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Research Paper

Lignosulfonate functionalized kaolin-Ag hybrid catalyst for highly effective dye decolorization



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ABSTRACT

In this work, the immobilization of silver nanoparticles on lignosulfonate functionalized kaolin composite (LSkaolin-Ag) was fabricated by a facile reduction method without additional reductant and stabilizer. Transmission electron microscopy, X-ray powder diffraction, and X-ray photoelectron spectroscopy, and Fourier transform infrared spectroscopy (FTIR) were used to confirm the successful preparation of LS-kaolin-Ag composite. The catalytic reduction tests on both cationic dye rhodamine B and anionic dye Congo red indicated the high catalytic activities of this as-prepared LS-kaolin-Ag composite. Meanwhile, this catalyst showed good recyclability for dye decolorization with just a little decrease of conversion percent in five successive reactions. These results suggest that LS-kaolin-Ag composite as an efficient and cost-effective catalyst shows great application potential for the decolorization of various organic dyes.

1. Introduction

Environmental pollution is a serious threat on the economic development, ecosystem diversity, and human health (Ren et al., 2018a, 2018b; Wang et al., 2018; Ye et al., 2017a, 2017b). Water bodies contaminated by various pollutants, such as heavy metals,(Long et al., 2011; Tang et al., 2018; Xu et al., 2012) organic pollutants, (Xiong et al., 2018; Yang et al., 2018a, 2018b; Yi et al., 2018; Zhou et al., 2018) and dyes, (Gong et al., 2009; He et al., 2018b; Joseph and Mathew, 2015) will exacerbate the crisis of water resources. Among those pollutants, organic dyes are one of the most observable pollutants that released from textile, leather, cosmetic and other industrial effluents, which have caused adverse impacts on the environment and human health due to their undesirable diverse colors and toxicity (Forgacs et al., 2004; Gong et al., 2009; He et al., 2018a). Great efforts have been made to deal with the problem of dye pollution, however, it is still an urgent issue to be solved. In recent years, with the development of nanotechnology, nanocatalysis has been considered as superior technology for water purification due to its high catalytic performance (Joseph and Mathew, 2015; Liu et al., 2013). Aiming at the pollution issue of dye wastewater, hitherto, many nanocatalysts have been prepared to remove dyes from aquatic environment (Chen et al., 2011; Fatimah et al., 2011; Joseph and Mathew, 2015; Qin et al., 2018; Souza et al., 2016).

Among various nanocatalysts, silver (Ag) nanoparticles as catalysts have been attracting extensive scientific interest due to their fascinating properties and important catalytic performance in dye removal (Ai et al., 2011; Joseph and Mathew, 2015). However, the easy aggregation and difficult separation of Ag nanoparticles markedly restrict their catalytic activity and recyclability. In this regard, the incorporation of Ag nanoparticles on insoluble supports has been verified as an efficient approach to enhance the dispersity and stability of Ag nanoparticles, thereby improving their catalytic performance (Dong et al., 2014; He et al., 2018c; Zou et al., 2012).

Although various solid materials have been used as supports for Ag nanoparticles, (Goscianska and Pietrzak, 2015; He et al., 2018c; Kurtan et al., 2016) it is necessary to seek cheap and environmental-friendly support materials for their production and application. Compared with the commercial and synthetic support materials, clay minerals, which are widely distributed in nature, have an increasing application as various nanoparticle supports owing to their economic and environmental advantages (Bagchi et al., 2014; Hashemian and Reza Shahedi, 2013; Lin et al., 2014; Ramprakash Upadhyay and Srivastava, 2016; Zhou, 2011). Furthermore, clay minerals can be used as efficient

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LS-kaolin-Ag

Scheme 1. Proposed synthetic process of LS-kaolin-Ag composite.



Fig. 1. TEM images of kaolin (A), LS-kaolin (B), LS-kaolin-Ag composite (C), and EDX spectrum of LS-kaolin-Ag composite (D).

adsorbents for dye adsorption, which is beneficial for the design and application of clay-based catalysts (Rawtani and Agrawal, 2012, 2013; Khatri et al., 2016; Adeyemo et al., 2017; Wang et al., 2017; Peng et al., 2017). Kaolin is one of the most widely used clay minerals for nanoparticle support due to its low-cost, abundance, eco-friendly, and

exceptional properties such as high versatility, thermal and mechanical stability (Chen et al., 2012; Hashemian and Reza Shahedi, 2013; Wang et al., 2011). Thus, kaolin shows great potential as support of Ag nanoparticles. As is well-known, chemical reduction is one of the powerful methods to fabricate Ag-based composite, which requires appropriate



Fig. 2. FTIR spectra of LS (a), kaolin (b), LS-kaolin (c) and LS-kaolin-Ag composite (d).

reductant for the reduction of Ag⁺ ions to form Ag nanoparticles (He et al., 2018c; Huang et al., 2017, 2018; Zhang et al., 2018a). Although the incorporation of Ag nanoparticles on kaolinite has been reported, the reducing agent of NaBH₄ is hazardous and the application is missing (Patakfalvi and Dékány, 2003; Patakfalvi et al., 2003). Thus, it is necessary to seek an effective and green reductant for the synthesis and application of Ag-based composite.

Recently, lignosulfonate (LS), a non-toxic and biocompatible macromolecule with abundant functional groups such as hydroxyl, sulfonic acid, and methoxy group, has been reported as reductant and stabilizer to synthesize Ag nanoparticles (Gao et al., 2018; Milczarek et al., 2013). A tentative reduction mechanism has been proposed as the reaction of silver-ammonia complex with the –OH groups (phenolic-OH and aliphatic-OH) on lignosulfonate molecules (Milczarek et al., 2013). In addition, lignosulfonate can also be used as surface modification molecules to enhance the adsorption ability of raw adsorbent materials towards heavy metals due to their combination with the functional groups on lignosulfonate chain (Gao et al., 2018; Yang et al., 2014). Inspired by the reduction and surface modification characteristics of lignosulfonate, a hypothesis of utilizing lignosulfonate functionalized kaolin as a support of Ag nanoparticles without additional reductant comes into mind.

To the best of our knowledge, no report is available on the

incorporation of Ag nanoparticles onto lignosulfonate functionalized clay composite. In this work, a novel LS-kaolin-Ag hybrid was fabricated by the utilization of lignosulfonate as reductant. Firstly, lignosulfonate was grafted onto kaolin surface to form lignosulfonate functionalized kaolin, then Ag nanoparticles are generated by the reduction of Ag⁺ ions. In order to evaluate the catalytic activity of asprepared hybrid, the decoloration of model dye pollutants, rhodamine B (RhB) and Congo red (CR), were conducted. Herein, we deem that this work can extend the development and application of Ag-based clay composite in wastewater treatment.

2. Materials and methods

2.1. Materials

Kaolin (Al₂Si₂O₉H₄), silver nitrate, and NaBH₄ were purchased from Sinopharm chemical reagent Co., Ltd. Sodium lignosulfonate (LS) was purchased from Xiya reagent. 3-aminopropyl-trimethoxysilane (APTMS), rhodamine B (RhB) and Congo red (CR) were purchased from Sigma-Aldrich. Ultrapure water was used for the preparation of solutions in all experiments.

2.2. Synthesis

The synthesis of LS-kaolin-Ag composite was based on the reduction nature of lignosulfonate, which has been reported in the synthesis of Ag nanoparticles (Milczarek et al., 2013). The proposed synthetic process is illustrated in Scheme 1. In the reaction procedure, LS-kaolin was first prepared. 1.6 g of kaolin powder was first dispersed in 400 mL ultrapure water for 2h of ultrasonication, and then 2mL of APTMS was added into the mixture under stirring for 30 min at room temperature. Afterwards, 400 mg of LS powder was added to the mixture and then transferred to a water bath at 80 °C while stirring for 12 h. The brown product was washed with ultrapure water and dried in an oven at 60 °C overnight to obtain the LS-kaolin composite. For the synthesis of LSkaolin-Ag composite, silver ammonia solution $([Ag(NH_3)_2]^+)$ was used as Ag precursor, which was prepared by adding dropwise ammonia solution into 10 mg/mL of silver nitrate until the precipitation just disappeared. 400 mg of LS-kaolin was added into a flask containing 200 mL untrapure water and 4 mL of prepared silver ammonia solution under stirring for 16 h at room temperature. The solid product was filtrated and washed with ultrapure water for several times, and dried in a vacuum oven at 50 °C overnight. The resultant product was LSkaolin-Ag composite. The as-prepared samples were further used for the following catalytic experiments.



Fig. 3. (A) XPS survey spectra of LS-kaolin and LS-kaolin-Ag composite; (B) Ag3d XPS spectrum of LS-kaolin-Ag composite.



Fig. 4. (A) Powder XRD pattern of LS-kaolin-Ag composite; (B) Nitrogen adsorption-desorption isotherms measured at 77 K for kaolin and LS-kaolin-Ag samples.



Fig. 5. The UV-vis absorption spectra change for the removal of (A) CR (100 mg/L, 50 mL) by LS-kaolin composite (20 mg) with the presence of NaBH₄ (10 mM), and (B) RhB (20 mg/L, 50 mL) by LS-kaolin composite (10 mg) with the the presence of NaBH₄ (2 mM).

2.3. Characteristic

The morphology of the samples was observed by using Transmission Electron Microscope (TEM) (JEOL, Japan) analysis. The chemical compositions of samples were determined by X-ray photoelectron spectroscopy (XPS) on ESCALAB 250Xi (Thermo Fisher Scientific, USA). X-ray powder diffraction (XRD) measurements were recorded on a D8 Advance powder X-ray diffractometer (Bruker, German) with a Cu Ka X-ray generator (40 kV, 100 mA). The samples for Fourier transform infrared spectroscopy (FTIR) measurement were prepared by mixing the dried sample powder with KBr (w/w 1:100) toghther and then compressed into thin pellets. The FTIR spectra were recorded with the pellets in 4000–400 cm⁻¹ region by using a Tensor 27 FTIR spectrometer (Bruker, Germany). The specific surface area of prepared samples was measured by the Brunauer-Emmett-Teller (BET) method.

2.4. Catalytic reduction tests

The catalytic reduction tests of LS-kaolin-Ag composite towards RhB and CR with the presence of NaBH₄ were carried out as follows. For the catalytic reduction of CR solution, 20 mg of catalyst was added to 50 mL of CR solution with different concentrations (50, 100, and 200 mg/L, respectively) and 10 mM NaBH₄ under stirring; 50 mL of 100 mg/L CR solution was mixed with different catalyst dosages (10, 20, and 30 mg,

respectively) and 10 mM NaBH₄ under stirring. For the catalytic reduction of RhB solution, 10 mg of catalyst was added to 50 mL of RhB solution with different concentrations (10, 20, and 40 mg/L, respectively) with 2 mM NaBH₄ under stirring; 50 mL of 20 mg/L RhB solution was mixed with different catalyst dosages (5, 10, and 20 mg, respectively) and 2 mM NaBH₄ under stirring. With the reaction proceeded, the color of dye solution gradually vanished due to the catalytic reduction. The catalytic activities of as-prepared samples were estimated by monitoring the absorption spectra change at the maximum absorption wavelength of dye with time using a UV-vis spectrometer (UV-2550, SHIMADZU, Japan). The corresponding blank experiments without catalyst and comparative experiments with LS-kaolin composite on dye decolorization were also conducted.

3. Results and discussion

3.1. Characterization studies

The characteristic analysis of kaolin has been reported in our previous study, (He et al., 2018b, 2019a, 2019b) therefore, the main characteristics of as-prepared samples were described here. The morphological characteristics of as-prepared samples analyzed by TEM are presented in Fig. 1. Compared with the structure of raw kaolin (Fig. 1A), the smooth surface turned into rough and some thin flakes



Fig. 6. The UV-vis absorption spectra change for the reduction process of CR (100 mg/L, 50 mL) by LS-kaolin-Ag catalyst with different dosage of (A) 0 mg, (B) 10 mg, (C) 20 mg, and (D) 30 mg in the presence of NaBH₄ (10 mM). (E) Catalytic rate curves of CR after the addition of catalyst and NaBH₄. (F) Plots of ln (A_t/A_0) versus reaction time for the reduction of CR.

were observed on the edge after the lignosulfonate modification on kaolin (Fig. 1B). On the other hand, the color of raw kaolin was obviously changed from white to brown after the modification (insets in Fig. 1), indicating the successful introduction of lignosulfonate. Furthermore, it could be clearly seen from TEM image of LS-kaolin-Ag composite (Fig. 1C) that some small Ag nanoparticles were well dispersed on the material surface. The EDX characteristic (Fig. 1D) further demonstrated the presence of element of Ag in LS-kaolin-Ag composite. Overall, the differences of TEM images suggested that Ag nanoparticles were successfully immobilized on the surface of LS-kaolin.

In addition, the composite formation was also analyzed by FTIR spectra measurement (Fig. 2). The peaks at 472 and 577 cm⁻¹ that observed at kaolin, and LS-kaolin, and LS-kaolin-Ag composite were corresponed to Si–O–Si and Si–O–Al, respectively (Fig. 2 b, c and d) (Jin et al., 2015). After the LS modification, the typical peak at 1043 cm⁻¹ (Fig. 2a), which was attributed to S=O symmetric stretching of the

-SO3 group on the LS chains, was disappeared due to the interaction of -SO₃⁻ with NH₂ group (Lü et al., 2010; Zhang et al., 2018b). In order to further confirm the modification of lignosulfonate and the synthesis of Ag nanoaprticles on kaolin surface, XPS analysis was used to determine the surface component and composition of samples (Chi et al., 2012). After modification, the characteristic elements of kaolin such as Al and Si were still observed in the XPS survey spectra of LS-kaolin and LSkaolin-Ag composites; however, their peak intensities decreased significantly as compared with those on kaolin due to the surface modification (He et al., 2018b). In addition, the increased content of C element was attributed to the successful introduction of lignosulfonate. The presence of N element was ascribed to the application of APTMS as linkage. Compared with the XPS survey spectrum of LS-kaolin composite, an obvious peak of Ag3d was observed in the XPS survey spectrum of LS-kaolin-Ag composite (Fig. 3A). Furthermore, the XPS spectrum of Ag3d of LS-kaolin-Ag composite showed two typical peaks at 368.3 eV



Fig. 7. The UV-vis absorption spectra change for the reduction process of CR (50 mL) with different dye concentration of 50 mg/L, (B) 100 mg/L, and (C) 200 mg/L by LS-kaolin-Ag catalyst (20 mg) in the presence of NaBH₄ (10 mM). (D) Catalytic rate curves of CR after the addition of catalyst and NaBH₄.

for Ag3d_{5/2} and 374.3 eV for Ag3d_{3/2}, respectively (Fig. 3B), indicating the metallic state of Ag in LS-kaolin-Ag composite (Chi et al., 2012; Xu et al., 2017). This finding could be further supported by the analysis of powder XRD pattern. As shown in Fig. 4A, the typical diffraction peaks could be readily indexed to face-centered-cubic structure of metallic Ag according to JCPDS card NO.04–0783. Due to the low content of Ag nanoparticles in the product as seen from EDX and XPS spectra, the XRD peak intensities of Ag nanoparticles were not high (Kurtan et al., 2016). Taking the above characteristic analysis together, the immobilization of Ag nanoparticles on lignosulfonate functionalized kaolin was successfully prepared.

Nitrogen adsorption-desorption isotherms of kaolin, and LS-kaolin-Ag samples measured at 77 K is presented in Fig. 4B. The BET surface area of LS-kaolin-Ag was 16.223 m^2/g , which was higher than that of kaolin (9.652 m^2/g). The relatively higher surface area could be beneficial for the contact of pollutant molecules with composite.

3.2. Application of LS-kaolin-Ag composite as catalyst for dye decolorization

CR and RhB as the model anionic and cationic dye pollutants, respectively, were selected to investigate the catalytic activity of LSkaolin-Ag composite in the presence of NaBH₄. In order to determine the catalytic property of LS-kaolin-Ag composite, LS-kaolin composite was firstly used in a control experiment for dye removal. As shown in Fig. 5, no obvious peak changes of dyes were observed, which was similar with the phenomena of catalytic reduction just in the presence of NaBH₄, indicating that LS-kaolin composite had negligible catalytic activity towards dye reduction when in comparison with LS-kaolin-Ag composite in the following sections. Therefore, a series of catalytic experiments were performed using LS-kaolin-Ag composite as catalyst.

CR is a benzidine-based anionic diazo dye with two -N=N- bonds on its molecular structure, which is non-biodegradable and toxic in aquatic environment (Ganapuram et al., 2015; Vimonses et al., 2009). It was chosen as a model anionic dye indicator in this study. The catalytic reaction was monitored by the changes of absorption spectra using UVvis spectrophotometer. Similar with the previous reports, CR aqueous solution shows the typical peaks at 498 nm ($\pi \rightarrow \pi^*$) and 343 nm ($n \rightarrow$ π^*) (Ganapuram et al., 2015; Vimonses et al., 2009). The effect of catalyst dosage on the decolorization of CR can be seen from Fig. 6. Obviously, without the catalyst, the dye color did not change in the mixture just with NaBH₄ within 30 min (Fig. 6A). On the other hand, the absorption spectra changed remarkably and dye color gradually vanished after adding the LS-kaolin-Ag composite to CR solution. Thus, the incorporation of Ag nanoparticles on LS-kaolin played a dominant role in CR decoloration as compared with the results in the treatments of LS-kaolin composite and without catalyst. The initiated catalytic process was attributed to the role of Ag nanoparticles that acting as electron relay to transfer the electrons from BH₄⁻ (donor) to the dye (acceptor) molecule (Khan et al., 2018). Meanwhile, the dye decolorization rate became much faster with the increase of catalyst dosage in the mixture. When the catalyst dosage was 30 mg in 50 mL of 100 mg/L CR solution, the completion of catalytic reduction just required about 8 min (Fig. 6D), which took about 12 min at 20 mg catalyst at same condition (Fig. 6C), whereas the dye reduction still proceeded after 30 min at 10 mg catalyst (Fig. 6B). At higher catalyst dosage, the content of Ag nanoparticles in composite was larger, which could increase the active sites on catalyst surface to facilitate the electron transfer speed and thereby enhancing the catalytic reduction. The pseudo-first order kinetics are commonly used to evaluate the reaction kinetics,



Fig. 8. The UV-vis absorption spectra change for the reduction process of RhB (20 mg/L, 50 mL) by LS-kaolin-Ag catalyst with different dosage of (A) 0 mg, (B) 5 mg, (C) 10 mg, and (D) 15 mg in the presence of NaBH₄ (2 mM). (E) Catalytic rate curves of RhB after the addition of catalyst and NaBH₄. (F)Plots of ln (A_t/A_0) versus reaction time for the reduction of RhB.

Table	1
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The catalytic kinetic parar	neters of RhB catalytic reduction.
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Catalyst mass	RhB solution	Rate constant	Correlation coefficient
0 mg	20 mg/L 50 mL	0.007 min ⁻¹	0.999
5 mg		0.028 min ⁻¹	0.946
10 mg		0.443 min ⁻¹	0.951
15 mg		2.067 min ⁻¹	0.956

which can follow the equation: $\ln (A_t/A_0) = -kt$, where A_t and A_0 are the absorbance of CR at time t and 0, respectively, and k is the rate constant that can be calculated from the slope of the linear plot (Ai et al., 2011). As seen from Fig. 6F, the calculated rate constants for CR reduction with LS-kaolin-Ag composite at 0, 10, 20, and 30 mg were 0.001, 0.049, 0.360, and 0.583 min⁻¹, respectively. This result further

indicated the importance of appropriate catalyst dosage in the catalytic reaction.

In addition, the effect of initial CR concentration (50, 100, and 200 mg/L) on the catalytic activity of LS-kaolin-Ag was also investigated. As shown in Fig. 7, the dye color almost completely faded within 1 min at 50 mg/L of CR solution, whereas the complete decoloration required about 12 and 30 min at 100 and 200 mg/L of CR solution, respectively. The reduction rate decreased with the increase of initial concentration of CR solution. At a fixed catalyst mass and NaBH₄ concentration in solution, the electron transfer rate is finite. However, with the increase of dye concentration, the competition among dye molecules to accept electrons from catalyst increased, thereby decreasing the catalytic activity of catalyst.

RhB, a cationic dye, was also used to investigate the catalytic activity of LS-kaolin-Ag composite in the presence of $NaBH_4$ under different catalyst dosages and dye concentrations. Without the catalyst,



Fig. 9. The UV-vis absorption spectra change for the reduction process of RhB (50 mL) with different dye concentration of 10 mg/L, (B) 20 mg/L, and (C) 40 mg/L by LS-kaolin-Ag catalyst (10 mg) in the presence of NaBH₄ (2 mM). (D) Catalytic rate curves of RhB after the addition of catalyst and NaBH₄.



Fig. 10. The reusability of LS-kaolin-Ag as catalyst for the reduction of RhB and CR by $NaBH_4$.

the decline of maximum absorption peak was insignificant, just at a very slow rate in the presence of NaBH₄ (Kurtan et al., 2015). In contrast, the addition of LS-kaolin-Ag composite with certain mass can effectively enhance the catalytic reaction as reflected in Fig. 8. The reduction mechanism was also attributed to the electron relay system (Kurtan et al., 2015). As seen from Fig. 8F, the calculated rate constants for RhB reduction with LS-kaolin-Ag composite at 0, 5, 10, and 15 mg were 0.007, 0.028, 0.443, and 2.067 min⁻¹, respectively. The plots of ln (A_t/A₀) versus time showed a good linear correlation (Table 1),

indicating that the reactions conformed to pseuso-first kinetics. Similarly, the high dye concentrations could inhibit the reaction process (Fig. 9). Herein, the set reaction conditions were different due to the difference in redox potentials of these dyes and NaBH₄; (Joseph and Mathew, 2015) however, the same reduction phenomena as the CR reduction were observed. Thus, this as-prepared LS-kaolin-Ag composite is an effective catalyst for dye decolorization.

3.3. Catalytic stability

A good stability and recyclability of catalyst is important for its practical application. Investigations on the recyclability of LS-kaolin-Ag composite on CR and RhB decoloration were carried out. After the completion of catalytic reaction, the catalyst was filtered and washed with ultrapure water and ethanol and then dried for the next cycle. Fig. 10 shows the recyclability of LS-kaolin-Ag composite for the decolorization of two dyes in five successive catalytic reactions. Similar with the previous reports, the conversion percent of dyes just decreased a little after each recycle, which may be attributed to the loss of catalyst during recycling (Kurtan et al., 2016, 2015). Therefore, more efforts should be paid to improve the stability of this as-prepared composite.

4. Conclusions

In summary, a novel LS-kaolin-Ag catalyst has been successfully fabricated by a facile reduction route without additional reductant, which was determined by the characteristic analysis of XRD, XPS, and TEM. The results show that LS-kaolin-Ag composite can be used as an efficient catalyst for the catalytic reduction of CR and RhB dyes in the presence of NaBH₄. Meanwhile, an appropriate catalyst dosage is necessary for the rapid dye decolorization. Importantly, this catalyst remains good stability and recyclability in dye wastewater treatment. These results indicate that this cost-effective catalyst has great potential in environmental applications.

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Conflict of interest

The authors declare that they have no conflict of interest.

Ethical approval

This article does not contain any studies with human participants or animals performed by any of the authors.

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