Preparation of silver-nanoparticle-loaded magnetic biochar/poly(dopamine) composite as catalyst for reduction of organic dyes

Hui Li [a,1], Danni Jiang [a,1], Zhenzhen Huang [a,1], Kai He [a,1], Guangming Zeng [a,*], Anwei Chen [b,*], Lei Yuan [a], Min Peng [a], Tiantian Huang [a], Guiqiu Chen [a]

[a] *College of Environmental Science and Engineering, Hunan University and Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha 410082, PR China*

[b] *College of Resources and Environment, Hunan Agricultural University, Changsha 410128, PR China*

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[*] Corresponding author: Tel.: + 86-731-88822829; Fax: +86-731-88823701.
E-mail address: zgming@hnu.edu.cn (G. Zeng), A.Chen@hunau.edu.cn (A. Chen).

[1] These authors contribute equally to this article.

Abstract

In the present study, Ag nanoparticles loaded on polydopamine coated magnetic biochar (MC-PDA-Ag) catalyst was prepared by *in-situ* reduction approach. The morphology, composition, and structure of MC-PDA-Ag were characterized by the transmission electron microscopy (TEM), the scanning electron microscope (SEM), X-ray diffractometer (XRD), X-ray photoelectron spectroscopy (XPS), and vibrating sample magnetometer (VSM). Catalytic reduction tests confirmed that MC-PDA-Ag catalyst showed excellent catalytic performance on the model dyes (MB, RhB, and MO) in the presence of $NaBH_4$. The reduction efficiency of MB exceeded 90% by MC-PDA-Ag even under different initial pHs (3-11) and different $NaNO_3$ concentrations (0-0.5 M) within 5 min, indicating that the MC-PDA-Ag catalyst has potential strong universal adaptability in dye wastewater treatment. Furthermore, no significant decrease in catalytic ability was observed after 5 recycles, and the catalyst could be separated by an external magnet, indicating that this as-prepared catalyst exhibited high reusability and easy separability. These results suggest that MC-PDA-Ag composite catalyst can be used as an efficient catalyst for the reduction of organic dyes, and shows great potential application in wastewater treatment.

Keywords:

Magnetic carbon; Silver nanoparticles; Catalytic performance; Catalytic stability; Water treatment

1. Introduction

With the rapid development of modern industry, environmental problems have begun to deteriorate gradually [1-3]. Especially, various organic pollutants are unavoidably released into the water bodies, causing a series of serious hazards to our water resource [4]. Among these organic pollutants, organic dyes have received great concerns, owing to their extensive production and application in many manufactures, such as leather, textile, cosmetics, and printing industry, etc [5-7]. Excessive emissions of organic dyes caused abnormal coloration of surface water, hinder sunlight penetration and reduction of oxygen dissolution, thus breaking the balance of aquatic ecosystems [8-12]. Meanwhile, these aromatic contaminants pose an immediate and potential toxicity to aquatic plants, aquatic animals, and microorganisms [13,14]. Furthermore, some aromatic pollutants can also cause carcinogenic and teratogenic effects in essential [4]. Up to now, a variety of treatment technologies have been applied to dispose organic dyes, including physical adsorption [15-17], catalytic reduction [18-21], membrane filtration [22], biodegradation [23,24], etc. Among these approaches, catalysis has been considered as one of the most efficient methods to purify effluent, showing benign practical and potential values in water treatment [25,26]. Therefore, it is worthwhile to further explore the development of effective catalysis for the treatment of dyes wastewater.

It is well known that catalysts are essential in catalytic reaction process, so the application of catalysts plays a crucial role in water purification [21,27]. With the development of modern nanoscience, nanoscale precious metal particles such as silver (Ag) and gold have been widely used as nanocatalysts, which has attracted great interest in scientific research. Ag nanoparticles (AgNPs) have been widely applied to the reduction and degradation of organic compounds due to their high catalytic activity [28,29]. However, bare AgNPs are easily aggregated during the catalytic process, thereby inhibiting their catalytic performance and practical application [30-32]. In order to overcome this drawback, the immobilization of silver nanoparticles on a desired support material has been regarded as an efficient method to increase the stability of AgNPs, which is conducive to the maintenance of the catalytic capacity of AgNPs [33,34]. Recently, biochar materials, converted from waste lignocellulosic biomass, have been used as nanoparticle carriers because of their advantages of low cost and easy availability compared with other matrix supporters (including graphene and carbon nanotubes) [35-40]. In addition, biologically derived carbon materials possess many outstanding properties, namely, high specific surface area, rich porosity, ample functional groups, excellent thermal stability, and chemical durability [41,42]. These vital properties make it an important nano-catalytic support material. For instance, Inyang et al. [43] reported a hybrid multi-walled carbon nanotube (CNT)-biochar nanocomposite material, Zhang et al. [44] reported a biochar-supported Zerovalent iron nanocomposite, and Zhang et al. [45] reported a biochar/AlOOH nanocomposite. However, it is not easy to recover these nanocomposites from solution. To achieve solid-liquid separation effectively, magnetic biochar has been developed for application due to the easy separation and recycling using external magnetic fields [45-47], which creates a broader prospect for the development and application of biochar materials [48,49].

In order to fabricate AgNPs on the support material, chemical reduction, one of the most effective methods, is often used for preparing the Ag-based composite material with the participation of a reducing agent [11,14,29]. In addition, in order to supersede the traditional toxic or hazardous chemical reducing agents such as hydrazinehydrate ($N_2H_4 \cdot H_2O$), sodium borohydride ($NaBH_4$), etc. Polydopamine, a green non-toxic polymer, has been selected as reducing agent for the synthesis of Ag-based materials [32,50]. It has been verified that the PDA monomers can self-polymerize under weak alkaline conditions at ambient temperature, and so the surface of the substrate material is covered with abundant amine groups and hydroxyl groups from the formed PDA, thereby promoting the reduction of the metal ions [51]. However, PDA as an adhesive and reductant for the preparation of AgNPs catalyst based on magnetic biochar has not been reported.

In this work, a novel cost-effective, environmentally friendly AgNPs loaded on polydopamine coated magnetic biochar (MC-PDA-Ag) catalyst material was prepared, in which PDA not only acted as a binder medium to connect the matrix of magnetic biochar and AgNPs, but also served as a reducing agent to reduce Ag^+ to Ag^0. We systematically studied its properties and its reduction capability by characterizing this as-prepared catalyst and performing the catalytic experiments. It was found that this catalytic material can enhance the reduction rate during the process of dyes decoloration by $NaBH_4$ solution, exhibiting excellent catalytic capacity, stability, and cyclicity. Therefore, this facile MC-PDA-Ag catalyst is capable of becoming a potential candidate for environmental remediation and the green synthesis process may contribute to its application in water purification.

2. Materials and methods

2.1. Materials

All reagents were used in this work without any further purification. Silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$), ammonia solution ($NH_3\cdot H_2O$), iron (III) nitrate nonahydrate ($Fe(NO_3)_3\cdot 9H_2O$) were purchased from Sinopharm Chemical Reagent Co., Ltd. Dopamine hydrochloride and Tris (hydroxymethyl) aminomethane (Tris) were obtained from HeFei BoMei Biotechnology Co., Ltd and Solarbin, Beijing, China, respectively. Methylene blue (MB), Rhodamine B (RhB), and methyl orange (MO) were purchased from Sigma-Aldrich. Besides, pine sawdust (PSD), used as the raw material for producing biochar, was a naturally abundant biomass waste obtained from a local timber treatment plant in Hengshui, China. The PSD was rinsed three times with ultrapure water, then dried in an oven at 85 ℃, then pulverized with a high-speed universal crusher, and finally sieved through a 100 meshes screen (0.15 mm) for further use.

2.2. Synthesis of composites

2.2.1. Synthesis of MC materials

Magnetic biochar material (MC) was prepared by pyrolysis of Fe loaded pine sawdust (Fe-PSD), which was synthesized through a biosorption process [37]. Firstly, 4 g of PSD and 400 mL of $Fe(NO_3)_3\cdot 9H_2O$ solution (2 mM) were added into a beaker, and stirred evenly at ambient temperature for 5 h. After completing the adsorption, the mixture was dried in an oven at 105 ℃ overnight, and sieved again with 100 meshes sieve (0.15 mm) to obtain the Fe-PSD powder. Then, Fe-PSD was transferred to a tube furnace for further calcining under a high purity nitrogen protection at a heating rate of 5 ℃ min^{-1}. After continuous pyrolysis for 2 h at 500 ℃, the MC was obtained from the tube furnace.

2.2.2. Synthesis of MC-PDA materials

Magnetic biochar-polydopamine (MC-PDA) composites were performed according to the report of Liu et al. [4]. Briefly, 400 mg of dopamine hydrochloride was dissolved into 200 mL of Tris-HCl (10 mM, pH=8.5) aqueous solution under stirring for 10 min, and 400 mg of MC material was dispersed into the former solution under room temperature for 24 h. After then, the suspension was filtered out, and the remaining residue was washed with ultrapure water and ethanol for several times, and dried at 50 ℃ in a vacuum oven. Finally, the obtained samples were MC-PDA composites.

2.2.3. Synthesis of MC-PDA-Ag materials

The experimental procedures of depositing AgNPs on MC-PDA composites were prepared according to the previous report [27]. 300 mg of the as-prepared MC-PDA was dispersed into 150 mL of the Tollens' reagent (silver ammonia solution, 10 mg mL^{-1}) under stirring for 24 h at ambient temperature. After separation of the suspension solution, the residue was washed with ultrapure water and ethanol several times, and dried under vacuum overnight. After that, the MC-PDA-Ag composites were obtained.

2.3. Characterization

The surface morphology of composites and microstructure of the coatings were confirmed by the high-resolution transmission electron microscopy (HRTEM, JEOL-2100F, Japan) and the scanning electron microscope (SEM, Sirion 200, FEI, USA) with an energy dispersive X-ray (EDX). The XRD pattern for MC-PDA-Ag was carried out by using a 18 kW rotating anode X-ray diffractometer (XRD, Rigaku Ultima IV, Japan) with a Cu Ka radiation source (30 kV/160 mA, λ=1.54056 Å). X-ray photoelectron spectroscopy (XPS, ESCALAB250, Thermo-VG Scientific, UK) served for the chemical binding information of the composites. The magnetic properties of composites were determined by using a vibrating sample magnetometer (VSM) at room temperature.

2.4. Catalytic reduction experiments

The aqueous reduction of MB dye with $NaBH_4$ solution was adopted as a main model reaction to investigate the catalytic activities of MC-PDA-Ag composites. In a typical reaction procedure, 10 mg of the MC-PDA-Ag was placed into a reaction tube containing 20 mL of MB aqueous solution (40 mg/L). Then, 20 mL of freshly prepared $NaBH_4$ solution (5.3 mM) was added into the solution with stirring at room temperature. When the mixed solution gradually faded from colored to colorless, the catalytic reaction was completed. The process of reaction could be monitored by the color weaken of dyes solution as indicated by the decrease in the maximum absorbance values (665 nm) of the MB solution UV-vis spectra. The catalytic reduction rate was calculated according to $(C_0\text{-}C_t)/C_0$, where C_0 is the initial concentration of dye solution, and C_t is the concentration of dye solution reaction at time t.

For comparison, different as-prepared catalysts (catalyst-free, MC, and MC-PDA) and different model dyes [MO and RhB] were employed for the catalytic reduction tests under the same procedure as MC-PDA-Ag and MB.

Meanwhile, MB was also used as a target pollutant to study the adsorption capacity of MC-PDA-Ag composites without the participation of $NaBH_4$. The main process is as follows: 10 mg of the MC-PDA-Ag, MC-PDA, MC was added to a reaction tube containing 40 mL of MB aqueous solution (20 mg/L), respectively. Then, after a certain period of adsorption, the quantitative mixture was taken for further solid-liquid separation, and finally the clarified solution was quantified by an UV-vis spectrophotometer (UV-2550, SHIMADZU, Japan).

In addition, the effects of initial solution pH and ionic strength on catalytic reduction experiments were also further evaluated. In the end, the cycle performance of MC-PDA-Ag was analyzed by separating the catalyst from solution and reusing for another test after washing three times.

3. Results and discussion

3.1. Synthesis and characteristics of composites

A schematic illustration of the synthesis route for MC-PDA-Ag composites were shown in Fig. 1. The Fe-loaded biomass waste was first converted into magnetic biochar material by high-temperature pyrolysis at 500 ℃ after drying. Then, the MC-PDA composites were achieved by mixing the MC particle into dopamine solution (pH = 8.5) under stirring, and the PDA coatings could be realized on the surface of MC due to the self-polymerization of dopamine. Afterword, MC-PDA-Ag composites were formed by depositing AgNPs on the surface of MC-PDA with silver ammonia solution, owing to the reducing capacity of PDA. The successful synthesis of MC-PDA-Ag composites were further verified using the characteristic analysis and the catalytic reduction experiment.

Please insert Figure 1

The morphology changes and elemental compositions of MC, MC-PDA, and MC-PDA-Ag samples were analyzed SEM-EDX. As shown in Fig. 2A and E, the MC matrix was a carbon skeleton, whose surface morphology was a clear porous structure and a smooth surface, which was consistent with the report of Tian et al [37]. The SEM images of MC-PDA (showed in Fig. 2B and C) displayed the successful implementation of the PDA spheres deposition process, resulting in a rough surface and abundant closely connected micro-spheres in MC. The size of PDA spheres was about 200 nm [52]. Meanwhile, the existence of N in the EDX image (showed in Fig. 2F) also manifested the PDA successfully wrapped the MC. In addition, PDA spheres coating almost completely wrapped the surface of MC-PDA, which might provide more in situ reductive sites owing to a larger surface area [50]. Fig. 2D demonstrated that irregular AgNPs were uniformly tight fixed on the MC-PDA surfaces, which might stem from the reducing ability of the catechols in PDA [50]. Additionally, after comparing three EDX spectra (Fig. 2E-G), it was found that the nitrogen element only appeared in the EDX spectra of MC-PDA and MC-PDA-Ag, and the relative higher content of silver element only appeared in the EDX spectra of MC-PDA-Ag. The presence of the Au element in all EDX spectra, combined with the results obtained by

XPS analysis, shows that Au wasn’t an element contained in the composites, and it was an element introduced by a gold plating process during using SEM. These results clearly demonstrate the successful PDA coating and the formation of AgNPs on the surface of MC-PDA-Ag composites.

Please insert Figure 2

In order to observe MC-PDA-Ag microstructures more clearly, HRTEM images were obtained (Fig. 3A and B). Fig. 3A revealed that the formed AgNPs were monodispersed on the MC-PDA support. Fig. 3B (inset) displayed the crystallite structure of Ag NPs by measuring the distances between the uniform crystal fringes. It was found that the observed spacing of 0.24 nm was related to the (111) crystal plane of metal Ag [27]. The crystal structures of MC and MC-PDA-Ag were confirmed by XRD analysis (Fig. 3C). As shown in the two XRD patterns, a broad and relatively weak characteristic peak was observed at $2\theta = 23.0°$, which owes to the amorphous carbon of biochar, consisted of aromatic carbon sheets oriented in a relatively random manner. The amorphous carbon is obtained by pyrolysis of lignocellulose in pine chips. [38]. Diffraction peaks marked with blue circles in XRD patterns were attributed to the formation of spinel cubic phase γ-Fe_2O_3 (JCPDF card No. 39-1346) and Fe_3O_4 crystallites (JCPDF card No. 26-1136) [27,28]. In addition, strong diffraction peaks of four Ag crystal planes were found at $2\theta = 38.8°$, 44.5°, 64.6° and 77.6° in the XRD pattern of MC-PDA-Ag, which corresponded to metallic silver (JCPDF card No. 65-2871) with a face-centered cubic crystal structure, indicating that large amounts of Ag^+ ions were successfully reduced to elemental Ag(0).

Please insert Figure 3

Please insert Figure 4

XPS was employed to analyze the composition elements and chemical binding information of material. Fig. 4A visualized the full scan spectrum of MC-PDA-Ag and indicated that the main elemental compositions of MC-PDA-Ag are C, N, O, Fe and Ag, which was in line with the EDX result (Fig. 2G). Fig. 4B showed that two distinct peak signals were observed at 368.23 and 374.23 eV, which were assigned to Ag 3d5/2 and Ag 3d3/2 of the representative binding energy of metallic Ag, respectively, indicating that AgNPs existed in the form of Ag^0 on the surface of MC-PDA-Ag. The C 1s region was comprised of four different peaks in Fig. 4C, among which the obvious peaks at 288.2 and 286.3 eV could be ascribed to C=O (quinone) and C-N/C-O-H [27,36], and the peak sites located at 285.1 and 284.5 eV could be assigned to C-H/C=C and C-C [35,52], respectively. Moreover, Fig. 4D showed that the N 1s spectrum was composed of three peaks. The first peak place situated at 401.7 eV was fitted with R-NH_2 (amine groups) of PDA, which might be due to the small quantity of noncovalently self-assembled dopamine co-existing with the covalently polymerized dopamine [51]. The other two peaks mapped at 400.5 and 399.58 eV could be attributed to R-NH-R/indole groups (substituted amines) and =N-R (imino groups) of PDA, respectively [53]. Meanwhile, The Fe 2p spectrum of MC-PDA-Ag was comprised of five peaks in Fig. 4E, among which the peak positions located at 711.4 and 724.5 eV were attributed to the Fe^{3+} [54], and the peak centered at 719.93 eV was characteristic of γ-Fe_2O_3 [38]. In addition, the peak positions located at 716.93 and 722.45 eV were assigned to the satellite peak and Fe^{2+} [54]. The results were consistent with the XRD results. The XPS turns out that the successful realization of magnetism in biochar, the formation of PDA coating, and the deposition of Ag nanoparticle on the MC-PDA-Ag.

Please insert Figure 5

Fig. 5 presented the magnetization hysteresis curve of MC, MC-PDA, and MC-PDA-Ag that obtained by using VSM at indoor temperature. Specific pertinent data revealed that the ferromagnetic properties of MC-PDA-Ag with a saturation magnetization (Ms) value of 2.76 emu g^{-1}, which was lower than those of MC (5.4 emu g^{-1}) and MC-PDA (4.9 emu g^{-1}). It indicates that the main reason for the decrease of Ms value of MC-PDA-Ag may be related to the deposited AgNPs, decrease of the proportion of magnetic properties and the formation of PDA coating also has a certain influence on it. Meanwhile, the Ms value also suggest that these materials can be separated from aqueous solution by an external magnetic field [55]. Furthermore, the inset of Fig. 5 displayed that MC-PDA-Ag composites could be efficiently separated from the solution by a permanent magnet, which demonstrated the magnetization process made the solid-liquid separation process easy.

3.2 Catalytic activity of MC-PDA-Ag towards MB dye

To investigate the catalytic reduction activity of MC-PDA-Ag on organic pollutants, MB was selected as a model pollutant during the reduction reaction process in the presence of NaBH$_4$. The process of catalytic reduction could be monitored by the time-dependent UV-vis spectra, due to the gradual disappearance of the dye color after the addition of the catalyst and $NaBH_4$ solution [21]. As shown in Fig. 6A, when MC-PDA-Ag and $NaBH_4$ were added to the MB solution, the absorption intensity of MB at 665 nm decreased quickly with the reaction time. The absorption peak of MB disappeared completely within 5 min, indicating that the MB aqueous solution could be entirely converted by $NaBH_4$ with the MC-PDA-Ag catalyst within 5 min. Meanwhile, the inset of Fig. 6A also displayed that the solution color also weakened from blue before the reaction to colorless. For comparison, the catalytic reduction process was also be monitored of MB solution in the presence of $NaBH_4$ using three different catalysts: MC-PDA, MC and catalyst-free. Fig. 6B showed that the absorption intensity of the MC-PDA had a significant decrease in the first minute and then a slight decrease in the next 4 min. The absorbance spectra of MC and catalyst-free exhibited only a slight decrease and almost no decrease within 5 min (Fig. 6C and D). The above results reveal that the catalytic activity of the MC-PDA-Ag in the reduction of MB by $NaBH_4$ is mainly concerned with the excellent performance of AgNPs deposited on the surface of MC-PDA.

Please insert Figure 6

Fig. 7A displayed the catalytic reduction rates of MB using different catalysts in the presence of $NaBH_4$ after 5 min of reaction. The catalytic reduction rates of MB were 99.09%, 26.90%, 17.03%, and 2.38% for MC-PDA-Ag, M-PDA, MC catalysts, and catalyst-free, respectively, demonstrating that successful loading of AgNPs on MC-PDA remarkably enhanced the catalytic reduction rate to MB solution. This was consistent with the conclusion obtained in Fig. 6. And the residual MB concentration in the solution was calculated by the calibration curve of absorbance *vs*. MB concentration (the inset of Fig. 7A). Meanwhile, in order to further evaluate the catalytic activity of MC-PDA-Ag for MB dye solution, the catalytic rate constant of MB was calculated to be 0.873 min^{-1} based on the fitting of catalysis data using pseudo first-order reaction kinetics in Fig 7B. The kinetic equation was described as $\ln(C_t/C_0) = -kt$, where C_0 is the initial concentration of MB, and C_t is the concentration of MB reaction at time t, and k is the rate constant. It was obvious that the catalytic rate constant of MC-PDA-Ag was the fastest among four reported similar catalysts in Table 1. In addition, Table 1 also displayed that MC-PDA-Ag had the shortest catalytic time for catalytic reduction of MB among these catalysts. These results manifest that MC-PDA-Ag has a significant advantage during reducing MB in the presence of $NaBH_4$.

Please insert Figure 7

Please insert Table 1

In order to understand the effect of the MC-PDA-Ag composites on the dye solution without the participation of $NaBH_4$, adsorption experiment was carried out. Fig. 8 showed the adsorption efficiencies of three different composites for MB dye molecules without $NaBH_4$. The result indicated the removal efficiency of MB by MC-PDA-Ag was 15.54% at the 5 min, while the catalysis degraded 99% MB in the presence of $NaBH_4$ within 5 min. This difference may be attributed to the MB molecule can fall off from the metal surface after the catalytic reaction, and then it can provide a contact site for the next MB molecule. The adsorption efficiency of

MC-PDA was higher than that of MC because its PDA layer had a large number of functional groups, which could enhance π-π stacking interactions and the electrostatic interaction between the PDA coating and the MB molecule [56]. The adsorption capacity of MC-PDA-Ag is mainly related to the introduced AgNPs. Since electron interaction can occur between the AgNPs embedded in the surface of the MC-PDA and the MB molecules, the Ag nanoparticle plays a dominant role in the adsorption process, which is in accordance with the result reported by Cui et al. [27]. The above results further indicate the catalytic reduction of MB dyes in the presence of $NaBH_4$ using MC-PDA-Ag composites can improve the catalytic efficiency and accelerate the reaction process.

Please insert Figure 8

Previous studies have collectively demonstrated that the reduction nature of MB molecules by $NaBH_4$ with AgNPs as catalyst is an electrochemical mechanism [27,57]. Because of AgNPs act as electronic relays, the catalytic reduction reaction between $NaBH_4$ and MB molecules can occur on the surface of AgNPs, indicating that the primary condition for the catalytic reduction reaction is that the MB and BH_4^- are adsorbed on the catalyst. In addition, BH_4^- is a nucleophile with a high electron injecting ability, which can promote the electron transfer from the donor $NaBH_4$ to the accepted dye molecules via metal nanoparticles. Similar mechanisms for other metal nanoparticles catalysts have also been presented in previous studies [57,58]. Therefore, it can be assumed that the catalytic reduction process in this work has also undergone a similar mechanism, which can be carried out in three steps: (1) the diffusion and competitive adsorption of the MB molecules and BH_4^- onto the surface of the AgNPs of MC-PDA-Ag; (2) the electrons donated by BH_4^- is injected to the electronic relay of AgNPs; and (3) MB dye molecules capture electrons from Ag NPs. Once a certain MB molecule acquires electron from the surface of MC-PDA-Ag catalyst, it would be immediately reduced and desorbed, and released a new reduction site for the next MB molecule or BH_4^- to ensure the continuity of the reduction reaction.

3.3. Effects of initial solution pH and ionic strength on the catalytic activity of MC-PDA-Ag

To evaluate the catalytic performance of MC-PDA-Ag towards MB dye at different initial pH value, five different solution pH (3.0, 5.0, 7.0, 9.0, and 11.0) were selected for the tests. Fig. 9 displayed the time-dependent reduction rate of MB aqueous solution with different initial pH values in 5 min. The reduction effect of MB was better under acidic (i.e., 3.0, 5.0) and alkaline (i.e., 9.0, 11.0) solution conditions than under neutral condition at 1 min. However, the difference gradually decreased with time. Finally, the MB was completely reduced at 5 min even under different solution pH. The result indicates that the initial pH of solution has no obvious effects on the catalytic activity of the MC-PDA-Ag composites for catalytic reduction of MB, showing an excellent stability and universal adaptability. Thus, it can be applied to wastewater treatment under various pH conditions.

Please insert Figure 9

In addition, the effect of solution ionic strength on the catalytic performance of MC-PDA-Ag for reducing MB in the presence of $NaBH_4$ was also investigated. In our work, the effect of ionic strength was conducted with $NaNO_3$ concentrations of 0, 0.001, 0.005, 0.01, 0.05, 0.1, and 0.5 M in the catalytic reduction system containing 40 mg/L of MB and 10 mg of the catalyst. Fig. 10 revealed that the reduction rate of MB reached 97% or more after 5 minutes of catalytic reaction in the presence of $NaNO_3$ concentration (0, 0.001, 0.005, 0.01, 0.05, and 0.1 M). However, when the $NaNO_3$ concentration reached 0.5 M, the MB removal efficiency decreased slightly and reached 93%. The result shows that solution ionic strength has negligible effect on the catalytic performance of MC-PDA-Ag towards MB dye.

Please insert Figure 10

3.4. Catalytic activity of MC-PDA-Ag towards other dye solutions

Numerous studies have shown that it is extremely urgent to remove various organic dye contaminants from water bodies [34,59]. Therefore, other dyes including RhB and MO were selected to further evaluate the catalytic performance of MC-PDA-Ag. The catalytic reduction process was also monitored by UV-Vis spectroscopy. It can be seen that the reduction of RhB and MO were completed within 7 and 20 min, respectively (Fig. 11A and B). These reduction results further confirmed that MC-PDA-Ag composites could be used as an efficient catalyst for the catalytic reduction of dyes in the presence of $NaBH_4$. However, there was a difference in the reduction tendency among various dyes, which might be related to the charge properties of different dyes and the hydrophobicity of different dyes [21,60]. Therefore, studies on the catalytic reduction of other single dyes or multiple dyes by MC-PDA-Ag should be further explored.

Please insert Figure 11

3.5. The recyclability of catalyst

The reusability of catalyst is a vital factor to assess the application performance of catalyst in wastewater treatment [41,61]. As shown in Fig. 12, the reduction rate of the MB in the presence of $NaBH_4$ by the regenerated MC-PDA-Ag composites as catalyst was determined with reaction for 5 min. After 5 cycles of reuse, the conversion rate of MB decreased slightly, indicating that the prepared MC-PDA-Ag composite has excellent cycle stability and high catalytic activity, which has tremendous application potential in practical wastewater treatment.

Please insert Figure 12

4. Conclusions

In this study, a novel MC-PDA-Ag catalyst was successfully fabricated by in-situ reduction with AgNPs loaded on the surface of the PDA-wrapped magnetic biochar material that originated from pine. The as-prepared MC-PDA-Ag catalyst displayed an excellent catalytic performance for the catalytic reduction of MB dye in the presence of $NaBH_4$. Meanwhile, the catalyst can maintain good catalytic performance over a wide initial solution pH range and ionic strength. Besides, MC-PDA-Ag also showed prominent catalytic property towards MO and RhB organic dyes. Importantly, the inherent magnetic property of MC-PDA-Ag endowed it prominent recyclability in dye wastewater. Therefore, MC-PDA-Ag is a promising cost-effective catalyst for dye reduction and has great potential applications in wastewater treatment.

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