ABSTRACT: In this work, a superabsorbent polymer, sodium polyacrylate, also known as water ball (WB), loaded with Ni, Cu, and Ag zero-valent metal nanoparticles (MNPs) was applied for environmental remediation. WBS loaded with Ni, Cu, and Ag NPs were evaluated for their catalytic performance against the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) and decolorization of methyl orange (MO), Congo red (CR), and methylene blue (MB) dyes. The apparent rate constants ($K_{app}$) for the reduction of 4-NP to 4-AP in the presence of Ni, Cu, and Ag NPs were $2.1 \times 10^{-1}$, $2.9 \times 10^{-1}$, and $4.6 \times 10^{-1}$ min$^{-1}$, respectively, indicating the strongest activity of WB loaded with Ag NPs as compared to the other two catalysts. Similarly, WB loaded with Ag NPs showed the highest $K_{app}$ values compared to the other two catalysts. Among all of the bacteria studied, except Providencia stuartii and Streptococcus mutans, the zone of inhibition of Ag was higher as compared to that of the Ni and Cu NPs, however, slightly low from that of the reference standard tetracycline TE30. Furthermore, the synthesized catalysts were extensively characterized through X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), field emission scanning electron microscopy (FESEM), and X-ray photoelectron spectroscopy (XPS) analyses.

1. INTRODUCTION

Various pollutants are responsible for the contamination of water, and the major contributors are the persistent organic pollutants due to their toxic and carcinogenic effects and are considered as the most noticeable pollutants, for instance, nitrophenols and dyes.$^{1-3}$ Nitrophenols and dyes are organic pollutants having deteriorating effect on human health and other living organisms. The U.S. Environmental Protection Agency (EPA) registered 4-NP, 2-nitrophenol, and 2,4-dinitrophenol as “Priority Pollutants” and made restrictions for controlling their concentrations in natural water to <10 ng/L (U.S. EPA, 1976).$^1$ The reason for the discharge of nitrophenols in the water resources is their extensive applications in industries. These organic pollutants have worst consequences on the kidney, liver, central nervous system, and blood. Therefore, their removal from the wastewater is of prime importance. Furthermore, it is well documented that approximately 10,000 dyes are commercially available, 70,000 tons of these is synthesized annually on an industrial level, and 10–15% of these dyes or their by-products are discharged into the water resources and are esthetically unfavorable.$^1-3$ Dyes make a foamy and brown layer on the surface of water, which further stops the diffusion of oxygen and air into the water, disturbing the life of aquatic flora and fauna.$^1$ Various procedures have been developed for the removal of dyes and detoxification of persistent organic pollutants, such as adsorption, filtration, membrane technology, advanced oxidation, photocatalysis, and recently the development of nanoscale materials.$^4-7$

Nanoscale materials offer significant environmental and technological breakthrough in the field of various scientific sectors such as medicine, drug delivery, sensing technology, water splitting, acceleration of chemical reactions, solar energy conversion, and environmental remediation.$^{1,8-14}$ Scientists are trying to design and discover cost-effective materials to reduce dreadful and hazardous waste materials.$^{15}$ In the resurgence of environmental remediation, there is always a need for cost-effective, nontoxic, economical, and productive materials. Metal nanoparticles (MNPs) are one of the most investigated and promising materials because of many characteristics, such as low cost, eco-friendly nature, and extraordinary catalytic potentials. Over the last few decades, synthesis of MNPs has been largely documented because of their unique electrical and optical properties as well as their small quantum size effect.$^{16,17}$ MNPs show high catalytic activity as compared to their bulk counterparts due to their small size quantum effect, although the bulk and nanoscale
materials are composed of the same constituents. Metal nanoparticles in the zero state are called zero-valent metal nanoparticles, which may be naked in the homogeneous state or supported on solid matrices like in heterogeneous catalysis. In supported zero-valent MNPs, metal ions are first adsorbed onto the supported materials such as TiO$_2$, MgO, ZnO, RhO$_2$, polymer, and polymer composites and then converted to their zero-valent state with a reducing agent. Many supported materials are documented in the literature to support MNPs; however, among them polymer and polymer-based composites are the most promising. Supported MNPs possibly affect the porosity of catalysts, redox potential, surface area, heterojunction, and facet selection, which probably modify the catalytic potential. The thermodynamic instability of MNPs is because of their high surface energy, high surface area, and active sites, therefore reducing the reactive and adsorption sites that further reduce the interfacial contact area of the NPs and the sample. Desigining and synthesis of materials with varied physiochemical features, required for various applications, have been carried out. Examples include fabrication of polymer materials and semiconductors to obtain high surface area; good conductivity; porous material; and enhanced physical, chemical, and biochemical characteristics.

Immobilization of NPs has been discussed in the literature on different supported materials. In the resurgence of the supported materials for cost-effective, economical, and non-toxic materials, superabsorbent polymers also known as water balls or water beads are one of the most effective materials for the stabilization of zero-valent MNPs. The chemical structure of the WB mainly includes sodium polyacrylate. The structure of acrylic acid, polyacrylic acid, and sodium polyacrylate are presented in Figure S1.

A superabsorbent polymer has the capability to absorb liquids more than its weight. Sodium polyacrylate is a type of cross-linked polymer composed of sodium atoms. Poly(acrylic acid) is the basic polymer composed of a carboxylic acid group on each repeating unit of the polymer chain; however, the sodium cation neutralizes the carboxylic acid groups on each repeating unit in the chain. The Na$^{+}$ exchanges between the polymer network and water, and hence, the sodium metal ion is replaced by the water molecule in the process of osmosis and thereby swells the polymer molecule in water. The cross-linkage of the chains prevents the molecule from being broken and dissolved in water. Sodium polyacrylate absorbs distilled water 700 times more than its weight; however, the water absorption capacity reduces to 300 times in tap water due to the presence of other metal ions. Various polymer composites with supported NPs
are reported in the literature for different applications.\textsuperscript{40-43} For instance, good antibacterial and mechanical properties of chitosan-ZnO NPs,\textsuperscript{44} high temperature tolerance of poly-(vinylidene fluoride)@SiO$_2$ NPs,\textsuperscript{45} and greater gas permeability of polysulfone/SiO$_2$ NPs.\textsuperscript{46} Similarly, lower flux and high porosity of polyethersulfone-aluminum oxide membranes showed higher porosity.\textsuperscript{47} Cellulose acetate-Fe$_3$O$_4$@Ag NPs and PES-cellulose acetate—carbon black-supported Cu NPs were successfully used for wastewater treatment.\textsuperscript{48} Superabsorbent polymers have vast application in additive manufacturing, water withholding and infiltration capability of a sandy soil, largely used in agriculture and horticulture sectors, used as bioadhesive in medical application.\textsuperscript{35,37,49,50}

Use of different solvents, complex methodology, and non-eco-friendly procedures makes other procedures invaluable. This method is superior as compared to other methods in the literature due to its simplicity and high catalytic potentials. Use of a superabsorbent polymer as a solid support for the stabilization of zero-valent metal nanoparticles will be useful in environmental remediation.

The purposes of this research are as follows:\textsuperscript{1} to explore the supporting and stabilization efficiency of WBs for MNPs,\textsuperscript{25} to explore the catalytic efficacy of the WB for the degradation of persistent organic pollutants,\textsuperscript{25} and to explore the antibacterial activity of the WB loaded with MNPs.

2. RESULTS AND DISCUSSION

2.1. X-ray Diffraction (XRD). The XRD patterns were investigated to determine the crystallinity of WB and the Ni, Cu, and Ag NPs loaded with it as mentioned in Figure 1a–d, respectively. The XRD patterns of the WB showing a broad hump at $2\theta = 22.8^\circ$ suggest the amorphous nature of the WB. The same amorphous nature was observed for Ni and Cu NPs.

Figure 2. XPS survey scan spectrum of WB and Ni, Cu, and Ag NPs loaded with it. The other spectrum corresponds to the expanded portion of Ni, Cu, and Ag NPs XPS spectra. The XPS spectrum was run from 0 to 1200 eV.
but the hump shifted a little bit from 2θ = 22.8° to 26.6°, showing the interaction of NPs with the WB. Besides, the amorphous phase, crystalline peaks were observed in Ni, Cu, and Ag NPs. In the XRD patterns of the WB loaded with Ni NPs, the crystalline peak appeared at 2θ = 43.5°, which corresponds to the (111) crystal plane (JCPDS card no. 04-0850) along with the amorphous phase of WB. Similarly, the crystalline nature of Cu NPs accompanied by the amorphous phase of WB appeared at 2θ = 43.5°, which corresponds to the face-centered-cubic (111) crystal plane (JCPDS card no. 04-0836). In the XRD spectrum of Ag NPs, several sharp crystalline peaks appeared. These peaks were centered at 2θ = 38.5°, 48.83°, 64.61°, and 77.75° corresponding to the (111), (200), (220), and (311) crystal planes (JCPDS card no. 04-0783). The data is in good agreement with the reported data in the literature. The amorphous phase of the WB did not appear in the Ag NP spectrum, and it might be due to the high intensity of the crystalline peaks, which suppressed the amorphous peak.

2.2. FTIR. Figure 1e−h displays the FTIR spectra of WB and of WB loaded with Ni, Cu, and Ag NPs, respectively. Various vibrational modes appeared in the FTIR spectrum of WB and its MNPs. For instance, the peak centered at 3300 cm⁻¹ defined the asymmetric stretching vibrations of the −OH group. The −OH asymmetric stretching vibration was observed in the range of 3000−3300 cm⁻¹ for the WB loaded with Ni, Cu, and Ag NPs as well as WB. The broadness of the peak suggests the H-binding in the catalyst. The WB indicated a peak at 1642 cm⁻¹, suggesting the presence of a carboxylate group, which also appeared in the FTIR spectra of all catalysts. The intensity decreased for the MNP-loaded WB spectra, which might be due to the interactions of NPs with the carboxylate group. Another peak at 647 cm⁻¹ appeared in the WB spectrum, indicating the bending vibration of the C–H group.

2.3. Thermal Stability. The thermal stability of the WB and the MNPs loaded with it was determined through TGA analysis. The effect of thermal stability on WB and the loaded MNPs was investigated under an inert atmosphere of nitrogen gas. A single-stage decomposition was observed in WB, where the onset of WB decomposition initiated at approximately 130 °C and terminated at 240 °C. A total of 66% weight loss was observed in WB, which might be due to the depolymerization and oxidation of the WB. After 240 °C, the WB showed a plateau region from 250 to 600 °C. The plateau region is characterized by no weight loss in the sample with an increase in temperature. On the other hand, the WB loaded with Ni, Cu, and Ag NPs showed a multistage decomposition process, which is usually observed because of the increment in the weight of the sample by the attachment of MNPs as well as the surface oxidation process with an increase in temperature. At a temperature around 50 °C, the loss in weight was 84.3% for Ni NPs, 79.3 for Cu NPs, and 61.8% for Ag NPs, as manifested in the inset of Figure 1i.

2.4. X-ray Photoelectron Spectroscopy (XPS). Figure 2 shows the XPS survey scan spectrum of WB and Ni, Cu, and Ag NPs loaded with it. The C 1s peak appeared for all of the catalysts at a binding energy of 284 eV, and the O 1s peak appeared at 531 eV. Similarly, Ni 2p and Ni 3s exhibited a small peak at 62 and 190 eV with the Auger line peak of Ni 2p at a binding energy of 1072 eV for Ni and a small peak for Ni 3p₃/₂. The appearance of other small peaks in Ni NPs indicated
the Ni²⁺, which may react with the surface molecules to form Ni(OH)₂. The formation of Ni²⁺ ions indicated the oxidation of Ni⁰ due to the long exposure of Ni⁰ in the XPS operation.⁵³,⁵⁴ The Cu survey scan shows Cu 2p peaks at a binding energy of 1072 eV, suggesting the single valance state of Cu. This proves the reduction of Cu²⁺ to Cu⁰ by the reducing agent. Similarly, Cu 2p₁/₂ and Cu 2p₃/₂ peaks appeared at binding energies of 932 and 945 eV, respectively.⁵⁵ In the survey scan spectrum of Ag NPs, one intense and two small peaks appeared for Ag⁰ and Ag¹⁺ along with other photoelectron, oxygen, and carbon peaks. The peaks for Ag 3d₅/₂ and Ag 3d₃/₂ appearing at 369 and 398 eV indicated the formation of Ag⁰, and an Auger peak of Ag 3d at a binding energy of 1072 eV indicated the formation of Ag¹⁺.⁵⁶ Again, the same reason can be provided here as explained above for the Ni NPs, that is, the longer exposure time of XPS operation that converts Ag⁰ into Ag¹⁺.

2.5. Field Emission Scanning Electron Microscopy (FESEM). The FESEM micrographs of MNP-loaded WBs were taken at both low and high resolutions. The left side of the micrograph is at low resolution, and right side is at high resolution. The working distance (WD) was constant for both low- and high-resolution images. WD for Cu NPs was 4.2 mm, and for Ni and Ag NPs, it was 4.4 mm. WD is the distance between the sample surface and the objective lens. The increasing working distance causes an increase in the depth of focus and probe size, which results in the decrease of image resolution; therefore, proper WD should be adjusted before the sample analysis.⁵⁷ Furthermore, the spot size for all of the MNPs was the same, for instance, 1 μm for the low resolution and 100 nm for the high resolution. All of the MNP-loaded WBs indicated clear spots of NPs and showed that the NPs stabilized in the internal area of WB, as manifested in Figure 3a,b. The Cu (3c,d) and Ag (3e,f) NPs stabilized on the surface of WB due to the surface interactions of NPs with the chemical functionalities of the WB.

2.6. Energy-Dispersive X-ray Spectroscopy (EDS). Figure 4a–e displays the FESEM plots and EDS spectra of WB loaded with Ni, Cu, and Ag NPs. EDS is one of the most authentic techniques for the elemental analysis of the synthesized materials. The EDS spectrum plotted the electron energy in keV vs counts/s. The C atoms appeared at 0.3 keV with 40.55, 7.93, and 7.45 wt % in WB loaded with Ni, Cu, and Ag NPs, respectively. Similarly, WBs are present in 32.58% by weight when loaded with Ni NPs, 6.80% by weight when loaded with Cu NPs, and 21.65% by weight when loaded with Ag NPs. EDS suggests no impurity in the catalysts.

2.7. Catalytic Potential of MNPs Supported on WB. The catalytic potential of the stated NPs was checked for the reduction of 4-NP and removal of highly colored dyes. Figure 5a–e displays the catalytic activity of WB loaded with MNPs against the reduction of 4-NP to 4-aminophenol (4-AP). The typical peak of 4-NP appeared at λₘ₅ₐₓ 318 nm and shifted to 400 nm by the addition of NaBH₄. The shift in the wavelength from 318 to 400 nm by the addition of NaBH₄ was due to an increase in conjugation. After the addition of NaBH₄, the pale yellow color of 4-NP changed to a deep yellow color. NaBH₄ abstracts the −OH proton of phenol and forms a phenolate anion in which the negative charge resides on the oxygen atom. The negative charge is more stabilized on a more electronegative atom as compared to a less electronegative atom; therefore, the negative charge on the oxygen atom delocalized...
predominantly as compared to the lone pair electrons of the $-\text{OH}$ group and thus shifted the wavelength toward the longer $\lambda_{\text{max}}$. Such a shift toward a longer $\lambda_{\text{max}}$ is known as a red shift.

Initially, no reaction was observed after mixing 4-NP and NaBH$_4$ as depicted in Figure 5a, but after the addition of WB loaded with Ni, Cu, and Ag NPs, the peak at 400 nm decreased in 10, 14, and 6 min, respectively. On the other hand, another peak originated at approximately 290 nm allocated for 4-AP. The time-dependent UV−vis spectra of Ni, Cu, and Ag NPs for the reduction of 4-NP are presented in Figure 5b−d, respectively. It was reported in the literature that NaBH$_4$ can be used for the reduction of 4-NP, but the reaction proceeds very slowly and is not considered as an economical reaction. The reaction with NaBH$_4$ is thermodynamically favorable, but not kinetically; therefore, an efficient catalyst is required to make the reaction kinetically favorable. The rate of reaction increases in the presence of MNPs in addition to NaBH$_4$. Therefore, it is worth noting that both MNPs and NaBH$_4$ are the prerequisites for this reduction reaction. Both NaBH$_4$ and the catalyst decrease the activation barrier of the reaction and thereby increase the rate of reaction. The decrease in the initial concentration of the 4-nitrophenolate anion centered at $\lambda_{\text{max}} = 400$ nm with respect to time $t$ is deduced from eq 1 (decrease in concentration = $C_t/C_0$), as manifested in Figure 5e, which indicated that Ag NPs loaded on WB have the potential to reduce 4-NP to 4-AP faster as compared to Ni and Cu NPs loaded on WB. To further check the catalytic efficiency, eq 2 was applied. It was observed that 98, 84, and 94% reduction of 4-NP to 4-AP took 10, 14, and 6 min, respectively, in the presence of WB loaded with Ni, Cu, and Ag NPs (Figure 5f).

Figure 5. UV−vis spectra of 4-NP + NaBH$_4$ (a) and WB loaded with Ni (b), Cu (c), and Ag NPs (d); various kinetics parameters obtained from $C_t/C_0$ (e); and % reduction of 4-NP to 4-AP (f). Experimental conditions: 0.1 mM 2.5 mL of 4-NP + 1 mM 0.5 mL of NaBH$_4$ solution and 20 mg of each catalyst.

Table 1. Various Kinetics Parameters for the Reduction of 4-NP and Decolorization of Dyes Using NaBH$_4$ as a Reducing Agent in the Presence of WB Loaded with Ni, Cu, and Ag NPs

| pollutants | apparent rate constant $K_{\text{app}}$ (min$^{-1}$) and adjacent $R^2$ value using WB loaded with Ni, Cu, and Ag NPs |
|------------|---------------------------------------------------------------------------------------------------------------|
| 4-NP       | 2.1 × 10$^{-1}$ and 0.9838                                                                                   |
| MO         | 1.5 × 10$^{-1}$ and 0.9439                                                                                   |
| CR         | 2.5 × 10$^{-1}$ and 0.95416                                                                                 |
| MB         | 2.5 × 10$^{-1}$ and 0.846                                                                                    |
| Ni         | 2.9 × 10$^{-2}$ and 0.9515                                                                                   |
| Cu         | 7.4 × 10$^{-2}$ and 0.9311                                                                                   |
| Ag         | 8.5 × 10$^{-2}$ and 0.7927                                                                                    |
|            | 4.7 × 10$^{-2}$ and 0.9333                                                                                    |

$^a$The values in the table are based on the relationship: $\ln(C_t/C_0) = -kt$. 

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which suggested the superior catalytic performance of Ag NPs. However, the apparent rate constant \( K_{\text{app}} \) and \( R^2 \) values were deduced from the linear relationship given in eq 3. The apparent rate constant \( K_{\text{app}} \) is \( 4.6 \times 10^{-1} \) for Ag, \( 2.9 \times 10^{-1} \) for Cu, and \( 2.1 \times 10^{-1} \) for Ni, suggesting the highest rate of reduction of 4-NP with Ag NPs. The apparent rate constant and \( R^2 \) values are provided in Table 1.

Furthermore, all of the three MNPs were applied against the discoloration of two anionic dyes, i.e., MO and CR, in the presence and absence of the catalyst using NaBH\(_4\) as a reducing agent following the same procedure as described above for 4-NP. The apparent rate constant and \( R^2 \) values are provided in Table 1.

Figure 6. Time-dependent UV–vis spectrum of MO decolorization in the presence of Ni NPs loaded on WB (a), % decolorization of MO in the presence of WB loaded with Ni, Cu, and Ag and without the catalyst (bare) (b), UV–vis spectrum of CR decolorization in the presence of WB loaded with Ni NPs (c), and % decolorization of CR with WB loaded with Ni, Cu, and Ag loaded and without the catalyst (bare) (d). Experimental conditions: 0.05 mM 2.5 mL of each dye + 1 mM 0.5 mL of NaBH\(_4\) solution and 20 mg of each catalyst.

Table 2. Comparison of the Present Work with the Relevant Work Reported in the Literature

| catalyst                                      | targeted materials | concentration of the targeted pollutant, mg/L | amount of the catalyst, g/L | reaction time | refs |
|-----------------------------------------------|--------------------|-----------------------------------------------|-----------------------------|---------------|------|
| poly(N-vinylimidazole) coated@Ag NPs         | 4-NP               | 27.6                                          | 2.5                         | 80            | 62   |
| PPI dendrimer (G4)-platinum nanocomposites    |                    | 0.35                                          | 0.3                         | 12            | 63   |
| poly(2-acrylamido-2-methyl-1-propylsulphonic acid)@Ni NPs |        | 14.38                                         | 1                           | 60            | 64   |
| carbon nanofibers@Ag NPs                     |                    | 16.68                                         | 0.03                        | 8             | 65   |
| sodium polycrylate@Ag NPs                    |                    | 13.9                                          | 6.7                         | 6             | this work |
| sodium polycrylate@Cu NPs                    |                    | 13.9                                          | 6.7                         | 10            | this work |
| sodium polycrylate@Ni NPs                    |                    | 13.9                                          | 6.7                         | 14            | this work |

which suggested the superior catalytic performance of Ag NPs. However, the apparent rate constant \( K_{\text{app}} \) and \( R^2 \) values were deduced from the linear relationship given in eq 3. The apparent rate constant \( K_{\text{app}} \) is \( 4.6 \times 10^{-1} \) for Ag, \( 2.9 \times 10^{-1} \) for Cu, and \( 2.1 \times 10^{-1} \) for Ni, suggesting the highest rate of reduction of 4-NP with Ag NPs. The apparent rate constant and \( R^2 \) values are provided in Table 1.

Furthermore, all of the three MNPs were applied against the discoloration of two anionic dyes, i.e., MO and CR, in the presence and absence of the catalyst using NaBH\(_4\) as a reducing agent following the same procedure as described above for 4-NP. For the removal of MO dye, NaBH\(_4\) was used as a reducing agent; however, no visible change in the reaction was observed. It was reported in the literature that NaBH\(_4\) is used for the decolorization of dyes, but the reaction proceeds very slowly and is not considered as an economical reaction; the same reason is provided for this slow rate as provided above for 4-NP. Figure 6a shows the UV–vis spectrum of MO decolorization using WB loaded with Ni NPs as a catalyst, and the typical peak of MO is centered at \( \lambda_{\text{max}} = 464 \) nm. The % removal formula shows that 90% of MO dyes disappeared in 15 min by Ni NPs, while 94 and 96% with Cu and Ag NPs in 4 min, respectively, using NaBH\(_4\) as a reducing agent (Figure 6b). The UV–vis spectra of Cu and Ag NPs for the decolorization of MO in the presence of NaBH\(_4\) are presented in Figure S2a,b, respectively. In the UV–vis spectrum of MO decolorization, a new peak originated at 250 nm, which indicated the presence of amine-group-containing molecules. Various kinetics parameters obtained from \( C_t/C_0 \) (Figure S2c) and the linear relationship using the pseudo-first-order kinetics are presented in Table 2. The \( K_{\text{app}} \) and \( R^2 \) values for MO decolorization using WB loaded with Ni, Cu, and Ag NPs obtained from pseudo-first-order kinetics are presented in Table 1. It is obvious from Table 1 and from the apparent rate constant \( K_{\text{app}} \) deduced from the linear relationship in \( C_t/C_0 = -kt \) that the rate of decolorization of MO per min with Ni (1.4 \( \times 10^{-1} \)) is slower as compared to that with Cu (7.4 \( \times 10^{-1} \))
and Ag \((8.6 \times 10^{-1})\). Furthermore, an induction period of 1 min was observed for WB loaded with the Ni catalyst represented as \(t_0\). The induction period is routinely encountered in catalysis and is generally considered as the diffusion of analyte on the surface of the catalyst. In kinetics, the induction period is a slow step, where the electrons rearrange themselves, and after the induction period, the rate of reaction swiftly increases (Table 2).

For CR decolorization, no obvious change was observed in the presence of NaBH4 and is represented in Figure S3a, and this reaction is represented as bare (without the use of catalyst); however, by the addition of WB loaded with Ni, Cu, and Ag NPs, CR decolorizes with the passage of time. Two peaks arise for CR at 350 and 490 nm due to the \(\pi-\pi^*\) and \(n-\pi^*\) transitions associated with the \(-C=\xi-C-\) and \(-N=\xi-N-\) excitations, respectively.49 Figure 6c shows the time-dependent UV-vis spectrum of CR + NaBH4 in the presence of Ni NPs, which decolorize the CR in 9 min. However, two additional peaks are observed at 285 and 250 nm for amine-group-containing molecules. Similarly, the % degradation of the CR dye shows that WB loaded with Ni NPs decolorizes 89% of CR in 9 min, while 86% discoloration was achieved in 20 min for Cu NPs and 100% with Ag NPs in only 6 min (Figure 6d). Again an induction period of 1 min was observed using WB loaded with Cu and Ag NPs. The UV–vis spectrum of CR decolorization using WB loaded with Cu and Ag NPs is shown in Figure S3b,c, and \(C_t/C_0\) (Figure S2d) indicates the strongest catalytic performance of Ag NPs. The linear relationship shows the fastest apparent rate constant \(K_{app}\) per min for Ag \(3.7 \times 10^{-1}\) min\(^{-1}\) and slowest for Cu \(8.5 \times 10^{-2}\) min\(^{-1}\). The \(K_{app}\) and \(R^2\) values for the decolorization of CR with Ni, Cu, and Ag NPs loaded on WB can be found in Table 1.

Moreover, all of the catalysts were also checked for the decolorization of MB dye in the presence of NaBH4. MB is a cationic dye related to the thiazine group of dyes and is used in a number of applications.58 In the absence of catalyst, no apparent change was observed with NaBH4. Therefore, both NaBH4 and the catalyst are required for the decolorization of MB. After the addition of NaBH4, the highly colored and oxidized MB dye converted to the colorless reduced form of MB known as leuco MB.59 The structures of MB and leuco MB are given in Figure S4. However, the borohydride itself does not completely reduce the dye even in excess amount. The peak of MB dye centered at \(\lambda_{max} = 665\) and 290 nm vanished in 12, 6, and 8 min in the presence of WB loaded with Ni, Cu, and Ag NPs (Figure 7a–c), respectively. Besides, a new peak arises at 255 nm due to the formation of leuco MB, which indicates the reaction progress. WB loaded with Ni NPs decolorizes 96% MB dye in 12 min, while Cu and Ag decolorize 94 and 96% of MB, respectively, in 6 min (Figure 7d). The \(K_{app}\) and \(R^2\) values obtained from the linear relationship are presented in Table 1, which indicated that the apparent rate constant \(K_{app}\) is highest for Ag NPs, that is, \(5.4 \times 10^{-1}\), which is higher than the other two.

### 2.8. Biological Activity

Microbial contamination is becoming one of the worst obstacles in pharmacology, health care products, water treatment, medical devices, babies’ toys, water purification systems, hospital appliances, surgery, food packaging, textiles, and many others. Antimicrobial agents received the attention of researchers in both academic and industrial sectors because it provides quality significance to other materials.60 WBs loaded with Ni, Cu, and Ag NPs were investigated for their biological potential against six pathogenic bacteria. The antibacterial activity of the WBs loaded with Ni, Cu, and Ag NPs were assessed against both Gram-negative (
Providencia stuartii, Escherichia coli, Salmonella enterica, Acinetobacter baumannii and Gram-positive (Bacillus pumilus, Staphylococcus aureus) bacteria, and the results obtained from the MNP-loaded WB were compared with the reference standard tetracycline TE30. Table 3 and Figure 8a–f indicate that all of the catalysts have low activity as compared to the reference standard tetracycline TE30; however, among all of the catalysts, Ag showed good inhibitory activity against A. baumannii (1.7 cm) and S. enterica (1.8 cm) as compared to Ni and Cu. For P. stuartii, the zone of inhibition is 1.5 cm for Ni, 1.4 cm for Cu, and 1.2 cm for Ag, while for standard tetracycline TE30, it is 2.5 cm. The highest antibacterial potential of Ag as compared to Ni and Cu against most of the bacteria might be due to the small size of the WB loaded with Ag NPs.

Table 3. Evaluation of Antimicrobial Activity of WB Loaded with Ni, Cu, and Ag NPs against Six Bacterial Strains; the Zone of Inhibition Was Measured in Centimeters

| bacterial strains | Ni   | Cu   | Ag   | standard tetracycline TE30 |
|-------------------|------|------|------|----------------------------|
| 1 Bacillus pumilus | 0.9  | 1.0  | 1.4  | 2.2                        |
| 2 Acinetobacter baumannii | 1.4 | 0.8  | 1.7  | 2.2                        |
| 3 Salmonella enterica | 1.2 | 0.9  | 1.8  | 2.2                        |
| 4 Escherichia coli | 1.4  | 0.9  | 1.4  | 2.3                        |
| 5 Providencia stuartii | 1.5 | 1.4  | 1.2  | 2.5                        |
| 6 Streptococcus mutans | 1.4 | 1.5  | 1.2  | 2.4                        |

Figure 8. Inhibition zone of WB loaded with Ni, Cu, and Ag NPs against B. pumilus (a), A. baumannii (b), S. enterica (c), E. coli (d), P. stuartii (e), and S. aureus (f).

After that, the surface atoms of the MNPs rearrange themselves and then proceed the reaction. During the addition of NaBH₄, the CR dye (diazo dye) gets converted into its hydrazine derivatives, where the reducing agent reduces the azo group; however, the color of the dye remains the same, but after the addition of WB loaded with Ni, Cu, and Ag NPs, CR is decolorized as shown in Figure 9.

The possible mechanism for the reduction of 4-NP is presented in Figure 10. After the addition of NaBH₄ to 4-NP, the H¹⁺ ion abstracts the –OH proton of the aromatic ring and changes the color from pale yellow to deep yellow. The deep yellow color is because of the formation of the 4-nitrophenolate anion appeared at λmax = 400 nm. After the addition of the catalyst, NaBH₄ and 4-nitrophenolate anion get adsorbed on the surface of the catalyst. The reduction of 4-NP to 4-AP is a six-electron transfer reaction, where the electron transfer is subsequently followed by H¹⁺ transfer. Figure 10 explains the single electron transfer mechanism for the decolorization of CR dye.
reduction of 4-NP to 4-AP. The reduction of 4-NP to 4-AP possibly occurred through the formation of a nitrene intermediate.

3. CONCLUSIONS
The WBs loaded with Ni, Cu, and Ag NPs have been synthesized using NaBH₄ as a reducing agent. The synthesized NPs have been used for the degradation of persistent organic pollutants and have shown antibacterial potential. Similarly, WB loaded with Ag NPs showed the highest \( K_{\text{app}} \) values for MO, CR, and MB decolorization, which were \( 8.6 \times 10^{-5} \), \( 3.7 \times 10^{-1} \), and \( 5.4 \times 10^{-3} \), respectively, which are higher than those for WB loaded with Ni and Cu NPs. The Ag catalyst showed the highest catalytic activity for the reduction of 4-NP; degradation of MO, CR, and MB; and inhibition of bacteria as compared to the Ni and Cu catalysts. The high catalytic potential of these catalysts will open a new window for the removal of persistent organic pollutants and pathogenic bacteria.

4. EXPERIMENTAL SECTION

4.1. Reagents and Materials. The reagents 4-NP, MO, CR, MB, and NaBH₄ were purchased from Sigma-Aldrich, while Cu(NO₃)₂·3H₂O, NiCl₂·6H₂O, and AgNO₃ were purchased from Deajung Korea and WB was purchased from the local market of District Swabi, KPK, Pakistan. Six strains of bacteria, that is, B. subtilis, A. baumannii, S. enterica, E. coli, P. stuartii, and S. mutans, were cultured for this experiment. Distilled water was used throughout the experiment.

4.2. Synthesis of WB-Supported MNPs or MNP-Supported WB. The WBs loaded with MNPs were prepared in two steps. In the first step, a specified amount of WBs was put in 0.3 M solution of nickel chloride, copper sulphate, and silver nitrate solutions, respectively, to saturate the adsorptive sites of the WBs for 48 h. In the second step, the WBs loaded with Ni, Cu, and Ag metal ions were treated with freshly prepared NaBH₄ solution and then applied for the reduction of 4-NP and degradation of MO, CR, and MB dyes, respectively, as manifested in Figure 11.

4.3. Instrumentation. A field emission scanning electron microscope (FESEM; JEOL, JSM-7600F model, Japan) was employed for analyzing the surface morphology and energy-dispersive X-ray spectrometry (EDS; Oxford system) for analyzing the elemental composition of the catalysts. The binding energy and elemental composition of the catalyst were determined through X-ray photoelectron spectroscopy (XPS; Thermo Scientific K-α KA1066 spectrometer, Germany). The crystalline and amorphous nature of the WB and its loaded MNPs were investigated through X-ray diffraction (XRD) with a Cu Ka radiation (\( \lambda = 0.154 \text{ nm} \)) source (Thermo Scientific diffractometer). For functional group determination of WB and MNP-loaded WB, an attenuated total reflectance (ATR) FTIR spectrophotometer (Thermo scientific) were employed. The thermal stability of the materials was determined through thermal gravimetric analysis and was recorded in an inert atmosphere using nitrogen gas, and the weight loss was observed at 30 °C sweep rate of temperature. The chemical reduction of 4-NP to 4-amino phenol and the degradation of various dyes were recorded in a time-dependent UV–vis spectrophotometer (Spectrolab, model UV2601).

4.4. Reduction of 4-NP and Decolorization of Dyes. The reduction of 4-NP to 4-AP was assessed by adding 2.5 mL of 0.1 mM 4-NP solution in a UV cuvette and 0.5 mL of freshly prepared 1 mM NaBH₄ solution. The \( \lambda_{\text{max}} \) of 4-NP appeared at 318 nm; however, by adding NaBH₄ solution, the \( \lambda_{\text{max}} \) extended to a longer wavelength, called red shift, that is, from 318 to 400 nm, allocated for the 4-nitrophenolate anion. To this solution in the cuvette, 20 mg of the catalyst was added, and the reaction was monitored periodically.

The discoloration of MO, CR, and MB was observed in a UV cuvette by the time-dependent UV–vis spectrophotometry by taking 2.5 mL (0.05 mM) of each dye + 0.5 mL of 1 mM freshly prepared NaBH₄ solution in a cuvette and with the addition of 20 mg of the catalyst, followed by monitoring the reactions periodically.

The various kinetics parameters were deduced from the following equations.

The decrease in the original concentration of 4-NP and dyes was determined through eq 1.

\[
\frac{C_t}{C_0} = \frac{A_0 - A_t}{A_0} \times 100
\]

where \( C_t \) is the final concentration of the analyte after the passage of some time \( t \) and \( C_0 \) is the initial concentration at \( t = 0 \). Similarly, the percent reduction of 4-NP to 4-AP and decolorization of dyes were determined from eq 2.

Similarly, the apparent rate constant \( K_{\text{app}} \) and adjacent \( R^2 \) values were determined from pseudo-first-order kinetics as described in eq 3.
\[ \frac{C_t}{C_0} = e^{-kt} \]  

4.5. Biological Assay. The nutrient agar plates were used for determining the antibacterial activity of WB and the MNPs loaded with it against six different strains of bacteria, including Gram-positive bacteria, that is, *B. subtilis* and *S. aureus* and Gram-negative bacteria, that is, *P. stuartii*, *E. coli*, *S. enterica*, and *A. baumannii*. The Kirby–Bauer disk diffusion method with slight modification was employed for determining the antibacterial activity. The nutrient agar medium plates were prepared, sterilized, and solidified. The bacterial cultures were swabbed on these plates, and then WBs and Ni, Cu, and Ag NPs loaded on them were placed on these nutrient agar plates containing six diﬀerent cultures of bacteria at 30 °C for 24 h. After that, the zone of inhibition of each culture was measured and compared with the results of the reference standard tetracycline TE30. The antibacterial activity was observed as the mean zone of inhibition in centimeters (cm) around the disk, and the results were replicated in triplicate.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at [https://pubs.acs.org/doi/10.1021/acsomega.9b044410](https://pubs.acs.org/doi/10.1021/acsomega.9b044410).

Chemical structures of acrylic acid, polyacrylic acid, and sodium polyacrylate; UV–vis spectra and % degradation of methyl orange and Congo red dye; and chemical structures of methylene blue and leuco methylene blue (PDF)

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

(1) Khan, S. A.; Khan, S. B.; Kamal, T.; Yasir, M.; Asiri, A. M. Antibacterial nanocomposites based on chitosan/Co-MCM as a selective and efficient adsorbent for organic dyes. Int. J. Biol. Macromol. 2016, 91, 744–751.

(2) Gupta, V. K.; Nayak, A.; Agarwal, S.; Tyagi, I. Potential of activated carbon from waste rubber tire for the adsorption of phenolics: effect of pre-treatment conditions. J. Colloid Interface Sci. 2014, 417, 420–430.

(3) Ajmal, M.; Demirci, S.; Siddiq, M.; Aktas, N.; Sahiner, N. Simultaneous catalytic degradation/reduction of multiple organic compounds by modifiable p (methacrylic acid-co-acrylonitrile)–M (M: Cu, Co) microgel catalyst composites. New J. Chem. 2016, 40, 1485–1496.

(4) Yao, T.; Guo, S.; Zeng, C.; Wang, C.; Zhang, L. Investigation on efficient adsorption of cationic dyes on porous magnetic polyacrylamide microspheres. J. Hazard. Mater. 2015, 292, 90–97.

(5) Ismail, M.; Khan, M.; Khan, S. A.; Qayum, M.; Khan, M. A.; Anwar, Y.; Akhtar, K.; Asiri, A. M.; Khan, S. B. Green synthesis of antibacterial bimetallic Ag–Cu nanoparticles for catalytic reduction of persistent organic pollutants. J. Mater. Sci.: Mater. Electron. 2018, 29, 20840–20855.

(6) Khan, S. A.; Arshad, T.; Faisal, M.; Shah, Z.; Shaheen, K.; Suo, H.; Asiri, A. M.; Akhtar, K.; Khan, S. B. Al–Sr metal oxides and Al–Cd layered double hydroxides for the removal of Acridine orange dye in visible light exposure. J. Mater. Sci.: Mater. Electron. 2019, 30, 15299–15312.

(7) McCullagh, C.; Skillen, N.; Adams, M.; Robertson, P. K. Photocatalytic reactors for environmental remediation: a review. J. Chem. Technol. Biotechnol. 2011, 86, 1002–1017.

(8) Khan, S. A.; Bello, B. A.; Khan, J. A.; Anwar, Y.; Mirza, M. B.; Qadri, F.; Farooq, A.; Adam, I. K.; Asiri, A. M.; Khan, S. B. Albizia chevalier based Ag nanoparticles: Anti-proliferation, bactericidal and pollutants degradation performance. J. Photochem. Photobiol, B 2018, 182, 62–70.

(9) Khan, S. A.; Khan, S. B.; Asiri, A. M. Toward the design of Zn–Al and Zn–Cr LDH wrapped in activated carbon for the solar assisted de-coloration of organic dyes. RSC Adv. 2016, 6, 83196–83208.

(10) Khan, S. A.; Khan, S. B.; Asiri, A. M. Core–shell cobalt oxide mesoporous silica based efficient electro-catalyst for oxygen evolution. New J. Chem. 2015, 39, 5561–5569.

(11) Khan, S. A.; Khan, S. B.; Asiri, A. M. Electro-catalyst based on cerium doped cobalt oxide for oxygen evolution reaction in electrochemical water splitting. J. Mater. Sci.: Mater. Electron. 2016, 27, 5294–5302.

(12) Khan, S. A.; Khan, S. B.; Asiri, A. M.; Ahmad, I. Zirconia-based catalyst for the one-pot synthesis of coumarin through Pechmann reaction. Nanoscale Res. Lett. 2016, 11, No. 345.

(13) Khan, S. A.; Khan, S. B.; Kamal, T.; Asiri, A. M.; Akhtar, K. Recent Development of Chitosan Nanocomposites for Environmental Applications. Recent Pat. Nanotechnol. 2016, 10, 181–188.

(14) Khan, S. A.; Khan, S. B.; Asiri, A. M. Layered double hydroxide of Cd-Al/C for the mineralization and de-coloration of dyes in solar and visible light exposure. Sci. Rep. 2016, 6, No. 35107.

(15) Arshad, T.; Khan, S. A.; Faisal, M.; Shah, Z.; Akhtar, K.; Asiri, A. M.; Ismail, A. A.; Alhobgi, B. G.; Khan, S. B. Cerium based photocatalysts for the degradation of acridine orange in visible light. J. Mol. Liq. 2017, 241, 20–26.

(16) Arora, R.; Srivastav, A.; Mandal, U. K. Polyamidane Based Polymeric Nanocomposite Containing TiO2 and Sm2O3 for Environmental and Energy Applications. Int. J. Mod. Eng. Res. 2012, 2, 2384–2395.

(17) JIANG, L. C. Phytoinhibition and Formulation of Allelopathic Extract of Mikania micrantha Kunth ex HBK as pre-emergent weed suppressant against Echinochloa colona (L.) Link. Doctoral Thesis, Universiti Putra Malaysia, 2018.

(18) Li, L.; Hu, J.; Shi, X.; Fan, M.; Luo, J.; Wei, X. Nanoscale zero-valent metals: a review of synthesis, characterization, and applications to environmental remediation. Environ. Sci. Pollut. Res. 2016, 23, 17880–17900.

(19) Sahiner, N.; Sagbas, S.; Aktas, N. Very fast catalytic reduction of 4-nitrophenol, methylene blue and eosin Y in natural waters using green chemistry: p (tannic acid)–Cu ionic liquid composites. RSC Adv. 2015, 5, 18183–18195.

(20) Sahiner, N.; Karakoyun, N.; Alpaslan, D.; Aktas, N. Biochar-embedded soft hydrogel and their use in Ag nanoparticle preparation and reduction of 4-nitro phenol. Int. J. Polym. Mater. Polym. Biomater. 2013, 62, 590–595.
(21) Ajmal, M.; Siddiq, M.; Al-Loheedan, H.; Sahiner, N. Highly versatile p (MAC)-M (Cu, Co, Ni) microgel composite catalyst for individual and simultaneous catalytic reduction of nitro compounds and dyes. RSC Adv. 2014, 4, 59562–59570.
(22) Sahiner, N.; Demirci, S. The use of M@ p (4-VP) and M@ p (VI) (M: Co, Ni, Cu) cryogel catalysts as a reactor in a glass column in the reduction of p-nitrophenol to p-aminophenol under gravity. Asia-Pac. J. Chem. Eng. 2019, 14, No. e2305.
(23) Khan, S. B.; Khan, S. A.; Marwani, H. M.; Bakhsh, E. M.; Anwar, Y.; Kamal, T.; Asiri, A. M.; Akhtar, K. Anti-bacterial PES-cellsulose composite spheres: dual character toward extraction and catalytic reduction of nitrophenol. RSC Adv. 2016, 6, 110077–110090.
(24) Bakhsh, E. M.; Khan, S. A.; Marwani, H. M.; Danesh, E. Y.; Asiri, A. M.; Khan, S. B. Performance of cellulose acetate-ferroc oxide nano composites supported metal catalysts toward the reduction of environment pollutants. Int. J. Biol. Macromol. 2015, 80, 763–774.
(25) Khan, S. A.; Khan, S. B.; Farooq, A.; Asiri, A. M. A facile synthesis of CuAg nanoparticles on highly porous ZeO /carbon black-cellsulose acetate sheets for nitro- and azo dyes reduction / degradation. Int. J. Biol. Macromol. 2019, 130, 288–299.
(26) Rehman, S.; Siddiq, M.; Al-Loheedan, H.; Sahiner, N. Cationic microgels embedding metal nanoparticles in the reduction of dyes and nitro-phenols. Chem. Eng. J. 2015, 265, 201–209.
(27) Sahiner, N.; Seven, F.; Al-Loheedan, H. Superporous cryogel-M (Cu, Ni, and Co) composites in catalytic reduction of toxic phenolic (VI)(M: Co, Ni, Cu) cryogel catalysts as reactor in a glass column in versatile p (MAc) supportinc Ag, Ni, and Cu nanoparticles through wetness impregnation for environmental remediation. Nano Process. Synth. 2019, 8, 309–319.
(28) Gopiraman, M.; Meng, D.; Saravananroothy, S.; Chung, I.-M.; Kim, I. S. Gold, silver and nickel nanoparticle anchored cellulose nanofibers as highly active catalysts for the rapid and selective reduction of nitrophenols in water. RSC Adv. 2018, 8, 3014–3023.
(29) Gopiraman, M.; Muneeeswaran, M.; Kim, I. Highly porous Ru/ C and Cu/C nanocatalysts derived from custard apple for rapid and selective reduction of p-nitrophenol. Nano Prog. 2019, 1, 30–36.
(30) Chen, D.; Zeng, Z.; Zeng, Y.; Zhang, F.; Wang, M. Removal of methylene blue and mechanism on magnetic γ-Fe2O3/SiO2 nano composite from aqueous solution. Water Resour. Ind. 2016, 15, 1–13.
(31) Abdul Khaliil, H. P. S.; Bhat, A.; Yusra, A. L. Green composites from sustainable cellulose nanofibers: A review. Carbohydr. Polym. 2012, 87, 975–979.
(32) Khan, S. A.; Ismail, M.; Anwar, Y.; Farooq, A.; Al Jhony, B. O.; Akhtar, K.; Shah, Z. A.; Nadeem, M.; Raza, M. A.; Asiri, A. M.; Bahadar Khan, S. A highly efficient and multifunctional biomass supporting Ag, Ni, and Cu nanoparticles through wetness impregnation for environmental remediation. Green Process. Synth. 2019, 8, 309–319.
(33) Hervés, P.; Pérez-Lorenzo, M.; Liz-Marzán, L. M.; Dzubiella, J.; Lu, Y.; Ballaluf, M. Catalysis by metallic nanoparticles in aqueous solution: model reactions. Chem. Soc. Rev. 2012, 41, 5577–5587.
(34) Natkanisz, P.; Kuśtworski, P.; Bielas, A.; Piwowarska, Z.; Michalk, M. Thermal stability of montmorillonite polyacrylamide and polyacrylamide polynan composites and adsorption of Fe (III) ions. Appl. Clay Sci. 2013, 75–76, 153–157.
(35) Zhuang, W.; Li, L.; Liu, C. In Effects of sodium polycrylate on water retention and infiltration capacity of a sandy soil. SpringerPlus 2013, 2, No. S11.
(36) Liu, Y.; Zheng, Y.; Wang, A. Enhanced adsorption of Methylene Blue from aqueous solution by chitosan-g-poly (acrylic acid)/ vermiculite hydrogel composites. J. Environ. Sci. 2010, 22, 486–493.
(37) Khanlari, S.; Jain, C.; Ali, I.; Chandra, S.; Agarwal, S. Removal of lindane and malathion from wastewater using bagasse fly ash—a sugar industry waste. Water Res. 2002, 36, 2483–2490.
(38) Saravanan, B.; Gupta, V.; Narayanan, V.; Stephen, A. Visible light degradation of textile effluent using novel catalyst ZnO-Co2O3. J. Taiwan Inst. Chem. Eng. 2014, 45, 1910–1917.
(39) Gupta, V. K.; Ali, I.; Saleh, T. A.; Siddiqui, M.; Agarwal, S. Chromium removal from water by activated carbon developed from waste rubber tires. Environ. Sci. Pollut. Res. 2013, 20, 1261–1268.
(40) Lahhari, S. M.; Isa, M. H.; Aumuddin Abudllah, M.; Lahhari, A. J. Microwave individual and combined pre-treatments on lignocellulose biomasses. IOSR J. Eng. 2014, 4, 14–28.
(60) Feng, Q. L.; Wu, J.; Chen, G.; Cui, F.; Kim, T.; Kim, J. A mechanistic study of the antibacterial effect of silver ions on *Escherichia coli* and *Staphylococcus aureus*. *J. Biomed. Mater. Res.* **2000**, *52*, 662–668.

(61) Aditya, T.; Pal, A.; Pal, T. Nitroarene reduction: a trusted model reaction to test nanoparticle catalysts. *Chem. Commun.* **2015**, *51*, 9410–9431.

(62) Murugan, E.; Jebaranjitham, J. N. Synthesis and characterization of silver nanoparticles supported on surface-modified poly (N-vinylimidazale) as catalysts for the reduction of 4-nitrophenol. *J. Mol. Catal. A: Chem.* **2012**, *365*, 128–135.

(63) Esumi, K.; Isono, R.; Yoshimura, T. Preparation of PAMAM– and PPI– metal (silver, platinum, and palladium) nanocomposites and their catalytic activities for reduction of 4-nitrophenol. *Langmuir* **2004**, *20*, 237–243.

(64) Kuroda, K.; Ishida, T.; Haruta, M. Reduction of 4-nitrophenol to 4-aminophenol over Au nanoparticles deposited on PMMA. *J. Mol. Catal. A: Chem.* **2009**, *298*, 7–11.

(65) Zhang, P.; Shao, C.; Zhang, Z.; Zhang, M.; Mu, J.; Guo, Z.; Liu, Y. In situ assembly of well-dispersed Ag nanoparticles (AgNPs) on electrospun carbon nanofibers (CNFs) for catalytic reduction of 4-nitrophenol. *Nanoscale* **2011**, *3*, 3357–3363.