area and number density of the particles produced for constant composition than the larger AgNPs. Thus PVP-capped AgNPs prepared show efficient photocatalysis for drug degradation at 25°C.

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