Study on Reduction of 4-nitrophenol by Magnetic Maize Straw Supported with Copper Nanoparticles

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Abstract

In this work, magnetic maize straw was prepared by the amidation process using renewable maize straw as starting material. After magnetic succinylated maize straw (Mag-S-MS) was mixed with cupric ions aqueous solution, Cu (II) could be captured by the amino and carboxylate groups. Then, the bonded Cu (II) was converted to valuable Cu nanoparticles (Cu NPS). It was characterized by SEM-EDS, XRD, XPS, and TGA, which indicated Cu NPS were formed successfully on Mag-S-MS without self-aggregation and oxidation. The above nanocomposites could be employed as a catalyst for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP). The effect of the dosage of Cu NPS loaded-Mag-S-MS, the initial concentrations of NaBH_4 and 4-NP were investigated, and a possible mechanism was discussed. The catalyst maintained relatively high catalytic activity after five cycle tests. Due to its superparamagnetic nature, it could be quickly collected from the aqueous solution under a magnetic field. These results could provide a method for using agricultural waste in nano catalytic reaction.

1. Introduction

In recent decades, water pollution has been a global environmental problem because of the indiscriminate disposal of industrial wastewater containing heavy metals and toxic organics. 4-nitrophenol (4-NP) is one of the essential agents in pharmaceuticals, dyes and pesticides. As it is difficult to degrade in the environment and harmful to human health, it has been classified as a priority pollutant by the Environmental Protection Agency (EPA) of the United States (Li et al. 2011). 4-aminophenol (4-AP) is less toxic and it is a valuable intermediate in synthesizing some medicines and cosmetics (Khan 2020). Converting 4-NP to 4-AP through an environmentally and efficient methods, toxic materials can be converted into useful substances. Metallic nanoparticles (MNPS) are the common catalysts in the reduction process, such as Au, Ag, Pd and Cu (Ding et al. 2017; Dong et al. 2017; Hareesh et al. 2016; Wang et al. 2020). Among them, Cu nanoparticles (Cu NPS) are relatively cheaper than the other noble metals. It is becoming a promising catalyst than those noble metals. Copper (II) is introduced into water by some industrial activities such as sensors, electronics, and biomedicines, which can cause severe damage to ecological systems. Therefore, it is a sustainable and green strategy to reduce Cu (II) in the industrial effluents to Cu NPS, which can be applied as a catalyst in transforming 4-NP to 4-AP.

Cu NPS are easy to form aggregation and be oxidized (Petri et al. 2009), which limited its practical applications. Much attention has been paid to obtain an effective solid support material to anchor Cu NPS. Over the years, numerous attempts have been focused on finding non-toxic, inexhaustible, and biodegradable composites from plant biomass (Akhtar et al. 2020; Su et al. 2019). Furthermore, when some functional groups such as carboxyl, amino, and hydroxyl are grafted into the supporting material, metal ions are immobilized spontaneously by electrostatic interactions, which can disperse the metal ions excellently to prevent self-aggregation (Liu et al. 2017). Maize straw (MS) is an abundant resource of agricultural waste in China, and millions of tons are produced every year. However, most of them are incinerated or abandoned, causing significant waste and pollution. Hence, the application of maize straw has drawn much attention to removing the toxic metal, which is one of the effective ways to make full

use of the abundant bioresource. Based on our previous research, the carboxylic acid functions on succinylated maize straw (S-MS) could adsorb heavy metal ions from the aqueous solution (Guo et al. 2015), which inspired us to serve S-MS as Cu NPS carrier.

It is worth emphasizing that the sustainability of the catalyst can be assessed by the possibility of its recovery. It is necessary to impart magnetic properties to the catalyst to be separated effectively by applying an external magnetic field (Reddy et al. 2013). Herein, we bonded amine-functionalized magnetite nanoparticles ($\text{NH}_2\text{-Fe}_3\text{O}_4$) with S-MS by the amidation process to obtain magnetic succinylated maize straw (Mag-S-MS). Then its remanent carboxylic acid functions were deprotonated by Na_2CO_3 to obtain the sodium salt of the carboxylates (Mag-NaS-MS) to capture Cu(II). Finally, the bonded Cu(II) ions on Mag-NaS-MS were converted into valuable Cu NPS by NaBH_4 , which presented a catalytic activity to reduce 4-NP into 4-AP.

2. Materials And Methods

2.1 Materials

Maize straw was harvested from Dalian, China. After being cut into 5 cm length pieces, it was mixed with 10% NaOH for 2 h at 25 °C. The alkalized solid was washed with deionized water to the neutral and dried at 80 °C in the oven. The above obtained solid was smashed to pieces with sizes 50-500 μm . A amount of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ was added into 100 mL distilled water to obtain the stock Cu(II) solution. All chemicals were analytical grade and were used as received.

2.2 Preparation of S-MS

S-MS was prepared by a chemical method according to (Guo et al. 2015). 1.0 g succinic anhydride and 0.5 g MS were first mixed with 50 mL of xylene. Then, 1.4 mL of triethylamine was added to the reaction mixture and refluxed for 8 h. The resultant solid was filtered and washed with ethanol and water.

2.3 Preparation of amine-functionalized magnetic nanoparticles

$\text{NH}_2\text{-Fe}_3\text{O}_4$ were prepared by a solvothermal method (Wang et al. 2006). After 3.0 g $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$, 2.0 g anhydrous sodium acetate, and 6.5 g 1,6-hexanediamine were dissolved in 30 mL of ethylene glycol, the solution was stirred vigorously at 50 °C for 30 min to obtain a transparent solution. This mixture was then transferred into a 50 mL Teflon-lined stainless steel autoclave and reacted at 198 °C for 6 h. The products were washed with water and ethanol and finally dried in vacuum at 50 °C.

2.4 Preparation of Mag-S-MS and Mag-NaS-MS

1g S-MS (5.8 mmol/g of carboxylic acid functions) and a certain amount of N,N'-diisopropylcarbodiimide (DIC) were added into a three-neck flask containing 50 mL dimethylformamide (DMF) and stirred at 30 °C for 2 h to activate the carboxylic acid functions. Then 0.3 g $\text{NH}_2\text{-Fe}_3\text{O}_4$ was added into the reaction

mixture and stirred for another 15 h. After the resulting black solid was separated by magnetic decantation, it was washed with deionized water and 95% ethanol. Afterward, the product was dried overnight through desiccation and was named Mag-S-MS.

Mag-NaS-MS was prepared through the alkalization process. Mag-S-MS was mixed with sodium carbonate solution (0.01 mol/L) for 2 h at 25 ± 2 °C. The product was washed with deionized water until the effluent was neutral. The sample, designated as Mag-NaS-MS, and was dried in vacuum at 50 °C.

2.5 Fabrication and catalytic performance of Cu NPS-loaded-Mag-S-MS

At 25 ± 2 °C, Mag-NaS-MS was shaken with Cu(II) solution (100 mg/L) on a thermostat water-wash shaker (SHZ-82 A, China) with a shaking speed of 150 rpm for 2h. After shaking, the Cu²⁺ loaded Mag-S-MS was washed with ultra-pure water several times to remove the unbonded Cu²⁺, Cu²⁺ loaded Mag-S-MS was shaken with 1M NaBH₄ for 2h on a thermostat water-wash shaker.

The catalytic reduction of 4-NP was conducted in a quartz cell containing a mixture of 0.3 mL of 4-NP (5×10^{-4} M), 1.2 mL of 0.01 M NaBH₄, and 1.5 mL of ultrapure water. To this mixture, a given amount of the nano composite (Cu NPS-loaded-Mag-S-MS) was incorporated as a catalyst. The catalytic reaction was recorded by UV-Vis spectrophotometer (VARIAN, SCAN-50) over the scanning range from 250 to 500 nm.

The rate constant (k) was measured as a function of time by recording the change in the intensity of the absorption peak at 400 nm. To study the reusability of the catalyst, the black solid was separated under a portable magnet. After being washed with ultra-pure water, it was used consecutively in the same reaction system.

2.6 Characterization and measurements

The functional groups present in Mag-S-MS were characterized by the FTIR spectrum (Perkin-Elmer, USA). The surface morphologies of all the specimens were obtained by a field emission SEM (JSM-6460, JEOL, Japan), equipped with an energy dispersive X-ray spectroscope (Oxford, British). XRD patterns were acquired on a Shimadzu XRD-6100 diffraction with CuK α radiation ($\lambda = 1.54060$ Å) from 5° to 80°. The magnetic properties of all samples were measured with a Lake Shore 7410 VSM at room temperature. Thermogravimetric analysis (TGA, Perkin-Elmer, USA) was performed from 25 °C to 600 °C at a heating rate of 10 °C /min under nitrogen flow. The XPS spectra were obtained by an X-ray photoelectron spectroscopy (Thermo VG ESCALAB 250, USA) equipped with an Al-K α X-ray source (1486.6 eV).

3. Results And Discussion

3.1 Preparation of Mag-S-MS and Cu NPS-loaded-Mag-S-MS

The synthesis route of Mag-S-MS is shown in Fig. 1. The carboxylic acid functions of S-MS were used to synthesize Mag-S-MS. DIC was used as a coupling agent to activate the carboxylic acid carbonyl and amine-functionalized magnetic nanoparticles were introduced through the formation of an amide bond (Gurgel et al. 2009).

There are two new strong bands at $1550\text{--}1650\text{ cm}^{-1}$ in the FT-IR spectra of Mag-S-MS, which correspond to the presence of amide function (Fig. 2b). The band at 1640 cm^{-1} corresponds to the N-H flexural vibration of the carbonyl of the amide function (Jr et al. 2007). The new band appears at 1550 cm^{-1} , corresponding to the angular deformation of the N-H bond of the amide function (Zhao et al. 2013). In addition, the appearance of a peak at 567 cm^{-1} in the FT-IR spectra of Mag-S-MS, which corresponds to the stretching vibrations of Fe-O (Hao et al. 2010), and demonstrates that the magnetic nanoparticles were introduced.

According to Guo et al. (2015), Mag-S-MS could be deprotonated and converted to its sodium salts (Mag-NaS-MS) by Na_2CO_3 . The anionic groups (COO^-) could anchor copper ions, the adsorption properties of Mag-NaS-MS toward Cu (II) were investigated by the batch adsorption experiments. The adsorption behavior and mechanism were discussed in Section S1 and S2 in Supplementary information, respectively. The carboxylate groups on Mag-NaS-MS played a critical role in adsorbing Cu (II) , which formed a monodentate structure with Cu (II) (Fig S6). The Cu (II) ions bonded through the amino and the carboxylate groups were well dispersed on the Mag-S-MS to inhibit the self-aggregation of the reduced Cu NPS .

The cupric ions adsorbed on Mag-NaS-MS were reduced in situ by NaBH_4 to Cu NPS , which were applied in the further catalytic degradation process.

3.2 Characterization

3.2.1 XRD analysis

Figure 3 shows XRD patterns of S-MS, $\text{NH}_2\text{-Fe}_3\text{O}_4$, Mag-S-MS, and Cu NPS -loaded-Mag-S-MS. For $\text{NH}_2\text{-Fe}_3\text{O}_4$, the peaks at $2\theta = 30.1^\circ, 35.5^\circ, 43.1^\circ, 53.4^\circ, 57.0^\circ$, and 62.6° are six characteristic peaks of Fe_3O_4 , which belong to the (220), (311), (400), (422), (511) and (440) planes of Fe_3O_4 , respectively (Hao et al. 2010). In the XRD pattern of S-MS, the broad peak at $2\theta = 20.9^\circ$ is considered as the amorphous cellulose phase (French 2014, 2020; Yao et al. 2020). Additionally, the diffraction peaks of S-MS and $\text{NH}_2\text{-Fe}_3\text{O}_4$ are both found for Mag-S-MS, indicating that the crystalline structure in the cellulose matrix and $\text{NH}_2\text{-Fe}_3\text{O}_4$ was not destroyed during amidation. Fig. 3d shows the XRD pattern of Cu NPS -loaded-Mag-S-MS. Comparing with Mag-S-MS, Cu NPS loaded-Mag-S-MS exhibits well crystalline intense peaks at 50.5° and 74.2° , which can be indexed to the (200) and (220) crystal planes of metallic Cu phase (JCPDS card no. 4-0836), respectively. These observed peaks suggest Cu NPS were obtained by the reduction of adsorbed copper ions from the solution. However, the characteristic peak at 43.3° of Cu (111) is not observed, which might be shielded by the peak of Fe_3O_4 .

3.2.2 SEM investigation

SEM images of S-MS and Mag-S-MS show that the Mag-S-MS surface is much rougher than S-MS (Fig. 4a, b). Fig. 4b displays the spherical structure of Fe_3O_4 nanoparticles in diameter between 50-85 nm were dispersed on the surface of S-MS. After being reduced by NaBH_4 in-situ, it was found that the synthesized copper nanoparticles had flower shapes (Fig. 4c), and its diameter was approximately 220-800 nm. The Cu NPS were uniformly dispersed on the surface of Mag-S-MS without aggregation, which are the potential catalytic sites.

From the EDS spectra, it can be found that there was no Fe element exists in S-MS, while the proportion of Fe in Mag-S-MS was 21.70%, which was introduced by the amidation reaction (Fig. 4d and Fig. 4e). There was no Cu element in Fig. 4d and Fig. 4e, but the distribution elements (Fe and Cu) can be observed in the EDS mapping (Fig. 4f inner image).

3.2.3 XPS spectroscopy

As shown in Fig. 5a, after adsorbing Cu^{2+} , the $\text{Cu}2p$ XPS spectra of Mag-S-MS are at 934.7 and 954.7 eV, which are vanished after the formation of Cu NPS-loaded-Mag-S-MS. XPS peaks for Cu in Cu NPS-loaded-Mag-S-MS are detected at 932.7 and 952.5 eV (Fig. 5b). The difference value (19.8 eV) is the result of the spin-orbit splitting of $\text{Cu}2p\ 3/2$ and $\text{Cu}2p\ 1/2$ (Zanganeh et al. 2018), which demonstrates metallic copper (Cu^0) is embedded in the carrier (Mag-S-MS) successfully.

3.2.4 Thermal properties

Figure 6 shows the TGA curves of Mag-S-MS and Cu NPS-loaded-Mag-S-MS. In the initial stage of 50-200 °C, only 3% weight loss is observed because of the evaporation of physically adsorbed water. The main thermal degradation is observed in the range of 200-400 °C, due to the thermal degradation of maize straw. In the third stage of 400-600 °C, after maize straw was burned off, the weight loss of Mag-S-MS and Cu NPS-loaded-Mag-S-MS are approximately 80.1% and 70.1%, respectively. The residual component increased indicates the existence of Cu nanoparticles, which is in accorded with the results of XRD and XPS. In summary, Cu NPS were successfully loaded on Mag-S-MS carrier.

3.2.5 Magnetic properties

The magnetization curves of $\text{NH}_2\text{-Fe}_3\text{O}_4$, Mag-S-MS, and Cu NPS-loaded-Mag-S-MS are displayed in Fig. 7. The zero coercivity and reversible hysteresis behaviors indicate the superparamagnetic nature of the magnetic adsorbents. In addition, the saturation magnetization of Mag-S-MS is reduced to 17.2 emu/g, for being introduced nonmagnetic S-MS, but higher than the reported magnetic straw (Song et al. 2015; Tian et al. 2011). In comparison to Mag-S-MS, the saturation magnetization of Cu NPS-loaded-Mag-S-MS is obviously reduced (11.5 emu/g), which could be due to the screening effect of Cu NPS gathering around Fe_3O_4 nanoparticles (Su et al. 2019).

The inset of Fig. 7 shows that Cu NPS-loaded-Mag-S-MS could be dispersed homogeneously without a magnetic field. However, it was drawn to the glass bottle side by a magnetic bar in 10 s. Therefore, Cu NPS-loaded-Mag-S-MS could be separated and collected easily from the treated solution via the use of an external magnetic field, which is beneficial to develop a recyclable catalyst for its practical applications.

3.3 Catalytic reduction of 4-NP

3.3.1 Mechanism of catalytic reduction of 4-NP

It is thermodynamically favorable process for the catalytic reduction of 4-NP to 4-AP in the presence of NaBH_4 because their standard electrode potential (E for 4-NP/4-AP = -0.76 V, $\text{H}_3\text{BO}_3/\text{BH}_4^-$ = -1.33 V) is 0.67, which is larger than zero (Khan 2020). As soon as 4-NP was mixed with an aqueous solution of NaBH_4 , the color of the solution was changing from light yellow to yellowish-green immediately, which indicated phenolate anions of 4-NP were formed (Khan et al. 2020). On the other hand, a strong absorption peak shifted from 317 nm to 400 nm, monitored by UV-Vis absorption spectroscopy, and it was almost unchanged in 1 h without the catalyst. However, the solution gradually became transparent within 10 minutes (Fig. 8) when Cu NPS-loaded-Mag-S-MS (4 mg) was added into the 4-NP solution. Meanwhile, the peak intensity at 400 nm decreased gradually with the increase of the peak intensity of 4-AP at 303 nm. The two absorption peaks were an isosbestic point, indicating the successful reduction of 4-NP to 4-AP without any side reaction.

There were numerous bubbles on the catalyst's surface, which suggested that the hydrolysis of NaBH_4 could be stimulated efficiently by the catalyst. The reduction mechanism could be illustrated in Fig. 9 when BH_4^- was adsorbed by the catalyst, it could provide the electrons on the surface of Cu NPS-loaded-Mag-S-MS. Subsequently, the electrons could transfer to the nanocomposite and produce the hydrogen atom, which could attack the 4-NP molecules and reduce the nitro group to the amino group (Khan et al. 2017). Therefore, the catalyst assisted the electron in transforming from electron donor (NaBH_4) to acceptor (4-NP) to cut down the energy barrier and make the reaction possible. According to the reduction mechanism, the catalytic rate might depend on the amount of catalyst, the initial concentrations of NaBH_4 and 4-NP.

3.3.2 Effect of each variable on 4-NP reduction

The influence of different dosages of Cu NPS-loaded-Mag-S-MS on the reduction time was carried out under the same conditions (0.05 mmol/L 4-NP, 4 mmol/L NaBH_4 , and 20 °C). The pseudo-first-order kinetics (Eq. 1) (Liu et al. 2017) can be used to evaluate the catalytic effect.

$$\ln \left(\frac{A_t}{A_0} \right) = -kt$$

where A_0 and A_t are the absorbance of 4-NP at the initial time and instant time, respectively. k is the pseudo-first-order rate constant (min^{-1}), t is the reaction time (min).

Based on the linear relationship in Fig. 10a, it can be found that the catalytic kinetics of the reduction reaction fit the pseudo-first-order reaction (Liu et al. 2017). Table S5 showed the rate constants (k) calculated from the slopes with the different amounts of the catalyst. It is a positive correlation between amounts of Cu NPS-loaded-Mag-S-MS and the k value, which demonstrated that increasing the amount of catalyst would provide more active sites for reducing 4-NP and accelerate NaBH_4 hydrolysis more efficiently.

As shown in the mechanism of catalytic reduction (Fig. 9), NaBH_4 and 4-NP were the electron donor and acceptor, respectively. The effect of the concentration of NaBH_4 and 4-NP on the reaction was tested. The plots of $\ln(A_t/A_0)$ against reaction time for different concentration of NaBH_4 and 4-NP were shown in Fig. 10b and Fig. 10c, respectively. From which it can be found that a linear fitting curve was obtained, indicating that this reduction reaction followed a pseudo-first-order kinetic reaction. The rate constants (k) calculated from the slope was shown in Table S5. The reduction rate was higher with the increase of NaBH_4 because the higher concentration of NaBH_4 could provide the more amounts of hydrogen atoms, which could accelerate the reduction of the nitro group. The reaction rate also depended on the concentration of 4-NP. It can be seen from Table S5 that increasing the 4-NP concentration reduces the reduction rate constant. When the 4-NP concentration was 0.017 mM, the reduction rate constant k was 0.46 min^{-1} , but when the initial 4-NP concentration was increased to 0.05 mM, the reduction rate constant k decreased to 0.24 min^{-1} . This might be due to the concentration of NaBH_4 in the reaction was constant, and as the concentration of 4-NP increased, there were not enough hydrogen atoms in the reaction, resulting in reduced catalytic efficiency and a prolonged reaction time.

3.3.3 Reusability of Cu NPS-loaded-Mag-S-MS

Repeated usability of the catalyst is one of the critical parameters for its practical applications. Under the same experimental conditions, the reusability study of Cu NPS-loaded-Mag-S-MS catalytic reduction of 4-NP was evaluated five times. Fig S7 shows the value A_t/A_0 improved 5% after five cycles, which indicated that the catalytic efficiency was reduced slightly. It was the result of NaBO_2 accumulating on the catalyst surface during the NaBH_4 hydrolysis (Su et al. 2019). Additionally, Cu NPS-loaded-Mag-S-MS can be isolated easily from the solution only via an external magnet. The above research results showed that Cu NPS-loaded-Mag-S-MS has good catalytic efficiency and reusability. This research provides an alternative reference method for recycling waste agricultural resources and waste heavy metals to achieve sustainable development goals.

4. Conclusion

In this study, a low-cost magnetic carrier for copper nanoparticles was fabricated. Cu (II) ions were captured from the aqueous solution by its amino and carbonyl groups. After in situ reduction of Cu (II)

ions with NaBH_4 , the analysis of XRD, XPS and TGA, it proved that Cu^{2+} was successfully reduced to metallic copper (Cu^0). SEM-EDS images showed flower-like Cu NPS was uniformly dispersed on the surface of Mag-S-MS with diameter of 220-800 nm. Cu NPS-loaded-Mag-S-MS exhibited remarkable catalytic performance in the catalytic reduction of 4-NP to 4-AP in the presence of NaBH_4 . The reduction process followed the pseudo-first-order kinetic reaction. Increasing the amount of catalyst and NaBH_4 can accelerate the reduction reaction, while increasing the concentration of 4-NP has the opposite effect. Due to its superparamagnetism, the catalyst can be easily separated from the solution by external magnetic force. The catalyst recycling test showed that the catalytic activity did not decrease significantly after 5 cycles. The results of this study indicated that Cu NPS-loaded-Mag-S-MS had the characteristics of low cost, good reusability, convenient separation and high catalytic efficiency. Therefore, the concept of using agricultural waste maize straw and heavy metal Cu(II) pollutants in wastewater to prepare Cu NPS-supported-Mag-S-MS catalyst and use it for 4-NP reduction to 4-AP is consistent with the concept of human beings sustainable development.

Declarations

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Figures

Figure 1

Preparation process for Mag-S-MS and Mag-NaS-MS

Figure 2

FTIR spectra of S-MS(a) and Mag-S-MS(b)

Figure 3

XRD patterns of S-MS(a), NH₂-Fe₃O₄(b), Mag-S-MS(c) and Cu NPS-loaded-Mag-S-MS(d)

Figure 4

SEM images of S-MS (a), Mag-S-MS (b) and Cu NPS-loaded-Mag-S-MS (c); EDS spectra of S-MS (d), Mag-S-MS (e); EDS mapping of Cu NPS-loaded-Mag-S-MS (f)

Figure 5

XPS Cu core level spectra of Cu2p after the adsorption of Cu(II) onto Mag-S-MS (a) and Cu NPS-loaded-Mag-S-MS (b)

Figure 6

TGA results of Mag-S-MS (a) and Cu NPS-loaded-Mag-S-MS (b)

Figure 7

Magnetic hysteresis loops of $\text{NH}_2\text{-Fe}_3\text{O}_4$ (a), Mag-S-MS (b) and $\text{Cu NPS-loaded-Mag-S-MS}$ (c); the inset illustrates the magnetic separation on $\text{Cu NPS-loaded-Mag-S-MS}$ from aqueous solution

Figure 8

Time-dependent UV-Vis absorption spectra for 4-NP with NaBH₄ and the addition of Cu NPS-loaded-Mag-S-MS (4 mg). The inset illustrated the reduction of 4-NP with NaBH₄ before and after catalyzed by Cu NPS-loaded-Mag-S-MS, which can be gathered by an external magnetic field

Figure 9

Figure 10

Kinetic linear fitting curves for the catalytic reduction of 4-NP with different catalyst dosages (a), the initial 4-NP concentrations (b) and the initial NaBH₄ concentrations (c)

Supplementary Files

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