Multifunctional Efficacy of Environmentally Benign Silver Nanospheres for Organic Transformation, Photocatalysis, and Water Remediation

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ABSTRACT: Highly crystalline and monophasic silver nanospheres with a high specific surface area of 57 m²/g have been synthesized by an environmentally benign rapid chemical reduction using L-alanine for catalytic transformation, photocatalytic degradation, and bacterial disinfection, which can provide an ample strategy for water remediation. Electron microscopic analysis confirms the spherical morphology of as-prepared silver nanoparticles with an average grain size of 20 nm. Silver nanospheres showed excellent catalytic activity for the catalytic hydrogenation and conversion (95.6%) of 4-nitrophenol to 4-aminophenol. Significant photocatalytic degradation proficiency was also shown for methylene blue (94.5%) and rhodamine B (96.3%) dyes under solar irradiation. The antibacterial behavior of Ala−Ag nanospheres was demonstrated through the disk diffusion antibacterial assay against Gram-positive (Escherichia coli) and Gram-negative (Staphylococcus aureus) bacteria. Multifunctional efficiency of as-prepared Ala−Ag nanospheres for water remediation has also been established.

1. INTRODUCTION
Illimitable human interventions and precipitous urbanization have led to natural water sources contamination, which can cause disarray in ecosystem. The clean drinking water scarcity is preeminent among the consequences of growing environmental crisis, which alarmingly threatens the well-being of mankind.1 Several hazardous organic compounds from chemical industries and runoffs from the textile industries constitute the main basis of water pollution and are termed as primary contaminants of industrial wastewater. Being a considerable source for nonaesthetic contamination, these effluents are carcinogenic and hazardous. Besides accumulation in water bodies, these perilous compounds can reduce the oxygen accessibility of microbes for biodegradation process by lessening the capacity of photosynthesis, which initializes many chemical reactions in wastewater through further oxidation, hydrolysis, and produces harmful waste materials.2−4 Consequently, their entire disarticulation is compulsory. Over the past few decades, integrating the principles of “green chemistry” with a wide and enhanced field of nanotechnology has attracted ample attention.5 The main aim of this research is environmentally benign designing and fabrication of nanomaterials with the advancement of additional sustainable processes.5 Studies on optical, electrical, biological activities, and pharmaceuticals like photonics, electronics, optoelectronics, catalysis, sensing, and pharmaceuticals.13,14 From past decades, researches have shown that size, shape, size distribution, and morphology of silver nanoparticles can be controlled by varying the synthesis methods, reducing agents, and stabilizing green chemistry.6−8 Following this strategy, silver nanoparticles (AgNPs) synthesis with the “green” route was elucidated through incorporating the preference of reducing and stabilization agent with solvent medium, which are environmentally sustainable.8 In spite of this, several procedures of green chemistry that synthetically control the Ag nanoparticles still require more advancement. However, methods of synthesis for nanoparticles of noble metals by employing biomolecules such as amino acids have also attracted the attention of researchers.5,9−12 Synthesis of silver and silver-based nanomaterials has been a dynamic area of research for executing nanotechnology due to their great importance in a wide variety of applications like photonics, electronics, optoelectronics, catalysis, sensing, biological activities, and pharmaceuticals.1,3,14
agents, which directly influences the optical, electromagnetic, and catalytic properties of silver nanoparticles.\textsuperscript{15}

Catalytic organic transformation and photocatalytic degradation are efficient methods of decontamination of water from hazardous contaminants to mineralized products. Nitrophenol and its derivatives, as a major class of industrial and environmental organic contaminants, cause a threat to the environment, whereas the obtained product after its reduction i.e., aminophenol (AP), is extensively employed in numerous useful fields such as analgesic and antipyretic drugs, including paracetamol, acetanilide, and phenacetin.\textsuperscript{16} The literature completely unveils the anthropogenic, noxious, and inhibitory nature of 4-nitrophenol (4-NP), whose exposure can lead to numerous health-related problems such as nausea; exhaustion; headaches; cyanosis; mutilate liver, central nervous system, and kidney; as well as damage to the blood of both animals and humans.\textsuperscript{2,17,18} Moreover, 4-NP is soluble in water and also gets stabilized to a great extent. Thus, the hydrogenation of nitroarones in aqueous medium using catalysts is being widely employed as a touchstone reaction to affirm the catalytic efficiency of these catalysts.\textsuperscript{19,20} Catalytic hydrogenation of 4-NP into aminophenol using sodium borohydride in aqueous medium by employing fabricated nanostructured materials as catalysts\textsuperscript{21} is found to be of great interest. Among the catalytic organic transformations, mainly nitroaromatics reduction to amino-aromatics on the surface of catalyst borohydride has arisen as model reactions, which magnificently appraise the catalytic properties of nanomaterials through kinetic parameters attained from the monitoring of an aqueous solution with real-time spectroscopic measurements.\textsuperscript{7,41}

Besides toxic organic compounds, different perilous dyes such as methylene blue (MB) and rhodamine B (RB) are extensively used in textile and food manufacturing units. It is reported that these nonbiodegradable dyes are highly toxic for aquatic species and can have carcinogenic effects on other living creatures, which proved them as the main source of pollutant to water bodies and to the environment. Nowadays, various water remediation systems and conventional methods like adsorption, ultrafiltration, and chemical and electrochemical methods for the treatment of industrial wastewater are used to treat wastewater, which generates secondary pollutants that lead to certain problems. Further, their accumulation in water bodies reduces the reoxygenation capacity, which causes eutrophication and sternly damages the aquatic flora and fauna by limiting sunlight penetration.\textsuperscript{23–27} Photocatalysis has shown remarkable interest in the application of photocatalysts for water purification and generation of molecular hydrogen. Especially, photocatalytic degradation is widely employed due to its simplicity, efficiency, and cost-effectiveness, and has attained considerable interest for less productivity of secondary pollution.\textsuperscript{28} Recently, metal nanoparticles-based photocatalysts attracted global interest to deal with comprehensive issues related to photodegradation of organic contaminants and molecular H\textsubscript{2} generation from water splitting using sunlight.\textsuperscript{29,30} Another issue of concern for global health is the alarming expansion of pathogenic bacteria and fungi, i.e., commonly multidrug-resistant microorganisms. Henceforth, novel bioengineered nanomaterials have been developed with the recent advancements in antimicrobial nanotherapy, which are widely explored as antimicrobial agents. The destruction of cell walls and nucleic acids, as well as the degradation of cell membranes confirms their antimicrobial activity. An inclusive range of Ag nanoparticles-enriched consumer goods eventually discovered their way through waste disposal streams and into industrial wastewater remediation systems.\textsuperscript{1–34} In view of the above, several antibacterial studies have been carried out to meet the challenges of biological applications.\textsuperscript{7,35,36} It has also been established in these studies that alanine readily interacts with biosystems and enhances the role of silver nanoparticles to accomplish the antibacterial effect.

A series of chemical methods such as citrate precursor,\textsuperscript{37} solvothermal,\textsuperscript{38} hydrothermal,\textsuperscript{39} and reverse micellar\textsuperscript{40} methods have been explored for the fabrication of various nanostructured materials. Several routes are also known for the preparation of silver nanoparticles with controlled size and shape.\textsuperscript{7,41–43} In the present study, we have developed an environmentally sustainable, cost-effective, and rapid methodology to synthesize Ag nanoparticles by employing alanine (essential amino acid) as a stabilizing, reducing, and capping agent for water remediation. Several characterization techniques such as X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM)/high-resolution TEM (HRTEM), UV–visible spectroscopy, Fourier transform infrared (FTIR) spectroscopy, Brunauer–Emmett–Teller (BET) surface area analysis, and thermogravimetric studies have been carried out to analyze the crystallinity, size, morphology, elemental composition, optical and thermal properties, and surface area of as-synthesized nanoparticles. Further, catalytic organic transformation, photocatalytic degradation, and antibacterial properties were also examined.

2. RESULTS AND DISCUSSION

2.1. Powder X-ray Diffraction (XRD) Studies. The crystalline structure, phase composition, and purity of as-prepared samples were determined by the powder X-ray diffraction technique. The XRD pattern of as-obtained Ala–Ag nanospheres and standard JCPDS pattern is given in Figure 1. The diffraction peaks of synthesized Ag nanoparticles at 2θ values of 38.102, 44.287, 64.475, and 77.43 correspond to the (111), (200), (220), and (311) lattice planes, which is in good agreement with the cubic phase of metallic silver according to JCPDS card no. 03-0921 with space group Fm\textsubscript{3}m. The impurity peaks corresponding to AgO and Ag\textsubscript{2}O could not be observed in the X-ray diffraction pattern, thus confirming the high purity of as-synthesized nanoparticles. It is clear from the XRD pattern that the synthesized Ag sample is highly crystalline and monophasic without any impurity. By employing the Debye–Scherrer eq 1, the average crystallite size of Ala–Ag nanoparticles was also measured as

$$D = \frac{K\lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

where D is the average diameter of crystallite, K is the shape factor of particle (0.89), β is the full width at half-maximum (FWHM) of the sample, λ is the wavelength of X-rays, and θ is the diffraction angle. The average crystallite diameter was found to be 20.9 nm, which agrees with the results of TEM analysis, as shown in Table 1.

2.2. Field Emission Scanning Electron Microscopy (FE-SEM) Studies. Microscopic studies of the as-prepared silver nanoparticles (AgNPs) were appraised by the FE-SEM technique to determine their surface morphology. Figure 2a shows the FE-SEM image of the as-prepared AgNPs, which depicts regular spherical shape with uniform size. From the inset of Figure 2a, it could be seen that the as-prepared silver
nanospheres exhibit rough surfaces and are aggregated to form larger particles, which is further confirmed from the gray color of nanoparticles. Energy-dispersive X-ray analysis (EDAX) was also carried out to identify the elements present in the as-prepared Ala−Ag NPs. In Figure 2b, the EDAX spectrum confirms the formation of AgNPs by displaying a strong signal in the region of silver. Metallic silver nanoparticles commonly reveal a distinctive optical absorption peak at approximately 3 keV. A weak peak was also noted at 3.2 keV, which must be due to surface plasmon resonance (SPR) of silver nanospheres. The count intensity of EDAX spectra in the silver region is relatively high as compared to other elements. Along with the peaks for silver and oxygen, two other unindexed peaks at 0.27 and 0.38 keV corresponding to carbon and nitrogen confirm the presence of biomolecule (alanine-containing amine group) bound to the Ag nanospheres surface. For comprehensive verification, X-ray elemental mapping of Ala−Ag nanospheres was performed to further examine the elemental distribution of the as-synthesized Ala−Ag NPs. Figure 2c,d shows the X-ray elemental mapping, which clearly demonstrates that silver was dispersed maximally (99.65%) and minutely (0.35%) and other elements like oxygen were present. Moreover, mapping of Ag was well defined with sharp contrast. Distribution of oxygen was due to the presence of L-alanine on the surface of Ala−Ag nanospheres. Thus, the acquired results indicate that L-alanine was proficient in the synthesis of spherical-shaped silver nanoparticles. Accordingly, the formation of Ala−Ag nanospheres was confirmed by these results.

2.3. Transmission Electron Microscopy (TEM) Studies. TEM/HRTEM studies were performed to further corroborate the morphology of the as-synthesized nanoparticles. Figure 3a,b depicts the TEM micrographs of the as-prepared Ala−Ag nanospheres at two different magnifications. The particle size distribution histogram is presented in Figure 3c, which shows the distribution of Ala−Ag nanospheres in the range of 5–45 nm with an average grain size of ~20 nm. Figure 3d shows the size distribution histogram of the as-synthesized Ala−Ag nanospheres.
HRTEM image for the as-synthesized nanospheres displaying the highly oriented lattice fringes. The lattice fringes observed in the HRTEM image (Figure 4a) and line intensity profile corresponding to this plane (Figure 4b) reveal the “d” spacing value of 2.464 nm, which corresponds to the dominant (111) crystal plane growth of crystalline silver. Figure 4c,d shows the HRTEM image and corresponding line intensity profile, which demonstrates the d spacing value of 0.154 nm that corresponds to the (220) crystal plane of silver nanoparticles. These observations are consistent with other studies.

2.4. UV–Visible Diffuse Reflectance Spectroscopy. The as-synthesized Ala−Ag nanoparticles were studied using diffuse reflectance spectroscopy to examine the optical properties, as shown in Figure 5. The reflectance data were used to determine $F(R)$, and absorbance was obtained by converting the reflectance of the as-synthesized product by employing the Kubelka–Munk function, as shown in the following equation

$$F(R) = \frac{\alpha}{s} = \frac{(1 - R)^2}{2R}$$

where $F(R)$ is the Kubelka–Munk function, $\alpha$ is the absorption coefficient, $s$ is the scattering factor, and $R$ is the reflectance of the material. Figure 5a shows the reflectance data obtained from the differential reflectance spectroscopy (DRS) analysis, and Figure 5b shows the plot of energy vs $(F(R)/Int)^2$ on x- and y-axes, respectively, which is employed to calculate the band gap by linear extrapolation. Plasmonic resonance was observed in optical reflectance spectra (Figure 5a), which exhibits a short-wavelength strong plasmon-induced attenuation at 390 nm and a long-wavelength SPR band in the near-infrared region that is attributed to silver nanoparticles. The estimated band gap value for the as-synthesized nanospheres agrees with previous reports and is found to be 2.58 eV.

2.5. Fourier Transform Infrared (FTIR) Spectroscopic Studies. FTIR study was carried out to explore the nature of interactions between the alanine molecules and as-synthesized silver nanoparticles. Figure 5c depicts the IR spectra, which show the appearance of specific peaks at 3143, 2997, 2420, 1619, 1424, 1362, and 1087 cm$^{-1}$. The bands at 1087 and 3143 cm$^{-1}$ correspond to amine and hydroxyl groups. Alanine exists in its zwitterionic form, and a broad absorption band appeared at about 3143 cm$^{-1}$, which is due to O-H stretching, suggesting the deprotonation of the amine group NH$_3^+$ by freeing NH$_2$ and complete COOH group. The vibration bands at 2420–2997 cm$^{-1}$ could be attributed to carbonyl species.

Figure 4. (a) HRTEM image showing lattice fringes of the (111) crystal plane, (b) line intensity profile of the corresponding plane, (c) HRTEM image showing lattice fringes of the (220) crystal plane, and (d) line intensity profile corresponding to this plane of Ala−Ag nanospheres.

Figure 5. (a) DRS, (b) Kubelka–Munk, (c) FTIR, and (d) thermal gravimetric analysis (TGA) plots of Ala−Ag Nanospheres.
This also a which evades the agglomeration, and also stabilizes the colloid. The coordination among the ions chemical or electrochemical means can be applied with amine groups for its easy reduction. The coordination among the ions of Ag⁺ and N atoms simplifies the reduction of Ag⁺ by diminishing the Ag⁺/Ag reduction potential. Though, the Ag⁺ ions are easily reduced, and metallic Ag gets oxidized in the same manner. Thus, once reduction occurs, it is necessary to stabilize Ag⁰ against new oxidation. The nanoparticles of Ag may interact with the amine group of the alanine and the amine groups coordinated to the Ag⁺ ions adsorbed over the surface of the nanoparticles can avoid agglomeration of reduced Ag⁺. Therefore, it facilitates the Ag⁺-ions reduction, which evades the agglomeration, and also stabilizes the colloid. This also affirms that l-alanine can be efficiently employed both as reducing and stabilizing agents for Ag nanoparticles synthesis.

2.6. Thermal Gravimetric Analysis (TGA) Studies. The thermal stability of the as-synthesized Ala–Ag NPs was estimated using TGA studies, as shown in Figure 5d. The weight loss pattern of the as-synthesized nanoparticles was recorded during thermal decomposition, as shown in the TGA curve. Ala–Ag nanoparticles show four significant weight losses at different temperature intervals as 0.81% (198 °C), 1.32% (217 °C), 1.87% (355 °C), and 2.5% (805 °C). Around 2.5% of weight loss from the original weight takes place between 40 and 805 °C due to the decomposition and elimination of organic groups present in the sample, which were employed in the synthesis procedure. The obtained TGA curve of Ala–Ag reveals weight loss in the temperature interval of 50–217 °C, which is attributed to the desorption of moisture. The minor weight loss occurs between 217 and 805 °C, which is due to the removal and decomposition of l-alanine molecules present in the catalyst after the reduction and passivation of silver atoms. Although, the weight/weight ratio of Ag/alanine precursor during the synthesis was almost equal to 2:1. However, the as-prepared sample was washed several times with water and ethanol, and during the washing process, which may lead to the removal of most of the organic moieties. Moreover, the drying temperature was 80 °C. Hence, low wt % weight loss was observed, which is attributed to loss of organic moieties like alanine.

2.7. Brunauer–Emmett–Teller (BET) Analysis. The impact of high surface area on the properties of nanostructured materials is an area of increasing significance for understanding, creating, and improving materials to have diverse applications. The key goal of catalytic reactions is to promote the rate of reaction with high yield and selectivity of the desired product. It is anticipated that this goal will be more closely approached through tailoring a catalyst, which offers higher surface area. The activity of synthesized nanoparticles in catalysis improved due to the high surface area because it offers more active sites on its surface, which leads to an increase in adsorption and reaction sites for the catalytic process. Therefore, surface area studies become the most imperative parameter before determining various applications. Surface area and pore size of synthesized nanoparticles were studied by N₂ adsorption–desorption measurements using the multipoint BET method. Figure 6a shows a mixed H2- and H3-type hysteresis loop for Ala–Ag nanoparticles followed by a type III BET isotherm. This indicates unrestricted multilayer formation as the lateral interaction between absorbed molecules shows stronger interaction compared to adsorbate and adsorbent surface. The porous nature of the material is confirmed through the wide and broad hysteresis loop with a delay in the process of condensation–evaporation. In this case, the pores are of a narrow bottleneck type along with platelike lamellar aggregates forming slit-shaped porous nanomaterials. The specific surface area of Ala–Ag nanospheres was found to be 57 m²/g. The Dubinin–Astakhov (DA) plot is displayed in
Figure 6b, which determines their pore radius, and it was found to be 15.2 Å. Figure 6c represents the plot of Barrett–Joyner–Halenda (BJH), which demonstrates the average pore size distribution calculated from adsorption points of nanoparticles. Based on the BJH model, the pore volume and average pore diameter were found to be 0.042 cc/g and 21.26 Å, respectively.

2.8. Catalytic Organic Transformation of 4-Nitrophenol (NP) to 4-Aminophenol (AP) over Ala–Ag Nanocatalyst. In different organic transformations, catalytic conversion of 4-NP to 4-AP with sodium borohydride is considered as a model reaction to investigate the proficiency of the as-synthesized Ala–Ag nanoparticles as a hydrogenation catalyst. After adsorption equilibrium, the reaction was observed by recording UV–visible absorption spectra over
different time variations in the concentration of 4-NP. Figure 7a shows the adsorption peak of 4-NP at 317 nm and near wavelength 400 nm in aqueous medium, and a red shift was observed on the consecutive addition of a fresh aqueous NaBH₄ solution. The yellow-colored solution changed to deep yellow immediately. This red shift is due to the formation of 4-nitrophenolate ion due to the alkaline condition instigated by adding NaBH₄. In the absence of catalyst, the peak owing to the 4-nitrophenolate ion does not undergo any change. However, on addition of catalyst, the adsorption peak at 400 nm is gradually reduced in intensity with time and a typical adsorption peak appeared at 300 nm for 4-AP as the reaction for catalytic reduction progressed. As a result, the deep yellow solution starts fading to colorless. The addition of catalyst did not affect the UV–visible absorption spectra of 4-NP because a very less amount of catalyst was used. Figure 7b depicts the absorption plot for the catalytic hydrogenation of 4-NP to 4-AP at various time intervals in the presence of Ala−Ag nanocatalyst. Figure 7c shows that in the absence of Ala−Ag nanocatalyst, the 4-nitrophenolate ion does not undergo transformation and the peak at 400 nm remains unaltered even after a couple of days. The hydrogenation process of 4-NP was carried out for 8 min and about 95.9% was get reduced to 4-AP, as revealed in Figure 7d. The relative change in the concentration (C/C₀) of 4-NP vs time during the conversion reaction of 4-NP in the presence of catalyst is represented in Figure 8a. The rate of hydrogenation of 4-NP is independent of the NaBH₄ concentration, as its initial concentration surpasses 4-NP concentration. Hence, the reaction rate can be assumed to be independent of NaBH₄ concentration and catalytic hydrogenation process can be elucidated with respect to 4-NP concentration according to pseudo-first-order kinetics.

\[-\ln \frac{C}{C₀} = kt\]  

(3)

where C and C₀ are the 4-NP concentrations at time t and initial concentration, respectively. The slope of the line signifies the rate constant \(k\) for the hydrogenation of 4-NP. Figure 8b reveals that the reaction followed kinetics of pseudo-first order by a linear relationship between ln(C/C₀) and time, and the rate constant \(k\) was calculated to be 0.076/min with the \(R²\) value found to be 0.97. To evaluate the stability and reusability of the as-prepared catalysts, multiple cycles of hydrogenation reaction of 4-NP were carried out. The catalyst was recovered from the reaction mixture by centrifugation and was washed and dried for further use. The results depicted in Figure 8c shows that the catalyst can be easily recycled by a simple centrifugation method, enabling the recovery and reuse of catalyst, and the activity of catalytic hydrogenation reaction of 4-NP is maintained over 94.2% even after three consecutive cycles, which exhibits the higher activity and better stability of the catalyst.

### 2.9. Mechanism of Catalytic Hydrogenation of 4-NP over Ala−Ag Nanocatalyst to 4-AP

The plausible mechanism of catalytic hydrogenation of 4-NP was proposed on the basis of the above observations, as shown in Figure 9. When the as-synthesized Ala−Ag nanoparticles were dispersed in the 4-NP aqueous solution in the presence of NaBH₄, a large amount of hydrogen dispersed on the surface of Ala−Ag nanoparticles due to the decomposition of NaBH₄. Seemingly, the decomposition reaction is accelerated by AgNPs. It is examined that NaBH₄ can not convert the nitro groups into amino groups, and the rate of NaBH₄ decomposition is an important step in nitroaromatic reduction. Hence, during hydrogenation of nitroaromatics, the subsequent hydrogen plays a key role rather than the direct reaction between NaBH₄ and nitroaromatics. The as-synthesized Ala−Ag NPs adsorbed the 4-NP molecules and [BH₄⁻] ions on their surface and initiated the electron transfer reaction, yielding H₂ and sodium metaborate (NaBO₂) as byproducts. This caused the cleavage of the H−H bond in H₂ due to the presence of AgNPs, and each hydrogen got attached to the Ala−Ag nanosphere surface, forming a metal−hydrogen bond. In this metal hydrogen structure, the negatively charged hydrogen can easily attack positively charged nitrogen in the nitro group of 4-NP, resulting in the reduction of nitro groups into nitroso groups. Further, reductive addition of two hydrogen atoms takes place to form hydroxylamine. Finally, this can be further hydrogenated to aniline derivatives.

### 2.10. Photocatalytic Eradication of Methylene Blue and Rhodamine B Dyes over Ala−Ag Nanocatalyst

The photocatalytic activity of the as-synthesized Ala−Ag nanoparticles was examined by degrading organic dyes, viz., methylene blue (MB) and rhodamine B (RB), under solar light irradiation. To perform the actual experiment, different control tests were done to corroborate the photocatalytic capability of the as-synthesized Ala−Ag nanospheres. The extent of degradation of dyes using Ala−Ag nanospheres as photocatalyst was monitored by the UV–visible spectroscopic technique. Figure 10 shows that in the absence of sunlight, dye solutions displayed minor degradation on the surface of catalyst. Likewise, when the degradation process was analyzed without any catalyst in the presence of sunlight, no degradation, i.e., no photochemical reaction, was noted. The eradication of dyes in the presence of sunlight irradiation was initially monitored by decoloration of dyes to colorless, after 60 min for MB and 35 min for RB. Figure 11a displays the UV–visible absorption spectra that indicate the decrease in peak intensity of MB and RB dyes at set intervals of time. It was observed that the optical absorption bands corresponding to MB and RB at 664 and 540 nm exhibited rapid degradation. It is shown in Figure 11b that under solar radiation using as-synthesized Ala−Ag NPs, the degradation rates were 94.5 and 96.3% of MB and RB, respectively, within 60 and 35 min. The percentage of photocatalytic degradation was calculated using the above-mentioned equation.

![Figure 9. Plausible mechanism of 4-NP hydrogenation to 4-AP by Ala−Ag nanocatalyst.](https://dx.doi.org/10.1021/acsomega.0c03584)
The kinetics of the dye degradation process was modeled by applying the Langmuir–Hinshelwood mechanism as mentioned above, which also covers the adsorption properties of the photocatalyst. Figure 12a shows the relative change in dye concentration ($C_t/C_0$) in the presence of catalyst with time. Figure 12b indicates that the degradation of the dye follows the pseudo-first-order kinetics. The value of rate constant ($k$) was found to be 0.036 and 0.091 min$^{-1}$ for MB and RB dyes, respectively. The reusability and durability of the as-prepared Ala–AgNPs photocatalyst was examined by performing a recycling study under identical conditions with the stock solution of MB, as shown in Figure 13. The stability of the Ala–AgNPs was tested for three successive recycling runs, which show the reusability and excellent cycle stability of the Ala–AgNPs.

2.11. Mechanism for Photocatalytic Activity of Ala–Ag Nanospheres. Generally, the mechanism followed by photocatalytic reactions over the catalyst surface involves light...
absorption, charge carrier generation, electron–hole pair (e\(^{-}\)/h\(^{+}\)) transportation, and surface oxidation–reduction reactions.\(^{55–57}\) Under sunlight irradiation, the as-prepared Ala–Ag NPs are photoexcited by absorbing the photons with \(h\nu\) energy, and because of the high SPR effect, they undergo plasmonic decay and later generate electron–hole pairs (e\(^{-}\)/h\(^{+}\)). Further, the oxidation–reduction reaction occurs on the Ala–Ag NPs surface and promotes the accumulation of dye molecules. By absorbing sunlight, the adsorbed dye molecules get excited and give its photogenerated e\(^{-}\)s to the conduction band of Ala–Ag NPs. These photogenerated e\(^{-}\)s further reduced the adsorbed O\(_{2}\) on the surface of the Ala–Ag photocatalyst to superoxide (O\(_{2}^{-}\)) radical anions and hydrogen peroxide (‘OOH) radicals. The photogenerated holes reacted with adsorbed molecules of water or hydroxyl (OH\(^{-}\)) ions to generate hydroxyl radicals (HO\(^{\bullet}\)) and oxidize adsorbed dye molecules. Finally, the generation of active species (radicals) supports the photodegradation, which further induces mineralization of dyes. The scavenger quenching experiments were performed to confirm the presence and role of active species in the mechanism during the photodegradation process of these dyes. Benzoquinone (BQ), isopropanol (IP), silver nitrate (AgNO\(_{3}\)), and ammonium oxalate (AO) are the various scavengers used in this study for O\(_{2}^{-}\), OH\(^{-}\), e\(^{-}\), and h\(^{+}\) respectively. As shown in Figure 14, by adding AO, a minimal inhibitory effect was observed, whereas BQ, IP, and AgNO\(_{3}\) reduce the photocatalytic activity of the catalyst to some extent. This suggests that the photogenerated electrons along with superoxide radicals (O\(_{2}^{-}\)) and then hydroxyl radicals (HO\(^{\bullet}\)) play a main role and act as the main reactive species in the photocatalytic dye degradation.

The catalytic hydrogenation conversion and photocatalytic degradation studies of the present work have been compared to the previously reported literature and are shown in Table 2. The elucidated mechanism of photodegradation of dyes over Ala–Ag NPs as photocatalyst is shown schematically in Figure 15, and equations are represented as

\[
\text{Ala–AgNPs} + h\nu \rightarrow \text{Ala–AgNPs}(e^{-} + h^{+})
\]  
\[
dye + h\nu \rightarrow \text{dye}^{\bullet}
\]  
\[
dye^{\bullet} + \text{Ala–AgNPs} \rightarrow \text{dye}^{\bullet\bullet} + \text{AgNPs}(e^{-})
\]  
\[
O_{2} + \text{Ala–AgNPs}(e^{-}) \rightarrow \text{Ala–AgNPs} + (O_{2}^{\bullet\bullet})
\]
2.12. Antibacterial Efficacy of the As-Synthesized Ala–Ag Nanoparticles. The antibacterial activity of the as-synthesized Ala–Ag nanospheres was examined to evaluate their ability to inhibit the growth of multidrug-resistant bacteria. The agar diffusion method was used to attain the antibacterial activity of Ala–Ag nanospheres by varying concentration. The lowest concentration of an antimicrobial drug that will constrain the growth of microorganisms after overnight incubation is biologically termed as the minimum inhibitory concentration (MIC). The MIC values of Escherichia coli (Gram-negative) and Staphylococcus aureus (Gram-positive) were found to be 80 and 100 μg/mL, respectively, which might be associated with the larger size of Ala–Ag NPs. Further, disk diffusion assay was performed to monitor the antibacterial efficacy by checking the bacterial growth inhibition on solid media. After incubation, the zone of inhibition of each Ala–Ag NP concentration was measured in millimeters, which indicates that Ala–Ag NPs have potent antibacterial properties since these are effective against both Gram-negative and Gram-positive bacteria. On increasing the concentration of Ala–AgNPs, the zone of inhibition increases, as depicted in Table 3. The inhibition zone of Ala–AgNPs was 14 mm in both E. coli and S. aureus with the same concentration. The images of disks are shown in Figure 16, which demonstrates the antibacterial behavior of Ala–Ag nanospheres against tested bacterial strains.

3. CONCLUSIONS

We have successfully synthesized silver nanospheres using a simple, environmentally benign, and cost-effective chemical reduction method. l-Alanine amino acid was utilized for the

Table 2. Comparison of Catalytic Hydrogenation and Photocatalytic Degradation

| catalyst          | amount | hydrogenation/photocatalysis | reaction rate/degradation (%) | references |
|-------------------|--------|-------------------------------|-------------------------------|------------|
| His-AgNPs        | 25 mg  | photocatalytic                 | 59                            | 47         |
| F-AgNPs          | 20 mg  | photocatalytic                 | 58                            | 58         |
| AgNPs (CN)       | 10 g   | photocatalytic                 | 75                            | 59         |
| Ala–Ag nanospheres | 1.5 mg | photocatalytic                 | 94.5                          | this work |
| Ala–Ag nanospheres | 1.5 mg | photocatalytic                 | 96.3                          | this work |
| Ultrathin silver film |       | hydrogenation                  | 80                            | 60         |
| AgNPs(1)/ZHL     | 10 mg  | hydrogenation                  | 80                            | 61         |
| Ala–Ag nanospheres | 0.001 mg | hydrogenation               | 95.9                          | this work |

Table 3. Zone of Inhibition (mm) on Different Concentrations (μg/mL) of Ala–Ag Nanospheres

| s. no. | concentration (μg/mL) | zone of inhibition (mm) |
|--------|-----------------------|-------------------------|
|        |                       | E. coli | S. aureus |
| 1      | 25                    | 10      | 9         |
| 2      | 50                    | 12      | 12        |
| 3      | 100                   | 14      | 14        |
| 4      | 150                   | 22      | 20        |
| 5      | gentamicin (5 μg/mL)  | 22      | 20        |

Figure 14. Scavenging effect on the photodegradation of MB and RB dyes over Ala–Ag NPs photocatalyst.

Figure 15. Schematic mechanistic representation of the photodegradation of MB and RB dyes using Ala–Ag photocatalyst nanospheres.

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preparation of silver nanospheres, which plays an important role as a stabilizing and capping agent, due to the structural potential of amino acids to interact with silver, which provides good colloidal stability to the silver nanoparticles, impelling their use in photocatalytic and catalytic reductions. The structural evaluation of the as-synthesized nanospheres was characterized using XRD, FESEM, TEM/HRTEM, UV-DRS, FTIR, TGA, and BET surface area analyses. The efficacy of the as-obtained Ala−Ag nanospheres toward catalysis, photocatalysis, and disinfection was explored to offer a simple solution for water remediation. The as-synthesized Ala−Ag nanospheres show an admirable catalytic efficiency of about 95.6% as a hydrogenation catalyst toward hydrogenation of 4-nitrophenol. Moreover, the excellent photocatalytic efficiency of Ala−Ag nanospheres for the degradation of organic dyes, methylene blue, and rhodamine B was revealed with 94.5 and 96.3% removals in only 60 and 35 min, respectively. Also, the as-prepared nanospheres displayed bactericidal effectiveness against both Gram-negative and Gram-positive bacteria. The development of alanine-assisted Ag nanoparticles offers an environmentally friendly and low-cost approach for wastewater treatments like catalytic transformation, photocatalytic degradation, and bacterial disinfection.

4. EXPERIMENTAL SECTION

4.1. Materials and Chemicals. Silver nitrate (Merck), L-ascorbic acid (Merck), L-alanine (Hi-Media), sodium borohydride (Thomas Baker), rhodamine B (Thomas Baker), 4-nitrophenol (SRL), benzoxquinone (Merck), ammonium oxalate (Merck), isopropanol (Merck), gentamycin (Sigma-Aldrich), Luria broth (Hi-Media), and Luria agar (Hi-Media). The bacterial strains of E. coli (MTCC 405) and S. aureus (MTCC 3160) were procured from the Microbial Type Culture Collection (MTCC), Institute of Microbial Technology (Chandigarh, India). Analytical grade chemicals were obtained and used without further purification. Washing and cleaning of glassware were done carefully with nitric acid followed by distilled water before use. Deionized water was utilized throughout the experiments.

4.2. Synthesis of Ala−Ag Nanospheres. In this synthesis method, aqueous solutions of silver nitrate (0.1 M) and L-alanine (0.1 M) were added in a beaker containing 10 mL of deionized water and kept stirring in an ice−water bath. In the next step, 0.1 M aqueous solution of ascorbic acid was injected into the mixture after 10 min with vigorous stirring, which played the role of a reducing agent. The obtained reaction mixture turns gray, and the reaction was terminated after 15 min. The as-acquired gray solution was centrifuged at 8000 rpm and washed several times. The collected precipitate was dried in a preheated oven at 80 °C. The dried sample was ground to collect the gray-colored silver nanoparticles. The schematic scheme of the synthesis steps is shown in Figure 17.

Figure 16. Disk diffusion assay of (A) E. coli and (B) S. aureus showing zone of inhibition in the presence of Ala−Ag NPs at concentrations of (b) 50 μg/mL, (c) 100 μg/mL, and (d) 150 μg/mL. The controls represent (G) gentamycin and (a) silver nitrate substrates.

4.3. Characterization Techniques. The as-synthesized material was initially analyzed by the powder X-ray diffraction (XRD) technique to determine its crystalline structure on a Rigaku Ultima IV X-ray diffractometer equipped with a Ni filter (for Cu Kα, λ = 1.5416 Å). The accurate lattice constants were attained by eliminating Kα2 reflections with a normal stripping procedure. Normal scans were recorded with a step size of 0.05° and a step time of 1 s in the 2θ range of 20−80°. A Leo Supra 50 VP energy-dispersive X-ray (EDAX) system (Carl Zeiss, Germany) was utilized for field emission scanning electron microscopy (FE-SEM) to analyze the morphology, chemical composition, and elemental distribution. To estimate the size and shape of the as-prepared nanoparticles, transmission electron microscopic (TEM) measurements were performed. For TEM/HRTEM imaging, nanoparticles were dispersed in water followed by ultrasonication for 20 min, after which the dispersed sample was drop-cast on commercially available carbon-coated copper grids. An FEI Tecnai G2 20 instrument was employed at the accelerating voltage of 200 kV. A PerkinElmer 365 double-beam UV−visible spectrophotometer was used for diffuse reflectance spectroscopy to record the absorbance spectra for photocatalytic activity and to estimate the optical properties of the as-synthesized nanoparticles. Before carrying out the UV−visible DRS measurements, the baseline and background corrections were carried out using BaSO₄ as a standard sample.

The infrared spectra of Ala−Ag nanoparticles were recorded on a PerkinElmer FT-IR spectrophotometer model IR affinity-1 on the sample powders diluted in KBr pellets. The thermal stability of the nanocatalyst was inspected by a PerkinElmer
STA 6000 thermal analyzer. A Brunauer–Emmett–Teller (BET) surface area analyzer (Nova 2000 e, Quantachrome Instruments Limited) was used to investigate the surface area and pore size of the as-synthesized Ala–Ag nanoparticles at liquid nitrogen temperature (77 K). Vacuum degassing was carried out to remove the surface contaminants and moisture by placing approximately 0.06 g of the sample in a sample cell at 120 °C for 3 h. The multipoint BET equation was applied to estimate the specific surface area. The pore size and pore volume distributions were also determined by Dubinin–Astakhov (DA) and Barrett–Joyner–Halenda (BJH) methods from the N2 desorption isotherms.

### 4.4. Catalytic Evaluations

The efficiency of Ala–Ag nanospheres in catalysis was monitored by performing catalytic hydrogenation of 4-NP to 4-AP. This catalytic conversion was carried out with 3 mL of 4-NP (1 × 10^{-4} M), and 20 μL of NaBH4 (0.1 M) was mixed in a quartz cell. Thereafter, 20 μL of a homogeneous dispersion (3 mg/mL) of nanocatalyst was added to the mixture of 4-NP and NaBH4. Further, the reaction mixture was analyzed by a UV–visible spectrophotometer to monitor the changes in solution with time, and the activation parameters were calculated for each reduction spectrum. The conversion was observed by a significant decrease in adsorption peak intensity at ≈400 nm, and the conversion percentage of the catalytic reduction was calculated using the following equation

\[
D(\%) = \left( \frac{C_0 - C_t}{C_0} \right) \times 100
\]  
(15)

The recycling experiment was also done by collecting the catalyst after centrifugation of the reaction mixture, followed by washing with deionized water and then reusing it up to three cycles.

### 4.5. Photocatalytic Evaluations

The photocatalytic properties of Ala–Ag nanospheres were studied by performing photodegradation of methylene blue and rhodamine B dyes as perishable water contaminants. Herein, 5 mL of 0.3 mg/mL homogeneous aqueous dispersion of the as-synthesized Ala–Ag nanoparticles was added distinctly in 50 mL (1 × 10^{-5} M) of two dye solutions. These aqueous dye solutions were kept in the dark for 1 h to obtain adsorption–desorption equilibrium of the dyes on the catalyst surface. Afterward, on a bright sunny day (New Delhi, 28.6139°N, 77.2090°E) between 10 a.m. and 3 p.m. (atmospheric temperature 32−36 °C), the suspended solutions were exposed to sunlight at an average intensity of ca. 40−50 mW/cm². About 4 mL of aliquots was drawn out at set intervals of time and centrifuged at once to collect the catalyst for performing recycling experiments. The reaction progress was observed at regular durations by employing UV–visible spectroscopy. The percentage of photocatalytic degradation was calculated using eq 15 as above. The protocols of degradation studies have been adopted as reported elsewhere.

### 4.6. Antibacterial Evaluations

#### 4.6.1. Minimum Inhibitory Concentration (MIC)

The MIC was carried out by the standard protocol of NCCLS document M7-A3 by the 96-well plate microdilution method (Jorgensen 1993). The MIC₀ was done in triplicate by broth dilution method, and the average value was considered. The result was compared by taking OD at 595 nm using a Multiskan GO Thermo Fisher Scientific spectrophotometer.

#### 4.6.2. Disk Diffusion Assay

The method of agar diffusion was performed to analyze the bactericidal effect of the as-synthesized Ala–Ag nanospheres against Gram-negative E. coli (MTCC-405) and Gram-positive S. aureus (MTCC-3160) bacteria. Disks with a diameter of 6 mm were kept on agar plates, and various concentrations of the as-synthesized Ala–Ag NPs (5 mg/mL aqueous suspension) were pipetted onto filter disks. Gentamycin (5 μg) dissolved in distilled water as a positive control and silver nitrate (50 μg) as a negative control were applied on the disk. At 37 °C, the Petri plates were incubated for 12 h for bacterial growth. The protocols of disk diffusion assay and minimum inhibitory concentration documented elsewhere were used to study the antibacterial properties of the as-synthesized Ala–Ag NPs.7,43

#### 4.6.3. Role of -Alanine

Amino acids are the building blocks of protein that easily get oxidized and consist of functional groups, namely, (−NH₂) amino and (−COOH) carboxyl with a side chain of (−R group). Mainly, amino and carboxyl groups undergo chemical transformations, while the −R group remains intact. Among the advanced biological approaches, the synthesis of nanocrystalline silver by assisting amino acids has been tested efficaciously. In fact, biomolecules can also act as a ligand and associates along the precursor metal-ion-forming complex. The molecules of amino acids when acting on behalf of capping agents can suppress the growth of nucleated particles and led to the formation of nanoparticles.46 The zwitterionic nature and pH-based charge reversibility allow their use as reducing and capping agents. Amino acids assist the production of AgNPs with varied sizes and shapes by playing the role of both reducing and capping agents. Amino acids such as alanine, histidine, tryptophan, methionine, asparagine, and glutamic acid have a strong affinity for Ag⁺ ions. Therefore, controlled nucleation of metal nanoparticles with defined shape and improved stability in several aqueous environments is successfully achieved using amino-acid-functionalized metal nanoparticles.47,48,64,65 The catalytic efficiency of the AgNPs for the reduction of methylene blue, congo red, and 4-nitrophenol by amino-acid-biosynthesized silver nanoparticles in aqueous media is also reported. The amino-acid-functionalized Ag NPs displayed good colloidal stability against dye solutions, which improve the catalytic efficiency of the AgNPs.46,48 Hence, these amino acids stabilize the as-synthesized nanoparticles as well as inhibit their agglomeration. Therefore, amino acids like alanine played the role of capping, reducing, and stabilizing agents during the synthesis of silver nanoparticles, which provide good colloidal stability to silver nanoparticles, which encouraged researchers to use them in catalytic and photocatalytic applications.

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REFERENCES

(1) Wang, Q.; Yang, Z. Industrial water pollution, water environment treatment, and health risks in China. Environ. Pollut. 2016, 218, 358–365.

(2) Sinha, T.; Ahmaruzzaman, M.; Adhikari, P. P.; Bora, R. Green and environmentally sustainable fabrication of Ag-SnO2 nanocomposite and its multifunctional efficacy as photocatalyst and antibacterial and antioxidant agent. ACS Sustainable Chem. Eng. 2017, 5, 4645–4651.

(3) Gupta, V. K.; Suhas. Application of low-cost adsorbents for dye removal—a review. J. Environ. Manage. 2009, 90, 2313–2342.

(4) Ahmad, T.; Farooq, U.; Phil, R. Fabrication and photocatalytic applications of perovskite materials with special emphasis on alkali-metal-based niobates and tantalates. Ind. Eng. Chem. Res. 2018, 57, 11–41.

(5) Hu, B.; Wang, S. B.; Wang, K.; Zhang, M.; Yu, S. H. Microwave-assisted rapid facile “green” synthesis of uniform silver nanoparticles: self-assembly into multilayered films and their optical properties. J. Phys. Chem. C 2008, 112, 11169–11174.

(6) Gilbertson, L. M.; Zimmerman, J. B.; Plata, D. L.; Hutchison, J. E.; Anastas, P. T. Designing nanomaterials to maximize performance and minimize undesirable implications guided by the principles of green chemistry. Chem. Soc. Rev. 2015, 44, 5758–5777.

(7) Ahmad, T.; Wani, I. A.; Manzoor, N.; Ahmed, J.; Asiri, A. M. Biosynthesis, structural characterization and antimicrobial activity of gold and silver nanoparticles. Colloids Surf., B 2013, 107, 227–234.

(8) Raveendran, P.; Barka, N.; Tamimi, M.; Assabbane, A.; Ait-Ichou, Y. Photodegradation of 2-naphthol in water by artificial light illumination using TiO2 photocatalyst: Identification of intermediates and the reaction pathway. Appl. Catal., A 2008, 334, 386–393.

(9) Hu, Y.; Yuan, C. Low-temperature preparation of photocatalytic TiO2 thin films from anatase sols. J. Cryst. Growth 2005, 274, 563–568.

(10) Bagheri, S.; Termeh Yousefi, A.; Do, T. O. Photocatalytic pathway toward degradation of environmental pollutants: structure, kinetics and mechanism approach. Catal. Sci. Technol. 2017, 7, 4548–4569.

(11) Sarina, S.; Waclawik, E. R.; Zhu, H. Photocatalysis on supported gold and silver nanoparticles under ultraviolet and visible light irradiation. Green Chem. 2013, 15, 1814–1833.

(12) Jiao, J.; Wan, J.; Ma, Y.; Wang, Y. Facile formation of silver nanoparticles as plasmonic photocatalysts for hydrogen production. RSC Adv. 2016, 6, 106031–106034.

(13) Flores-Lopez, L. Z.; Espinoza-Gómez, H.; Somoranthan, R. Silver nanoparticles: Electron transfer, reactive oxygen species, oxidative stress, beneficial and toxicological effects. Mini review. J. Appl. Toxicol. 2019, 39, 16–26.

(14) Naaz, F.; Farooq, U.; Ahmad, T. Ceria as an Efficient Nanocatalyst for Organic Transformations, Nanocatalysts; 1st ed.; Sinha, I., Ed.; Intech Open: London, U.K., 2019; pp 1–31.

(15) Iravani, S.; Korbekandi, H.; Mirmohammadi, S. V.; Zolfaghari, B. Synthesis of silver nanoparticles: chemical, physical and biological methods. Res. Pharm. Sci. 2014, 9, 385–406.
(36) Teixeira, L. D.; Silva, O. N.; Migliolo, L.; Fensterseifer, I. C.; Franco, O. L. In vivo antimicrobial evaluation of an alanine-rich peptide derived from Pleuronectes americanus. Peptides 2013, 42, 144–148.

(37) Ahmad, T.; Lone, I. H. Citrate precursor synthesis and multifunctional properties of YCrO₃ nanoparticles. New J. Chem. 2016, 40, 3216–3224.

(38) Khatoon, S.; Ahmad, T. Synthesis, optical and magnetic properties of Ni-doped ZnO nanoparticles. J. Mater. Sci. Eng. B 2012, 2, 325–333.

(39) Ahmad, T.; Phul, R. Magnetic iron oxide nanoparticles as contrast agents: hydrothermal synthesis, characterization and properties. Solid State Phenom. 2015, 232, 111–145.

(40) Ahmad, T.; Ganguli, A. K. Structural and dielectric characterization of nanocrystalline (Ba,Pb)ZrO₃ developed by reverse micellar synthesis. J. Am. Ceram. Soc. 2006, 89, 3140–3146.

(41) Wani, I. A.; Ganguly, A.; Ahmad, J.; Ahmad, T. Silver nanoparticles: ultrasonic wave assisted synthesis, optical characterization and surface area studies. Mater. Lett. 2011, 65, S20–S22.

(42) Wani, I. A.; Khatoon, S.; Ganguly, A.; Ahmad, J.; Ganguli, A. K.; Ahmad, T. Silver nanoparticles: Large scale solvothermal synthesis and optical properties. Mater. Res. Bull. 2010, 45, 1033–1038.

(43) Wani, I. A.; Khatoon, S.; Ganguly, A.; Ahmad, J.; Ahmad, T. Structural characterization and antimicrobial properties of silver nanoparticles prepared by inverse microemulsion method. Colloid Surf., B 2013, 101, 243–250.

(44) Badi’ah, H. I.; Seedeh, F.; Supriyanto, G.; Zaidan, A. H. Synthesis of silver nanoparticles and the development in analysis method. IOP Conf. Ser.: Earth Environ. Sci. 2019, 217, No. 012005.

(45) Kaviya, S.; Santhanakalashmi, J.; Viswanathan, B.; Muthumary, J.; Srinivasan, K. Biosynthesis of silver nanoparticles using Citrus sinensis peel extract and its antibacterial activity. Spectrochim. Acta, Part A 2011, 79, 594–598.

(46) Jyoti, K.; Baunthiyal, M.; Singh, A. Characterization of silver nanoparticles synthesized using Urticodiaca Linn. leaves and their synergistic effects with antibiotics. J. Radiat. Res. Appl. Sci. 2016, 9, 217–227.

(47) Suganthi, S.; Vignesh, S.; Mohanapriya, S.; Sundar, J. K.; Raj, V. Microwave-assisted synthesis of L-histidine capped silver nanoparticles for enhanced photocatalytic activity under visible light and effective antibacterial performance. J. Mater. Sci.: Mater. Electron. 2019, 30, 15168–15183.

(48) Chandra, A.; Singh, M. Biosynthesis of amino acid functionalized silver nanoparticles for potential catalytic and oxygen sensing applications. Inorg. Chem. Front. 2018, 5, 233–257.

(49) Shen, X. S.; Wang, G. Z.; Hong, X.; Zhu, W. Nanospheres of silver nanoparticles: agglomeration, surface morphology control and application as SERS substrates. Phys. Chem. Chem. Phys. 2009, 11, 7450–7454.

(50) Shoieb, T.; Siu, K. W. M.; Hopkinson, A. C. Silver ion binding energies of amino acids: use of theory to assess the validity of experimental silver ion basicties obtained from the kinetic method. J. Phys. Chem. A 2002, 106, 6121–6128.

(51) Bhu, D. K.; Misra, A. Synthesis of worm like silver nanoparticles in methyl cellulose polymeric matrix and its catalytic activity. Carbohydr. Polym. 2012, 89, 830–835.

(52) Veerakumar, P.; Velayudham, M.; Lu, K.; Rajagopal, S. Polyelectrolyte encapsulated gold nanoparticles as efficient active catalyst for reduction of nitro compounds by kinetic method. Appl. Catal., A 2012, 439–440, 197–205.

(53) Sun, J.; Fu, Y.; He, G.; Sun, X.; Wang, X. Catalytic hydrogenation of nitrophenols and nitrotoluenes over a palladium/graphene nanocomposite. Catal. Sci. Technol. 2014, 4, 1742–1748.

(54) Jishma, P.; Roshmi, T.; Snigdha, S.; Radhakrishnan, E. K. Kinetic study of gold nanoparticle mediated photocatalytic degradation of Victoria blue. 3 Biotech 2018, 8, No. 97.

(55) Farooq, U.; Ahmad, J.; Alshehri, S. M.; Ahmad, T. High surface area sodium tantalate nanoparticles with enhanced photocatalytic and electrical properties prepared through polymeric citrate precursor route. ACS Omega 2019, 4, 19408–19419.

(56) Ahmad, T.; Phul, R.; Alam, P.; Lone, I. H.; Shahazad, M.; Ahmed, J.; Ahamed, T.; Alshehri, S. M. Dielectric, optical and enhanced photocatalytic properties of CuCrO₂ nanoparticles. RSC Adv. 2017, 7, 27549–27557.

(57) Mavaei, M.; Chahardoli, A.; Shokooshina, Y.; Khoshroo, A.; Fattahi, A. One-step synthesized silver nanoparticles using isonitrile: evaluation of photocatalytic, and electrochemical Activities. Sci. Rep. 2020, 10, No. 1762.

(58) Wang, L.; Lu, F.; Liu, Y.; Wu, Y.; Wu, Z. Photocatalytic degradation of organic dyes and antimicrobial activity of silver nanoparticles fast synthesized by flavonoids fraction of Psidium guajava L. leaves. J. Mol. Liq. 2018, 263, 187–192.

(59) Sumi, M. B.; Devadiga, A.; Vidy Shetty, K.; Saidutta, M. B. Solar photocatalytically active, engineered silver nanoparticle synthesis using aqueous extract of mesocarp of Cocos nucifera (Red Spicata Dwarf), J. Exp. Nanosci. 2017, 12, 14–32.

(60) Zakaria, M. A.; Menazea, A. A.; Mostafa, A. M.; Al-Askar, E. A. Ultra-thin silver nanoparticles film prepared via pulsed laser deposition: synthesis, characterization, and its catalytic activity on reduction of 4-nitrophenol. Surf. Interfaces 2020, 19, 100438–100443.

(61) Quites, F. J.; Azvedo, C. K.; Alves, E. P.; Germino, J. C.; Vinhas, R. C.; Landers, R.; Terezo, A. J.; Atvars, T. D. Ag nanoparticles-based zinc hydroxide-layered hybrids as novel and efficient catalysts for reduction of 4-nitrophenol to 4-aminophenol. J. Braz. Chem. Soc. 2017, 28, 106–115.

(62) Ahmad, T.; Phul, R.; Khatoon, N.; Sardar, M. Antibacterial efficacy of Ocimum sanctum leaf extract-treated iron oxide nanoparticle. New J. Chem. 2017, 41, 2055–2061.

(63) Jaffat, H. S.; Alduajili, N. H.; Hassan, A. J. A. Antimicrobial activity of silver nano particles biosynthesized by lactobacillus mixtures. Res. J. Pharm., Biol. Chem. Sci. 2017, 8, 1911–1924.

(64) Phul, R.; Kaur, C.; Farooq, U.; Ahmad, T. Ascorbic acid assisted synthesis, characterization and catalytic application of copper nanoparticles. Mater. Sci. Eng. Int. J. 2018, 2, 90–94.

(65) Roy, M.; Mukherjee, P.; Mandal, B. P.; Sharma, R. K.; Tyagi, A. K.; Kale, S. P. Biomimetic synthesis of nanocrystalline silver sol using cysteine: stability aspects and antibacterial activities. RSC Adv. 2012, 2, 6496–6503.