Upgraded Valorization of Biowaste: Laser-Assisted Synthesis of Pd/Calcium Lignosulfonate Nanocomposite for Hydrogen Storage and Environmental Remediation
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Cite This: ACS Omega 2020, 5, 5888−5899

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ABSTRACT: Laser ablation in liquid (LAL), one of the promising pathways to produce nanoparticles, is used herein for the modification of the abundant biowaste, calcium lignosulfonate (CLS), adorning it with palladium nanoparticles (Pd NPs). The ensuing Pd/CLS nanocomposite, fabricated via a simple stirring method, is deployed for hydrogen storage and environmental cleanup studies; a hydrogen storage capacity of about 5.8 C g$^{-1}$ confirmed that Pd NPs serve as active sites for the adsorption of hydrogen. Additionally, the novel, sustainable, and reusable nanocomposite also exhibits superior catalytic activity toward the reduction of hexavalent chromium [Cr(VI)], 4-nitrophenol (4-NP), and methylene blue (MB) in an aqueous solution in a short time; the synthesized nanocatalyst could be reused for at least eight successive runs.

INTRODUCTION
It is universally known today that growing global pollution problems at an alarming rate are responsible for major irreparable damages to the environment. The rapid industrialization is liable for several environmental impacts on humans’ life, such as climate change, water pollution, water scarcity, and unhealthy air, among others. Besides, depleting natural resources need to be envisaged as a sensitive matter. Meeting the society’s demands requires alternative biofriendly and sustainable energy resources that do not contribute to much polluting emissions such as fuel cells. Hydrogen produced from water is one of the renewable energy forms that embraces this definition.$^{2,3}$

Aiming for this sustainable target, the design and synthesis of novel materials in a greener fashion from renewable and abundant resources has been the main objective.$^{4−6}$ Among the bio-based materials, after cellulose, lignin is the most widely known naturally occurring biopolymer$^{7}$ comprising of cross-linked amorphous copolymer bonded together by means of different C−O−C and C−C linkages. The ineptest characteristic of lignin would be impermeability, which possibly can be addressed by introducing various functional groups in lignin,$^{5}$ sulfonation being more adaptable for application in industrial products.$^{7,8}$ The enhancement of its water-soluble properties is the consequence of hydrophilic groups, such as sulfonate, phenolic hydroxyl, as well as alcoholic hydroxyl.$^{9}$ In the presence of sulfonic groups, carbon chain, hydrophobic groups, along with hydrophilic groups, lignosulfonate (LS) shows good surface activity and acts as a catalyst.$^{10}$ According to the production process deployed, diverse ion-based LS can be obtained as calcium, sodium, or magnesium lignosulfonates.$^{8}$ LS, a three-dimensional network structured polyphenolic compound, can be simply oxidized electrochemically$^{7}$ and makes an ideal substrate to decorate with nanoparticles thus modifying and fine-tuning its properties for high-end applications,$^{6}$ namely, for energy storage and in catalysis.$^{7,11}$

Synthesis of nanocomposite-based materials for the hydrogen storage study has been one of the active research fields; nanocomposites encompassing nickel, palladium, platinum, and some metal oxide have the ability for hydrogen adsorption and desorption.$^{12}$ Among these metals, Pd shows a unique ability for adsorption of hydrogen atom because of its structure,$^{13,14}$ and adorning Pd NPs on such materials can
turn them into effective catalysts for adsorption/desorption of hydrogen atoms\textsuperscript{15} and also reduction/degradation of environmental pollutants;\textsuperscript{16–24} such activity for hydrogen storage has been studied in nanocomposites, including Si wafer\textsuperscript{15} and single- and multiwalled carbon nanotubes.\textsuperscript{22,23}

Environmental contamination comprises water-, soil-, and air pollution that has been commonly caused by using poisonous/hazardous chemicals, namely, nitrophenols, heavy metals, and organic dyes, among others.\textsuperscript{15,17–19,24} Two main types of pollutants such as nitro compounds and toxic dyes are mostly used in diverse industries, e.g., drugs, papers, ceramics, cosmetic printing, food processing, and especially textiles. The toxic nitrophenols (especially 4-NP) are largely responsible as the main environmental pollutants\textsuperscript{25,26} and must be converted into harmless aminophenols (especially 4-AP) that are prospective intermediates and precursors for pharmaceuticals, synthetic resins, pesticides, and dyes ideally via a reductive protocol.\textsuperscript{17,18,26–28} Another hazardous heavy metal in wastewater is [Cr(VI)], produced during some large-scale industrial processes. Trivalent chromium [Cr(III)], in contrast, has 100-fold less toxicity and can be efficiently eliminated via the formation of insoluble hydroxides in water under controlled conditions.\textsuperscript{17,29–31} Consequently, it is obligatory to develop efficient, ecofriendly, and sustainable methods for the treatment of nitro compounds, organic dyes, and heavy metals, thus addressing both the energy demand and environmental issues; the assembly of nanocomposites and modified nanoparticles does inspire newer strategies for the degradation of pollutants and environmental remediation.\textsuperscript{32–38}

Nanoparticle fabrication by laser ablation in liquid (LAL) is an enticing approach\textsuperscript{39–44} that provides a simple method that is adaptable for various media and conditions; Pd NPs have been produced by LAL and examined for their catalytic\textsuperscript{42} and energy storage applications,\textsuperscript{45} electrochemical means being the promising option to store hydrogen.\textsuperscript{12} The main advantage is that it does not require extreme conditions, e.g., compression and condensation.\textsuperscript{34} Cyclic voltammetry (CV) is an indispensable technique for a wide range of materials to study adsorption/desorption of hydrogen. In an alkaline environment, the CV technique shows water decomposition and adsorption and desorption of hydrogen atoms by means of working electrode\textsuperscript{42,45} whereas UV–vis spectroscopy complements as a convenient method to monitor the conversion processes.

Introducing a new nanocomposite based on an abundant, renewable, and biofriendly material and utilizing a safe method to generate Pd NPs are the first aim of this paper. In search of improving hydrogen storage properties, LS was decorated with Pd NPs wherein the LAL process was deployed to fabricate Pd NPs. Finally, Pd\textsubscript{x}/CLS nanocomposite was constructed via a straightforward method (Figure 1a). The hydrogen adsorption/desorption of metal NPs was studied by electrochemical means in 1 M KOH as medium. CV and cyclic life performance were carried out to assess the electrochemical behavior of the electrodes. Besides, catalytic performance of the prepared Pd\textsubscript{x}/CLS nanocomposite was investigated to reduce and degrade environmental pollutants, namely, 4-NP and methylene blue (MB) with NaBH\textsubscript{4} and Cr(VI) with biomass-derived formic acid (HCOOH) in water.

\section*{RESULTS AND DISCUSSION}

\textbf{Hydrogen Storage Mechanism.} CV is an acceptable method to study the electrochemical behavior of materials. In the present work, to investigate hydrogen adsorption/desorption, we applied CV tests to the CLS and Pd\textsubscript{x}/CLS electrodes and also to the pure stainless-steel mesh, which is the substrate of the nanocomposite electrode. By applying potential in an alkaline solution, at first, water decomposition (\textit{H\textsubscript{2}O} + e\textsuperscript{–} → H + OH\textsuperscript{–}) was observed. This generated hydrogen tends to adsorb onto nanocomposites because of the electrode electric polarization under the applied potential. When the potential begins to decline, the liberated hydrogen atoms lead to recombination with OH\textsuperscript{–} to form H\textsubscript{2}O. In the anodic and cathodic direction, the equation involved is

\begin{equation}
[W] + n\text{H}_2\text{O} + ne\textsuperscript{–} \leftrightarrow [\text{WH}_n\text{]} + n\text{OH}^\text{–}
\end{equation}

where [W] represents the working electrode host cites. 

\textbf{Nanocomposite Characteristic.} XRD pattern was studied crystallographically for the synthesized product. In addition, XRD was carried out to evaluate the influence of Pd NPs on the structure of Pd\textsubscript{x}/CLS. Subsequently, the XRD pattern of Pd\textsubscript{x}/CLS and Bragg’s law were applied for estimation of the lattice parameter of Pd. Figures 2a–d shows the XRD pattern of CLS and Pd\textsubscript{x}/CLS, respectively; sharp peaks indicate that all synthesized samples are well crystallized. The strong and sharp peaks of CLS suggest that it exists as ultrathin nanosheets, which make an ideal space for loading of Pd NPs.\textsuperscript{46} The XRD pattern of Pd\textsubscript{100}/CLS shows two strong reflection peaks at 40.119 and 68.121° associated with arrangement of (111) and (220) planes of Pd (JCPDS 46-1043). These diffraction peaks were assigned to Pd structure, forming the successful formation of Pd\textsubscript{100}/CLS. These two strong reflection peaks at 40.119 and 68.121° associated with arrangement of (111) and (220) planes of Pd (JCPDS 46-1043). These diffraction peaks were assigned to Pd structure, thus confirming the successful formation of Pd\textsubscript{100}/CLS. When curves were meticulously compared, a significant decrease in intensity was observed around 26.62, 29.3, and 36.4° owing to the immobilization of Pd NPs. It is interesting to note that Pd has a face-centered cubic structure; the lattice parameter of Pd can be achieved using XRD pattern and following the equation (Bragg’s law)\textsuperscript{37}

\begin{equation}
d_{\text{lad}} = \frac{\lambda}{2 \sin \theta}
\end{equation}
where $a$ is the lattice parameter of the cubic crystal; $h$, $k$, and $l$ are the Miller indices of the Bragg plane; $\lambda$ is the wavelength of the X-ray radiation used; and $d_{hkl}$ is the distance between layers in a crystal. The strong and sharp diffraction peak of the (111) Bragg plane was employed to estimate lattice parameters of all samples. Moreover, the mean crystalline sizes were gauged by Scherrer’s equation:

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

where $\lambda = 0.154$ nm, $\beta$ is the full width of half-maximum intensity (FWHM) in radians, and $\theta$ is the Bragg diffraction peak. The calculated results by using eqs. 2, 3, and 4 are presented in Table 1. Our procedural increase in time did not affect the mean crystalline sizes, which is considered an obvious benefit.

| sample name    | $2\theta$ | $hkl$ | $D$ (nm) | $a$ (Å) |
|----------------|-----------|-------|----------|---------|
| Pd15/CLS       | 40.02     | 111   | 19.89    | 3.89    |
| Pd30/CLS       | 40.01     | 111   | 19.89    | 3.88    |
| Pd100/CLS      | 40.04     | 111   | 19.88    | 3.89    |

FT-IR provides analysis to justify the presence of functional groups in the materials. Figure 3 shows representative FT-IR spectra, recorded in the wavenumber range 400–3800 cm$^{-1}$, for CLS and Pd100/CLS. The comparison of the spectrum of lignin$^8$ and CLS (Figure 3a) shows the same main structural features of the samples. This is undoubtedly beneficial because the sulfonation did not alter the main structure and change just appeared in the lignin chains.$^8$ The most characteristic infrared bands of CLS appeared at 3000–3500 cm$^{-1}$ (Figure 3) associated with the OH stretching.$^8,46,49$ As shown in Figure 3b, the spectrum of Pd100/CLS shows the same peaks as CLS.

Figure 2. XRD pattern for (a) CLS, (b) Pd15/CLS, (c) Pd30/CLS, and (d) Pd100/CLS.

Figure 3. FT-IR spectrum for (a) CLS and (b) Pd100/CLS.

The Pd NPs’ immobilization on CLS did not generate any significant peaks but simply influenced the intensity of functional groups; the intensity of the main peaks of CLS and Pd100/CLS is presented in Figure 3.

The surface structure is studied in terms of the adsorption/desorption N$_2$ at 77 K on the CLS and Pd100/CLS surface, and the results are shown in Figure 4 and summarized in Table 2. Figure 4a shows the N$_2$ adsorption/desorption isotherm of the samples, which suggests that the adsorption hysteresis loop in the $P/P_0$ range is from 0.7 to 0.99. This is likely due to the filling and draining of the mesopores by capillary condensation and usually attributed to bottleneck pores.$^{33}$ While comparing
N2 adsorption for CLS and Pd100/CLS, in the range of $P/P_0 = 0.8−0.99$, a sharp increase of accumulation of N2 in the pores and the vacant space of Pd100/CLS becomes apparent. This leads to the conclusion that Pd100/CLS has a large surface area because of the aggregated Pd NPs.50,51 Pore structure (BJH) of the samples is depicted in Figure 4b, and the major peaks of CLS and Pd100/CLS were about 2.7 and 1.2 nm, respectively. BET results determined that surface properties of Pd100/CLS significantly increased in comparison with initial CLS. Interaction between Pd NPs and the surface of CLS leads to increase of mesoporous volume; consequently, the size and pore volume of CLS increased after Pd NPs’ loading.52 The increasing surface area is probably due to the doping effect and the formation of new pores because of the loading Pd NPs on the CLS surface,50 and this enhancement of surface area and pore volume offers a good opportunity to adsorb and store hydrogen.

The different magnification of SEM analyses for CLS nanocomposites are shown in Figure 5a,b, depicting that CLS has a ravelinike morphology with disparate porosity. It is envisaged that such a structure provides ideal space for attaching nanoparticles. The SEM images for Pd100/CLS (Figure 5c,d) confirmed the presence of Pd NPs on the CLS surface; Pd NPs appeared aggregated and did not show the regular morphology.

To scrutinize the present Pd NPs on the CLS surface, TEM analysis was performed for Pd100/CLS (Figure 6). Light gray thin films are CLS nanosheets interconnected in a disorderly arrangement, as corroborated by another report.53 Spherical-type structures were formed in some regions, indicating that Pd NPs aggregated with each other, the space between Pd NPs and CLS surface being the generated porosity. The average diameter of Pd NPs is estimated, with Image J software, to be about 8 nm. These results are in acceptable agreement with the BET and SEM analysis.

Figure 7 depicts SEM image of the ensuing electrodes with rough structures for easy access of active cites at the surface between electrodes and electrolyte medium.

Figure 8 shows the EDS analysis of nanocomposites and resulting electrodes. Figure 8b,d confirms the presence of Pd NPs in the nanocomposite.

Cyclic Voltammetry Studies. To comprehend the electrochemical conduction of samples, CV study was performed in a three-electrode cell filled with 1 M KOH at a sweep rate of 50 mV s$^{-1}$ using a stainless-steel mesh substrate deposited with CLS and Pd100/CLS. Figure 9a shows CV curves of the mesh substrate (curve I) and CLS electrode (curve II). According to the CV curves, the results suggest that the mesh substrate has no evident peaks in this potential window; i.e., it does not adsorb and desorb hydrogen. Throughout Figure 9, the CV curve of CLS shows minor faradic peaks, which means that the CLS can adsorb and desorb a little hydrogen. To take into account Pd NPs’ performance in adsorbing and desorbing hydrogen, the CV curve of Pd15-100/CLS is presented in Figure 9. As apparent, all curves show oxidation and reduction peaks, demonstrating that hydrogen was adsorbed and desorbed on the surface of the working electrodes. In the cathodic direction, in the scan to negative potential, the CV curve of Pd15-100/CLS shows a reduction peak (C) due to water decomposition, H formation, and adsorption at the electrode surface.44 In contrast, in the anodic direction, an oxidation peak (A) shows hydrogen desorbing on the surface of Pd15-100/CLS electrode, due to the faradic reaction. The reduction peak is associated with hydrogen adsorption on the Pd surface.12 The produced hydrogen was adsorbed and stored on the surface of the working electrodes. In the cathodic direction, in the scan to negative potential, the CV curve of Pd15-100/CLS shows a reduction peak (C) due to water decomposition, H formation, and adsorption at the electrode surface.44 In contrast, in the anodic direction, an oxidation peak (A) shows hydrogen desorbing on the surface of Pd15-100/CLS electrode, due to the faradic reaction. The reduction peak is associated with hydrogen adsorption on the Pd surface.12 The produced hydrogen was adsorbed and stored on the surface of the working electrode due to the polarization created by the applied potential. These potential peaks, in the cathodic and anodic process, show a quasireversible electrochemical reaction appearing on the Pdx/CLS electrodes. To assess the influence of Pd NPs in hydrogen adsorption/desorption, the oxidation and reduction peak currents, i.e., $I_A$ and $I_C$, are compared and listed in Table 3. The immobilization Pd NPs on CLS has a
meaningful effect on the oxidation and reduction peaks, thus emphasizing that Pd is an effective catalyst for hydrogen adsorption and desorption.

**Cyclic Life Performance.** The amount of hydrogen desorbed can be measured by the integration of the anodic peak. The total charge related to hydrogen desorption can be associated with the integral of the curve where atoms are being desorbed. Given that the electrode/electrolyte interface act as a capacitor, the measurement of \( Q_{H} \) is done by assuming a baseline to separate the double layer and faradic region. This part of the CV curve, pertaining to Pd100/CLS, is presented in Figure 10a. The red area corresponds to the double-layer capacitance, and the white area shows the amount of hydrogen desorption. The integration is defined by following equation

\[
Q_{H} = \frac{1}{\theta} \int_{0.85}^{0.35} (I_a - I_{dl}) dE
\]

where \( \theta \) is the sweep rate, \( dE \) is the potential window, and \( I_a \) and \( I_{dl} \) are the current due to the anodic peak and double-layer charging, respectively.

To investigate the cyclic life performance of Pd100/CLS, a CV curve for 100 cycles was obtained. By using eq 4 and CV data, \( Q_{H} \) was estimated and drawn as a function of the cycle’s number in Figure 10b. As the curve shows, the amount of hydrogen charge decays with the increase in the cycle number. In the first 20 cycles, a 43% decrease in \( Q_{H} \) is probably due to the oxidation of the electrode; \( Q_{H} \) decrease during scans maybe due to the separation of Pd100/CLS from the electrode surface.

**Catalytic Studies of Pdx/CLS Nanocomposites for Reduction of Environmental Pollutants.** In this work, Cr(VI), MB, and 4-NP were subjected to the reduction/degradation process using Pdx/CLS nanocomposite as a sustainable and recoverable catalytic nanosystem and HCOOH or NaBH\(_4\) as reducing agents in aqueous media. The reduction is important and the main chemical reaction in industrial organic chemistry, which is performed via an electron-transfer change. The progress of the conversion processes was checked via UV−vis analysis; Cr(VI), 4-NP, and MB have a typical absorption peak at 350, 317, and 664 nm, respectively.
Cr(VI) reduction to Cr(III) was examined by deploying HCOOH and K₂Cr₂O₇ as a hydrogen donor and chromium source, respectively, in the presence of Pd₁₅/CLS and Pd₁₀₀/CLS nanocomposites at 50 °C. The mechanism of Cr(VI) reduction by Pdₓ/CLS nanocomposite was studied using hydrogen transfer of HCOOH and electron transfer between oxygen as a ligand to Cr(VI) metal in solution (Scheme 1). HCOOH was first decomposed to hydrogen and carbon dioxide after adsorption onto nanocomposite surface; Cr₂O₇²⁻ was then converted to Cr(III) by the formation of bubbling H₂ gas (eqs 1 and 2, Scheme 1).

After the addition of HCOOH and beginning of the Cr(VI) reduction, the peak at 350 nm completely vanished within 2 min (Figure 11), with the disappearance of the yellow color. Without the addition of Pdₓ/CLS nanocomposites and formic acid, the reduction of Cr(VI) did not occur and no color change was discernable even after 3 h (Table 4, entries 1 and 6). As shown in Table 1, in the presence of the CLS, the reduction of Cr(VI) was not completed even after 1 h (Table 1, entry 2). The CLS serves as a support and stabilizing agent and decreases the agglomeration of Pd NPs, providing a synergistic effect in the reduction process. The best results were attained using 5.0 mg of Pd₁₀₀/CLS and 1.0 mL of aqueous HCOOH solution at 50 °C within 120 s (158 s) (Table 4, entries 4 and 7).

Additionally, the catalytic prowess of Pd₁₅/CLS and Pd₁₀₀/CLS nanocomposites was studied toward 4-NP reduction to 4-AP; the mechanism for this process by Pdₓ/CLS nanocomposites, via an electron-transfer reaction using NaBH₄ at ambient temperature, is depicted in Scheme 2. The reduction process can be performed by the adsorption of the BH₄⁻ ions on the Pdₓ/CLS surface and the transfer of active hydrogen species via the π−π stacking interactions; the reduction process can be catalyzed using Pd NPs along with the formation of a metal hydride complex. As shown in Scheme 2, the formed 4-AP was finally desorbed from the Pdₓ/CLS surface and another catalytic cycle can start anew.

During the reduction reaction, the electron transfers between BH₄⁻ ions (reductant) and Pd NPs (oxidant) can result in the disappearance of a chiastic SPR at λ_max ~317 nm and appearance of a new SPR at 297 nm (Figure 12). Upon the addition of Pdₓ/CLS nanocomposites to the reaction solution and start of the reduction reaction, the peak intensity at 317 nm quickly shifted to 400 nm and decreased with the concomitant disappearance of the yellow color within 60 s at ambient temperature. The peak observed at λ_max ~400 nm was associated with the produced 4-nitrophenolate ions following the addition of NaBH₄ to 4-NP solution, disappearing after the 4-NP reduction. The reduction process was examined with time variation using various amounts and conditions, and results are summarized in Table 5. In the absence of the Pdₓ/CLS nanocomposites and NaBH₄ reductant, no reaction and obvious color change was observed (Table 5, entries 1 and 6). The catalytic performance of the Pd₁₅/CLS and Pd₁₀₀/CLS nanocomposites became apparent in the reduction of 4-NP to 4-AP (Table 5, entries 3–12); the Pd₁₅/CLS and Pd₁₀₀/CLS nanocomposites are much more reactive than CLS (Table 5, entry 2). Additionally, CLS, as a support, prevents the...
aggregation of Pd NPs. In addition, the catalytic activity of the Pd100/CLS nanocomposite is better than Pd15/CLS in a comparatively shorter time period. As shown, the reduction of 4-NP to 4-AP was quickly completed within 60 s using 7.0 mg of Pd100/CLS nanocomposite as a highly active nanocatalyst and 100 equiv of NaBH4 (Table 5, entry 12). Additionally, the reaction time for the reduction reaction increased to 83 and 75

Figure 8. EDS analyses of (a) CLS, (b) Pd100/CLS nanocomposite, (c) CLS electrode, and (d) Pd100/CLS electrode.

Figure 9. CV curves of (a) mesh substrate (curve I) and CLS electrode (curve II) (b–d) Pd100/CLS electrodes in 1 M KOH at the 50 mV s⁻¹ sweep rate; A and C represent the oxidation and reduction peaks, respectively.

Table 3. CV Data for CLS and Pdx/CLS

|       | $I_p$ (A g⁻¹) | $E_p$ (V) | $I_{op}$ (A g⁻¹) | $E_{op}$ (V) |
|-------|---------------|-----------|------------------|-------------|
| CLS   | −0.1          | −1.04     | 0.03             | −0.7        |
| Pd15/CLS | −0.15        | −1.01     | 0.18             | −0.7        |
| Pd30/CLS | −0.5         | −1.11     | 0.31             | −0.7        |
| Pd100/CLS | −1.85        | −1.02     | 1.3              | −0.7        |

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s in the presence of 50 or/and 79 equiv of the NaBH4 solution, respectively (Table 5, entries 10 and 11).

For the other pollutant, MB, a similar method was repeated to assess the catalytic ability of the Pd\textsubscript{x}x/CLS nanocomposites and the results are reported in Table 6; generally, Pd\textsubscript{100}/CLS nanocomposites could reduce MB solution in a short span of time. The investigation of the MB reduction was performed by recording the process of the UV absorption spectra at $\lambda_{\text{max}}$ $\sim$ 664 nm (Figure 13). According to the obtained results, no color change was observed without assistance of Pd\textsubscript{100}/CLS nanocomposites and NaBH\textsubscript{4} reductant even after 60 min (Table 6, entries 1 and 4). The obtained results (Table 6) depict that the Pd\textsubscript{15}/CLS has weaker performance for the MB reduction, and a relatively slower reaction rate was observed in comparison with Pd\textsubscript{100}/CLS. The best activity for the MB reduction was obtained using 3.0 mg of Pd\textsubscript{100}/CLS nanocomposite; further increments of its amount did not improve the results (Table 6, entries 5 and 6).

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**Table 4. Optimization of Conditions for the Cr(VI) Reduction by Pd\textsubscript{x}/CLS Nanocomposites and HCOOH at 50 °C**

| entry | catalyst (mg) | HCOOH (mL) | time |
|-------|---------------|-------------|------|
| 1     | CLS (5.0)     | 1.0         | 3 h\textsuperscript{a} |
| 2     | Pd\textsubscript{15}/CLS (3.0) | 1.0 | 3:40 min |
| 3     | Pd\textsubscript{15}/CLS (5.0) | 1.0 | 2:38 min |
| 4     | Pd\textsubscript{100}/CLS (7.0) | 1.0 | 3 h\textsuperscript{a} |
| 5     | Pd\textsubscript{100}/CLS (3.0) | 1.0 | 2:15 min |
| 6     | Pd\textsubscript{100}/CLS (5.0) | 1.0 | 2 min |

\textsuperscript{a}No reaction. \textsuperscript{b}Not complete.

**Scheme 2. 4-NP Reduction Mechanism Using Pd\textsubscript{x}/CLS Nanocomposite**

For the other pollutant, MB, a similar method was repeated to assess the catalytic ability of the Pd\textsubscript{x}/CLS nanocomposites and the results are reported in Table 6; generally, Pd\textsubscript{x}/CLS nanocomposites could reduce MB solution in a short span of time. The investigation of the MB reduction was performed by recording the process of the UV absorption spectra at $\lambda_{\text{max}}$ $\sim$ 664 nm (Figure 13). According to the obtained results, no color change was observed without assistance of Pd\textsubscript{x}/CLS nanocomposites and NaBH\textsubscript{4} reductant even after 60 min (Table 6, entries 1 and 4). The obtained results (Table 6) depict that the Pd\textsubscript{15}/CLS has weaker performance for the MB reduction, and a relatively slower reaction rate was observed in comparison with Pd\textsubscript{100}/CLS. The best activity for the MB reduction was obtained using 3.0 mg of Pd\textsubscript{100}/CLS nanocomposite; further increments of its amount did not improve the results (Table 6, entries 5 and 6). Since both, the adsorption of reactants and electron-transfer process from the BH\textsubscript{4}$^-$ to MB take place on the Pd surface, the Pd\textsubscript{100}/CLS nanocomposite is much more reactive than CLS. CLS, as a support, prevents the aggregation of Pd NPs, and its synergic effect is important in the reduction process.

**Catalyst Recyclability.** The Pd\textsubscript{100}/CLS nanocomposite revealed excellent reusability and recyclability for catalyzing the
4-NP reduction using NaBH₄ under equivalent empirical conditions. The easy separation of the synthesized Pdx/CLS allows it to be collected and removed from the reaction mixture via simple filtration. After carrying out the reduction process, the used nanocatalyst can be collected, washed with distilled water and ethanol, and then dried for the consecutive cycle. Figure 14 depicts that Pd100/CLS catalyzed the reduction of 4-NP with declined product yield of only 3% after eight consecutive runs.

**CONCLUSIONS**

Commercial lignosulfonate (CLS) was modified by means of Pd NPs to accomplish hydrogen storage in alkaline medium, and the same catalyst was equally efficient for the environmental cleanup of common pollutants in aqueous medium. Characterization techniques, viz., XRD, FT-IR, BET/BJH, SEM, EDS, and TEM, were deployed to study the surface of the representative samples. The results show that the LAL process managed to fabricate Pd NPs and their subsequent deposition procedure on CLS was successful. The electrochemical study has shown an encouraging hydrogen storage capacity due to the loading of Pd NPs, which was about 5.8 C g⁻¹; Pd NPs serve as active sites for the hydrogen adsorption. The present study also illustrates that Pdx/CLS nanocomposites have exceptional catalytic activity and stability for the reduction of common environmental pollutants in water, namely, 4-NP and MB with NaBH₄ and Cr(VI) with HCOOH.

**EXPERIMENTAL SECTION**

**Instruments and Reagents.** Commercial calcium lignosulfonate (CLS) with an ideal formula was used. Powder X-ray diffraction patterns were applied to characterize the structure

![Figure 12](https://example.com/fig12.png)

**Figure 12.** UV–visible spectra of the NaBH₄-induced reduction of 4-NP using 7.0 mg of Pd100/CLS nanocomposite.

**Table 5.** Optimization of 4-NP Reduction (2.5 × 10⁻³ M) Using Pdx/CLS Nanocomposites and NaBH₄ at Ambient Temperature

| entry | catalyst (mg) | NaBH₄ (equiv) | time (min) |
|-------|---------------|--------------|------------|
| 1     | CLS (7.0)     | 100          | 170ᵃ       |
| 2     | Pd15/CLS (5.0) | 100          | 14:51      |
| 3     | Pd15/CLS (7.0) | 100          | 2:55       |
| 4     | Pd15/CLS (7.0) | 79           | 4:30       |
| 5     | Pd15/CLS (7.0) | 100          | 2:30       |
| 6     | Pd100/CLS (5.0) | 0.0          | 50ᵇ       |
| 7     | Pd100/CLS (5.0) | 50           | 3:5       |
| 8     | Pd100/CLS (5.0) | 79           | 2:20       |
| 9     | Pd100/CLS (5.0) | 100          | 2:5       |
| 10    | Pd100/CLS (7.0) | 50           | 1:23       |
| 11    | Pd100/CLS (7.0) | 79           | 1:15       |
| 12    | Pd100/CLS (7.0) | 100          | 1         |

ᵃNo reaction.ᵇNot complete.

**Table 6.** Optimization for the Reduction of MB (3.1 × 10⁻⁵ M) Using Pdx/CLS Nanocomposites and NaBH₄

| entry | catalyst (mg) | NaBH₄ (M) | time |
|-------|---------------|-----------|------|
| 1     | CLS (3.0)     | 5.3 × 10⁻³ | 60 minᵃ |  |
| 2     | Pd15/CLS (3.0) | 5.3 × 10⁻³ | 150 minᵇ |  |
| 3     | Pd100/CLS (3.0) | 0.0       | 5 s   |  |
| 4     | Pd100/CLS (3.0) | 5.3 × 10⁻³ | 60 minᵃ |  |
| 5     | Pd100/CLS (5.0) | 5.3 × 10⁻³ | 1 s   |  |
| 6     | Pd100/CLS (5.0) | 5.3 × 10⁻³ | 1 s   |  |

ᵃNo reaction.ᵇNot complete.
of samples (XRD, Unisantis xmd300 model), the wavelength of 1.5405 Å, and the 2θ range 10–80°. A UV–vis spectrophotometer (Hitachi, U-2900, λ = 200–700 nm) was employed to record the reduction of MB, 4-NP, and Cr(VI). A scanning electron microscope (Cam scan MV2300), equipped by an energy dispersive X-ray spectrometer (EDS), was used to determine the morphologies and the elemental analysis of nanocomposites and electrodes, respectively. To measure the chemical environment of samples, Fourier transform infrared (FT-IR, Thermo Nicolet) spectra were acquired. Brunauer–Emmett–Teller (BET, BELSORP-mini II) and Barret–Joyner–Halenda (BJH) analysis were deployed to study pore size and surface morphology of samples. The presence of Pd NPs on CLS was visualized by using a transmission electron microscope (Zeiss-EM10C-100 kV). In addition, cyclic voltammetry was deployed to determine the electrochemical characteristics of the samples.

**Synthesis of Pd-Loaded CLS.** To produce colloidal Pd NPs, a bulk piece of palladium was ultrasonically cleaned in distilled water and acetone. The Pd target (99.9%, Aldrich) is positioned at the cell bottom filled with deionized water. The ablation process was carried out according to our earlier described procedure. The LAL process was performed, the color of deionized water turned black, affirming the presence of Pd NPs in deionized water. To prevent agglomeration and reduce the rate of production for Pd NPs due to absorption laser beam by NPs, the LAL process was carried out in 3, 6, and 20 stages, each stage being of 5 min for Pd15/CLS, Pd30/CLS, and Pd100/CLS, respectively. In each stage, 5 mL of deionized water was used in a way that about 2 mm water covers the whole target surface. After 5 min, the colloidal Pd NPs were extracted, and the LAL process, repeated with fresh deionized water. Finally, LAL was performed for different time periods: 15, 30, and 100 min. After the LAL process, CLS was added to the Pd NP colloidal solution and stirred with a magnetic stirrer for 24 h at room temperature. Finally, the ensuing nanocomposite was filtered and dried at ambient temperature in a dust-free atmosphere. According to LAL time, the nanocomposites were labeled Pdx/CLS, where x represents the ablation time (x = 15, 30, and 100 min). The schematic of the whole procedure is depicted in Figure 1a.

**Electrode Preparation.** CLS and Pdx/CLS were used to create the electrodes: about 2 mg of the samples was added into deionized water (3 mL) and sonicated for 15 min. A stainless-steel mesh (200 mesh, 0.36 cm²) was used as the substrate, which was washed by acetone and deionized water, respectively. Then, the electrodes were prepared by the drop casting method on the substrate and dried at room temperature (Figure 1b).

**Electrochemical Instrumentation.** All electrochemical measurements were made at ambient temperature by an autolab (PSTAT204) using a three-electrode cell composed of a working electrode, a reference electrode (Ag/AgCl), and a counter electrode (Pt plate). The KOH electrolyte was prepared at 1 M concentration. For minimizing the ohmic drop of electrolyte, reference electrode was placed close to the surface of the working electrode. CV measurements of the working electrodes were carried out in a potential range of −1.3 to 0 V with a scanning rate of 50 mV s⁻¹.

**General Procedure for the Reduction of Cr(VI).** To assess the reduction of Cr(VI) to Cr(III), an aqueous K₂Cr₂O₇ solution (3.4 × 10⁻⁵ M, 25 mL) was first mixed with Pdx/CLS nanocomposite (5.0 mg) and then a HCO₂H solution (1.0 mL, 88%) was added at 50 °C under constant stirring. UV–vis analysis was employed to monitor the process; the Cr(VI) aqueous solution has an absorption peak at 350 nm. After fading of the solution color (light yellow), the Pdx/CLS nanocomposite was removed, washed with EtOH and deionized H₂O, and utilized again in sequential cycles.

**4-Nitrophenol (4-NP) Reduction.** The efficacy of the Pdx/CLS nanocomposite was also evaluated in the 4-NP reduction to 4-AP using NaBH₄. In this experiment, 7.0 mg of Pdx/CLS were dispersed into aqueous 4-NP solution (2.5 mM, 25 mL) and then freshly prepared NaBH₄ solution (25 mL, 250 mM) was added under stirring at room temperature. The yellow color of the solution disappeared and it became colorless, indicating the completion of reduction. After affirming the end of the reduction process by UV–vis spectroscopy, Pdx/CLS was filtered off, washed with deionized H₂O, dried, and then reused for subsequent runs.

**Methylene Blue (MB) Reduction.** In this investigation, Pdx/CLS nanocomposite (3.0 mg) and aqueous MB solution (25 mL, 3.1 × 10⁻⁵ M) were shaken under stirring at room temperature for 60 s. A freshly prepared aqueous NaBH₄ solution (25 mL, 5.3 × 10⁻³ M) was quickly added to the mixture and was allowed to stir at room temperature while the above solution rapidly became colorless. At the end, the nanocomposite was similarly separated, washed, dried, and utilized in the following cycles with no significant changes in the catalytic activity.

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Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The supports provided by the Bu-Ali Sina University and the University of Qom are appreciated. RSV gratefully acknowledges the support from the Operational Program Research.
Development and Education—European Regional Development Fund, project no. CZ.02.1.01/0.0/0.0/16_019/0000754 of the Ministry of Education, Youth and Sports of the Czech Republic.

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