

# Reduction of 4-Chlorophenol by Mg and Mg–Ag Bimetallic Nanocatalysts

Jignasa N. Solanki and Zagabathuni Venkata Panchakshari Murthy\*

Department of Chemical Engineering, Sardar Vallabhbhai National Institute of Technology, Surat 395007, Gujarat, India

**ABSTRACT:** Mg nanocatalyst is successfully synthesized in the present study using wet chemical method via the chemical reduction of magnesium sulfate and a reducing agent (sodium borohydride). Size/size distribution characterization is performed by dynamic light scattering (DLS) and scanning electron microscopy (SEM). Subsequently, 4-chlorophenol compound reduction is systematically studied with Mg catalyst. An ultraviolet–visible light (UV–vis) spectrophotometer is used to study the absorption spectra of in situ reduction reaction with time. Gradual disappearance of the peak corresponding to chloro compounds reveals the degradation of chloro compounds with time. Furthermore, the appearance of a new peak reveals the formation of a respective product (phenol). Mg–Ag bimetallic nanocatalyst is also synthesized via an equivalent chemical method and analogous reduction is performed with the catalyst. The performance of the Mg–Ag bimetallic catalyst is compared with that of the Mg nanocatalyst. Superior dechlorination percentage is observed with the Mg–Ag bimetallic nanocatalyst.

## 1. INTRODUCTION

With the development of industry, several types of pollutants are discharged into the environment; among them, phenolic wastes are typical contaminants that are considered to be hazardous and priority toxic pollutants listed by the USEPA (United States Environmental Protection Agency). Phenolic contaminants present in wastewater, even at low concentration, are toxic. Because of their biorefractory, bioaccumulation, and carcinogenic potential, treatment of these contaminants is very important. Chlorophenols have been widely used as important raw materials for production of pesticides and various synthetic compounds. They are persistent, toxic, and ubiquitously distributed environmental contaminants. The ever-increasing discharge of these compounds into the environment has caused various problems in water and wastewater treatment systems, because they cannot be effectively treated by traditional technologies such as biological degradation or photo catalysis.<sup>1</sup> Accordingly, it is of critical environmental importance to seek for sound technologies for the treatment of wastewater with chlorophenolic contaminants.

A wide variety of processes including advanced oxidation processes, photolysis, photocatalysis, ozonation, and catalytic ozonation have been reported for the removal of 4-chlorophenol.<sup>2</sup> A huge amount of research has been done on the biodegradation of 4-chlorophenol.<sup>3–5</sup> However, reductive dechlorination of 4-chlorophenol necessitates severe anaerobic conditions and an extended acclimation period. To provide a favorable redox potential for dechlorination, it is also difficult for implementation at an industrial scale. Aerobic degradation of 4-chlorophenol is also studied;<sup>6,7</sup> however, the products may be toxic.

Recently, catalytic dechlorination of chlorinated compounds has been reported successfully,<sup>8–17</sup> because it leads to reactions that are much faster than biodegradation. Moreover, reaction can be conducted even at room temperature and pressure. Dechlorination reduction is possible with a single corroding zerovalent metallic catalyst like  $\text{Fe}^0/\text{Mg}^0$  alone with direct electron transfer

to the adsorbed substrate. Bimetallic systems can dechlorinate more efficiently, since it is made of two metals. The first metal is in zerovalent form (with a negative reduction potential), which produces nascent hydrogen when in contact with water by anodic corrosion. The second metal with a relatively high positive reduction potential (such as  $\text{Ag}^+/\text{Ag}^0$ ,  $\text{Pd}^{4+}/\text{Pd}^0$ ) acts as the hydrogenating catalyst. Furthermore, it converts the produced nascent hydrogen to form a metal hydride (M-H), which reacts with the target substrate to reduce it.<sup>18</sup>

However, the bimetallic catalysts reported are not of nanoscale and the bulk scale catalysts have inferior catalytic performance. Nanometallic catalysts can be considered as highly efficient catalysts. Because of their nanoscale size, the ratio of surface area to volume is high. Hence, the contact between reactants and catalyst increases dramatically, resulting in better efficiency. At the same time, because of their insolubility in the reaction solvent, they can be separated out easily from the reaction mixture. Thus, nanoscale catalysts can combine the advantage of heterogeneous as well as homogeneous catalysts and offer unique activity with high selectivity. Today, nanocatalysts can be significantly useful in chemical industrial applications, and, with growing usage, the market potential also has begun to be realized.<sup>19</sup>

Many methods have been exploited for the synthesis of mono-disperse metallic nanocatalysts in the past few years; templated synthesis, wet chemical methods, and reaction in microemulsion are some of the most important methods. Among all these methods, wet chemical methods are most suitable for the synthesis of Mg and Mg–Ag bimetallic nanocatalysts.<sup>20,21</sup>

Although the reduction of chlorophenols is reported with a Mg–Ag bimetallic catalyst by Patel and Suresh,<sup>22</sup> the catalyst was a bulk bimetallic catalyst. To the best of our knowledge, the use of

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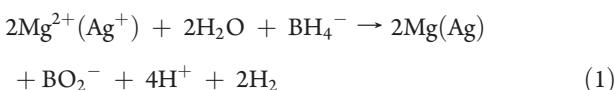
a nanoscale bimetallic Mg–Ag catalyst has not been reported for the reduction of 4-chlorophenol. Moreover, in comparison with reported dechlorination and hydrodechlorination studies with metallic or bimetallic systems involving use of catalysts such as Pd, Pt, and Au,<sup>22–25</sup> the present system may be less expensive and an alternative for field scale application.

In the present study, magnesium nanocatalysts with controlled size are synthesized in our laboratory via wet chemical methods. Size/size distribution characterization is performed by dynamic light scattering (DLS) and scanning electron microscopy (SEM). A Mg–Ag bimetallic nanocatalyst is also synthesized via an equivalent chemical method. Subsequently, 4-chlorophenol compound reduction is systematically studied with Mg catalyst. UV–visible spectrophotometer is used to study the absorption spectra of in situ reduction reaction with time. The gradual disappearance of the peak corresponding to chloro compounds reveals the degradation of chloro compounds with time. Furthermore, the appearance of a new peak reveals the formation of the respective product (i.e., phenol). Percentage conversion is calculated with reference absorption spectra of a pure 4-chlorophenol solution. A similar reduction study is performed with a Mg–Ag bimetallic nanocatalyst and the performance of the same is compared with that of a Mg nanocatalyst.

## 2. EXPERIMENTAL PROCEDURE

**2.1. Materials.** Sodium borohydride ( $\text{NaBH}_4$ , 95%) was purchased from Merck, Mumbai, India. Silver sulfate ( $\text{AgSO}_4$ ) and magnesium sulfate ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), each of analytical grade, were obtained from SD Fine Chemicals, Mumbai, India. Distilled water was used to prepare all of the aqueous solutions. All the chemicals were used without further purification. A high-speed stirrer (Remi, India), with speeds from 0 to 1000 rpm, was used for catalyst preparation.

**2.2. Nanocatalyst Preparation with Wet Chemical Reduction.** Synthesis of the nanoscale Mg–Ag particles was carried out using sodium borohydride ( $\text{NaBH}_4$ ) as the reductant. The process is as shown in eq 1:



A mixture of 4.0 g of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and 1 g of  $\text{AgSO}_4$  were dissolved in 200 mL of distilled water with constant speed stirring at 100 rpm at room temperature ( $25 \pm 2^\circ\text{C}$ ) in a 500-mL beaker. The desired mass ratio of Mg to Ag in the synthesized nanoscale Mg–Ag particles was 4:1. The  $\text{NaBH}_4$  solution was prepared by dissolving 2 g of  $\text{NaBH}_4$  in 130 mL of distilled water. Upon the dropwise addition of  $\text{NaBH}_4$  solution to the prepared solution (containing Mg and Ag ions), black particles were formed and then the mixture was stirred for an additional 20 min. The particles (Mg–Ag bimetallic nanocatalyst particles) were then isolated by filtration. To get rid of the excess borohydride, the particles were washed several times by distilled water. The particles were then dried overnight. Similarly, the synthesis of Mg nanoparticles (nanocatalyst particles of monometallic Mg) was performed by dissolving 5.0 g of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  in 200 mL of distilled water with constant speed stirring (100 rpm). The  $\text{NaBH}_4$  solution was added dropwise, followed by stirring, filtration, washing, and drying in similar way (to Mg–Ag bimetallic nanocatalyst particles preparation) as that previously discussed.

**2.3. Reduction Studies with Mg and Mg–Ag Nanocatalysts.** The prepared catalyst was used for the reduction of 4-chlorophenol. The standard aqueous solution of 4-chlorophenol was prepared with a concentration of 10 mg/L. A calibration graph was prepared to calculate the concentration of 4-chlorophenol in the reaction mixture at various time intervals. For that, UV–vis spectra were recorded with 4-chlorophenol sample solutions of known concentrations (1 mg/L to 10 mg/L) and absorbance data were obtained. The graph of concentration versus absorbance at peak wavelength ( $\lambda_{\max} = 506 \text{ nm}$ , corresponding to the presence of 4-chlorophenol) was then plotted. A linear relation (concentration as a function of absorbance) with an error of <0.6% was obtained.

After the addition of  $\text{NaBH}_4$  solution (reducing agent) and catalyst (0.05 g of the catalyst to 100 mL of reaction mixture), the compound was then mixed in a continuously stirred batch reactor under constant stirring at 400 rpm. The progress of the reaction with time was studied by recording the UV–vis spectra on filtrated reaction mixture (no catalyst present), which caused a gradual decrease with time in the absorbance value at peak wavelength. This absorbance value was used to identify the unknown concentrations of reaction mixture, using a linear relationship.

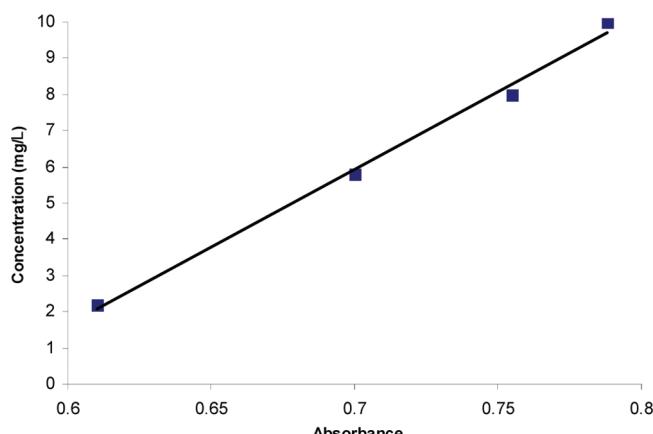
**2.4. Characterization.** Characterization of the catalyst powder was done by scanning electron microscopy (SEM) and particle size analysis (PSA). An SEM microscope (Hitachi, Model S-3400N) at an accelerating voltage of 15 kV was used to obtain the images of the sample containing prepared nanoparticles. Size distribution was determined with PSA using dynamic light scattering (DLS) (Malvern Instruments, U.K.), and the hydrodynamic diameter of the nanoparticles was determined from the diffusion constant of the particles ( $D$ ), using the Stokes–Einstein equation, via DLS, by its in-built function:

$$d_h = \frac{KT}{3\pi\eta D}$$

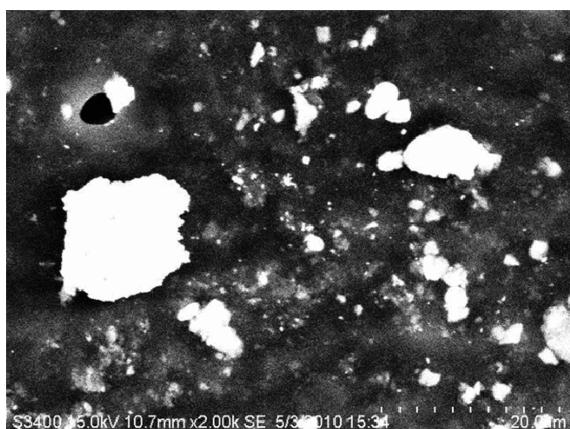
where  $K$  is the Boltzmann constant,  $T$  the absolute temperature,  $\eta$  the viscosity of the medium, and  $d_h$  the hydrodynamic diameter of the particles.<sup>26</sup> The mean size (average diameter), with cumulated analysis, of the particles was obtained in-built via DLS, by fitting a single exponential to the correlation function. Absorption spectra were recorded with a Hach, USA UV–vis spectrophotometer. Reaction progress is studied systematically by recording absorption spectra at various time intervals. And, the variations in both the absorption maxima and corresponding wavelengths with time were observed.

## 3. RESULTS AND DISCUSSION

**3.1. Characterization of 4-Chlorophenol Solutions.** In order to determine the concentrations of reaction mixture at various time intervals, 4-chlorophenol solution characterization was studied. In order to obtain a calibration graph, UV–vis spectra were recorded with 4-chlorophenol sample solutions of known concentrations (1 mg/L to 10 mg/L), as discussed previously. Maximum absorbance was observed at a wavelength of 506 nm (the  $\lambda_{\max}$  of 4-chlorophenol). The graph of concentration versus absorbance (at  $\lambda_{\max} = 506 \text{ nm}$ ) was plotted as shown in Figure 1. A linear fit of the data (with <0.6% error) was obtained and confirmed. The unknown concentrations of 4-chlorophenol in reaction mixture (at various time intervals) were then calculated at observed absorbance (corresponding to  $\lambda_{\max}$  for 4-chlorophenol)



**Figure 1.** Calibration graph of 4-chlorophenol concentration versus absorbance at  $\lambda_{\text{max}}$  (506 nm).



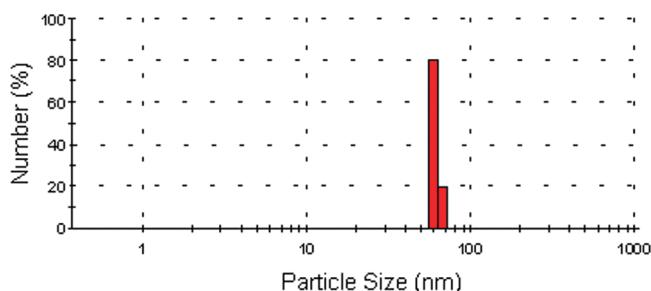
**Figure 2.** Scanning electron microscopy (SEM) image of synthesized Mg nanocatalyst particles.

using the linear fit. The dechlorination percentages were then estimated by subtracting  $C_{r,t}$  (ratio of 4-chlorophenol concentration at time  $t$ , to that of initial 4-chlorophenol concentration) from unity.

**3.2. Dechlorination of 4-Chlorophenol with Mg Nanocatalysts.** *3.2.1. Scanning Electron Microscopy of the Mg Nanocatalyst.* Figure 2 presents the SEM image of the laboratory-synthesized nanoscale Mg. It is observed that the diameters of the nanoscale Mg catalyst ranged from  $\sim 100$  to  $\sim 500$  nm. However, the particles tend to aggregate together to form chain structures, which might result from the interaction between small particles.

*3.2.2. Particle Size Distribution Analysis of the Mg Nanocatalyst.* Figure 3 indicates dynamic light scattering (DLS) size distribution histograms of a Mg nanocatalyst synthesized using the wet chemical reduction method. The diameters of the nano-scale Mg observed vary from 55 nm to 75 nm, which is not in close proximity to that observed from scanning electron microscopy.

*3.2.3. Dechlorination of 4-Chlorophenol Solutions with Nano Mg Catalyst.* The 4-chlorophenol reduction by  $\text{NaBH}_4$ , with a Mg nanocatalyst, is carried out in a continuously stirred batch reactor. The reaction progress—including the disappearance and appearance of reactants and products, respectively—is extensively studied in the literature by recording UV-vis spectra



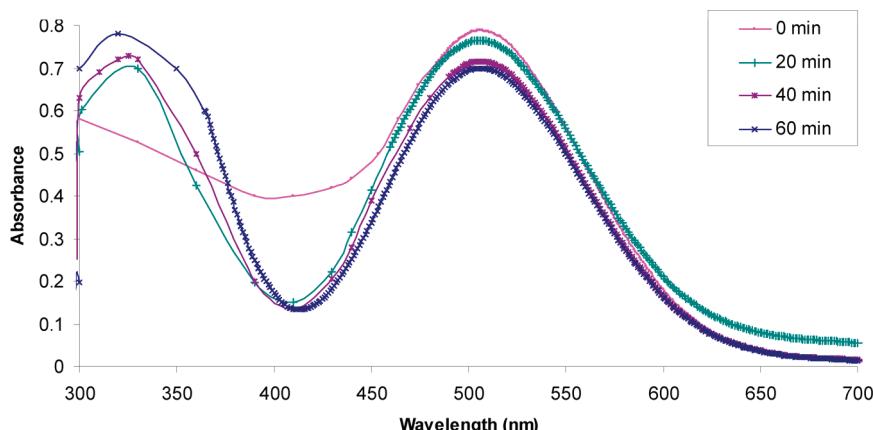
**Figure 3.** Dynamic light scattering (DLS) size distribution histograms of synthesized Mg nanocatalyst particles.

with time.<sup>28–35</sup> Consequently, in the current study too, the reaction progress is studied appropriately in a similar manner by recording UV-vis spectra at different time intervals (0, 20, 40, and 60 min). Immediately after the addition of aqueous solution of  $\text{NaBH}_4$  as a reducing agent (time  $t = 0$ ), the absorption peak observed at 511 nm (corresponding to 4-chlorophenol) did not shift, even after 24 h in the absence of catalyst, which suggests the absence of any reaction.

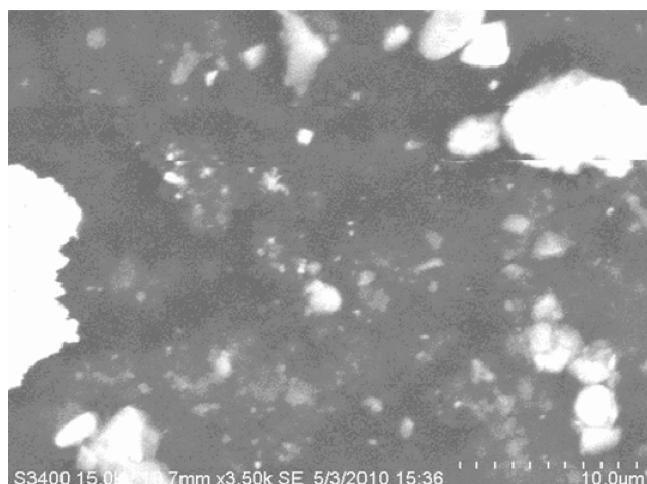
Addition and proper mixing of 0.05 g of the catalyst to 100 mL of the reaction mixture caused a gradual decrease of the peak height, as shown in Figure 4 (511 nm), which is attributed to the reduction of 4-chlorophenol. The surface of the Mg nanocatalyst initially provides the adsorption sites for 4-chlorophenol compounds. Thus, a Mg nanocatalyst can effectively reduce or dechlorinate 4-chlorophenol, which is qualitatively and quantitatively monitored by the gradual disappearance of the peak height (Figure 4). The quantitative measurements of the degree of percentage dechlorination was calculated using the linear fit (at the observed absorbance corresponding to  $\lambda_{\text{max}}$  for 4-chlorophenol), as discussed in section 3.1. After 60 min, the extent of dechlorination is observed to be only 48%.

A new peak has appeared at 330 nm, which is attributed to the presence of new product. Dechlorination of 4-chlorophenol would commonly result in phenol as a product.<sup>22</sup> Even then, to confirm that the new product is phenol, standard aqueous phenol solutions of known concentrations were prepared first. UV-vis spectra then were recorded on standard phenol solutions, so that the peak wavelength thus obtained can be compared with that obtained for the new product for the reaction mixture. The peak wavelength obtained with standard phenol solution was observed to be 329 nm, comparable to that of the new product (330 nm). Hence, it is implicated that the new product obtained is phenol. The presence of phenol as the new product is also confirmed by confirming the corresponding wavelength at which the peak for phenol is observed in other standard literature as well.<sup>27</sup> The successive increase of the intensities of the absorption spectra at 330 nm is observed during the course of the reaction. It implies an increase in the product amount with time. To know the total time required for the total reduction of 4-chlorophenol (99% dechlorination), the dechlorination was carried over for a long time interval. It was observed that a dechlorination percentage of 99% was achieved in 142 min. Hence, in order to obtain further improvement in the extent of dechlorination, a Mg–Ag bimetallic nanocatalyst is used.

**3.3. Dechlorination of Chlorophenols with Mg–Ag Nanocatalysts.** *3.3.1. Scanning Electron Microscopy of Nanocatalyst.* A scanning electron microscopy (SEM) image of synthesized Mg–Ag nanocatalyst is shown in Figure 5. The bimetallic



**Figure 4.** UV-vis spectra for dechlorination of 4-chlorophenol solution by synthesized Mg nanocatalysts with time at 0 min (pink curve with data points, ●), 20 min (teal curve with crosses, +), 40 min (purple curve with asterisks, \*), and 60 min (blue/black curve with times signs, ×).

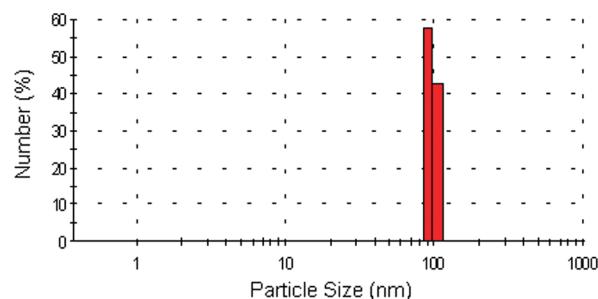


**Figure 5.** SEM image of synthesized Mg–Ag nanocatalyst particles.

particles are observed to be 100–200 nm in size (average diameter), compared to the 100–500 nm range observed for a monometallic Mg nanocatalyst (Figure 2). Nevertheless, the bimetallic particles are smaller in comparison, the particles tend to aggregate together to form chain structures which might result from the interactions between small particles.

**3.3.2. Particle Size Distribution Analysis of the Nanocatalyst.** Figure 6 shows the DLS size distribution histograms of bimetallic Mg–Ag nanocatalysts equivalent to histograms of Mg nanocatalysts (Figure 2). The diameters of the bimetallic Mg–Ag catalyst particles are found to vary from ~80 nm to ~110 nm, which are bigger in comparison with that of monometallic Mg nanocatalyst particles. However, the Mg–Ag nanocatalyst particle sizes obtained from SEM and DLS histograms are in close proximity, to some extent.

**3.3.3. Dechlorination of 4-Chlorophenol Solutions with Mg–Ag Nanocatalyst.** The 4-chlorophenol reduction by a Mg–Ag nanocatalyst is carried out in a continuously stirred batch reactor. The reaction progress is quantitatively monitored spectrophotometrically at different time intervals (0, 20, 40, and 60 min). Before the addition of NaBH<sub>4</sub>, the absorption peak at 511 nm is observed, which is the characteristic absorption peak



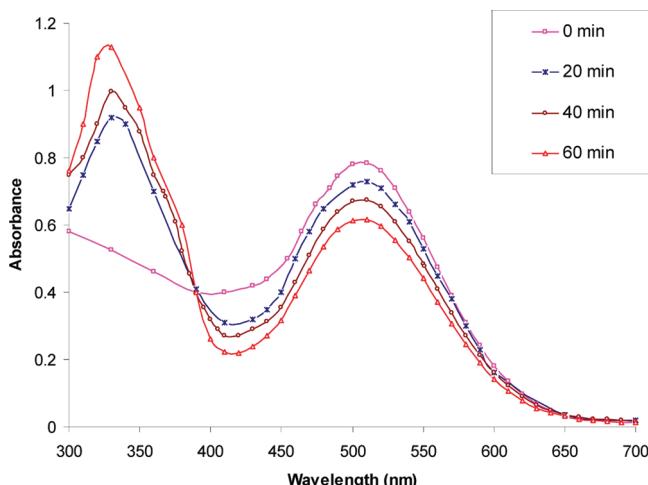
**Figure 6.** DLS size distribution histograms of synthesized Mg–Ag nanocatalyst particles.

( $\lambda_{\max}$ ) of 4-chlorophenol. After the addition of an aqueous solution of NaBH<sub>4</sub> as a reducing agent, the intensity corresponding to this peak remained almost unchanged, even for 24 h, with a minor decrease of the intensity in the absence of catalyst, which represents the absence of any reaction.

The addition and proper mixing of 0.05 g of the catalyst to 100 mL of the reaction mixture leads to a slow decrease in the characteristic peak height (511 nm), as shown in Figure 7. This is due to the successful reduction of 4-chlorophenol to phenol. The surface of Mg–Ag bimetallic nanocatalysts provides the adsorption sites for 4-chlorophenol compounds. Once again, the dechlorination was carried over for a long time interval and it was observed that a dechlorination percentage of 99% was achieved in 118 min.

This decrease is also accompanied by the appearance of a new peak at 330 nm (Figure 7), attributed to the presence of new product, which was confirmed to be phenol, since  $\lambda_{\max}$  (at which peak absorbance is obtained) was 330 nm, which is comparable to that of  $\lambda_{\max, \text{phenol}}$ . The successive increase of the intensities of the absorption spectrum at 330 nm is observed during the course of the reaction, which represents an increase in the product amount with time.

**3.4. Catalyst Performance.** The 4-chlorophenol reduction studies reported in standard literature are compared with the present dechlorination study. In the present study, with bimetallic nanocatalysts, 79% dechlorination is achieved within only 60 min, and 99% dechlorination is achieved within 118 min. Although the results of the dehydrochlorination of 4-chlorophenol by



**Figure 7.** UV-vis spectra for dechlorination of 4-chlorophenol solution by a synthesized Mg–Ag nanocatalyst with time at 0 min (pink spectrum with open boxes, □), 20 min (blue/black spectrum with times signs, ×), 40 min (burnt orange spectrum with open circles, ○), and 60 min (red spectrum with open triangles, Δ).

palladium-supported catalysts (bulk catalyst) were quite reasonable, as the conversion degree achieved amounts to be 99% by Calvo et al.<sup>23</sup> However, it is worth mentioning here that the addition of formic acid was necessary to produce hydrogen in that case. In addition, a high temperature (50 °C), as well as a high molar ratio of formic acid/4-chlorophenol (500), was required for batch reduction. Hence, dehydrochlorination is certainly not an inexpensive technique, in comparison with dechlorination. Calvo et al.<sup>23</sup> also attempted to make it more economic. Hence, they studied dehydrochlorination in a continuous (fixed-bed) reactor; nevertheless, they required a high molar ratio of 250. In addition, the degree of conversion declined to 95%.

The dechlorination percentage obtained was 95% in another study<sup>24</sup> (dehydrochlorination of 4-chlorophenol, along with other chlorophenols); however, the optimum conditions obtained were again severe, such as high temperature (75 °C), high pressure (2.4 bar), and an additional requirement of a H<sub>2</sub>/N<sub>2</sub> (1:1) gas stream. Moreover, the high conversion was favored only at high temperature and space-time. Although 2-chlorophenol has been found to be an easily dehydrodechlorinated compound, 4-chlorophenol was found to be the most refractory one.

An almost-complete reduction of chlorophenols over palladium/carbon was studied<sup>25</sup> by hydrodechlorination. The degree of dechlorination was above 98%. Hydrogen has been used as a reducing agent; hence, a pressure apparatus was necessary for reduction. However, with the usage of hydrazine as the reducing agent, a pressure apparatus was not required.

The dechlorination study<sup>22</sup> with bulk-size bimetallic Mg–Ag catalyst also reported that a poorer removal of chlorophenols was obtained in the absence of any acid. It was found that the addition of acetic acid could only improve the dechlorination percentage. The optimized dosage of acetic acid found was ranging from 87 mM to 175 mM, which would add to the total cost of dechlorination.

In the present study, within 60 min, the dechlorination percentage obtained was 48% with a monometallic Mg nanocatalyst. On the other hand, with a bimetallic nanocatalyst, within the same time frame, the dechlorination percentage was observed to

be 79%. Hence, in similar time intervals, the dechlorination percentages obtained with a bimetallic nanocatalyst are higher than that obtained with a monometallic Mg nanocatalyst. Not only that, almost-complete reduction of 4-chlorophenol with 99% dechlorination was also possible. The total time required to achieve 99% dechlorination was 142 min for a Mg catalyst. Compared to that, almost total dechlorination (99%) was achieved within only 118 min with a Mg–Ag bimetallic nanocatalyst. Hence, it may be clearly said that the performance of the bimetallic catalyst is higher than that of the monometallic Mg catalyst.

#### 4. CONCLUSIONS

Mg and bimetallic Mg–Ag nanocatalysts are successfully synthesized with a wet chemical method. Size analysis with scanning electron microscopy (SEM) and dynamic light scattering (DLS) revealed that the prepared nanocatalysts are 100–500 nm in size. Batch experiments were carried out to investigate the dechlorination performance of these laboratory-synthesized particles. Ultraviolet-visible light (UV-vis) spectroscopy study of dechlorination with Mg nanocatalysts was carried over. It depicts a possible reduction by a successive decrease in peak height at 511 nm with time, as well as the appearance of a new peak at 330 nm, attributed to the appearance of a new product: phenol. Moreover, increases in the intensities of new peaks depicts an increase in the product amount with time. However, within 60 min, the observed percentage of dechlorination of 4-chlorophenol is only 48%. Systematic study of the progress of the reaction with a bimetallic nanocatalyst resulted in much faster dechlorination. The extents of the decrease of intensity of the peak height at 511 nm at equivalent times are observed to be much higher than that observed with Mg (single) nanocatalysts. This is due to a higher extent of dechlorination at equivalent time intervals. Moreover, a new peak attributed to phenol appears at 330 nm and increase in intensity is again observed with time. Not only that, the extent of increase in peak height at equivalent times is also observed to be much higher in comparison with that of Mg nanocatalyst. Within 60 min, the observed percentage dechlorination of 4-chlorophenol is 79%, which is much higher than that with a Mg (single) nanocatalyst. Moreover, a reduction of 4-chlorophenol with 99% dechlorination was possible within 142 min with a Mg nanocatalyst, while it took only 118 min with a Mg–Ag bimetallic nanocatalyst. This result clearly shows that a faster rate of dechlorination of 4-chlorophenol can be obtained with a bimetallic Mg–Ag nanocatalyst, in comparison with a Mg nanocatalyst.

#### ■ AUTHOR INFORMATION

##### Corresponding Author

\*Tel: 0091 261 2201642, 0091 261 2201648. Fax: 0091 261 2227334. E-mails: zvpm2000@yahoo.com, zvpm@ched.svnit.ac.in.

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