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Fabrication of ploydopamine—kaolin supported Ag nanoparticles as effective catalyst for rapid dye decoloration

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HIGHLIGHTS

• Polydopamine-kaolin-Ag (PDA-kaolin-Ag) composite was prepared by an *in-situ* reduction method.

- This as-prepared catalyst showed high catalytic activity towards Rhodamine B and other dye decoloration.
- PDA-kaolin-Ag catalyst exhibited good catalytic stability and recyclability.

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ABSTRACT

In this work, silver nanoparticles supported on polydopamine-kaolin composite (PDA-kaolin-Ag) was fabricated by an *in-situ* reduction method with PDA as both reductant and stabilizer. The morphology, composition, and structure of PDA-kaolin-Ag composite were characterized by transmission electron microscopy (TEM), X-ray powder diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The catalytic reduction tests confirmed the importance of PDA modification and high catalytic activities of this as-prepared PDA-kaolin-Ag composite towards a model dye Rhodamine B. The catalytic reduction processes followed pseudo-first order kinetics. Meanwhile, this catalyst showed excellent stability and recyclability for dye decoloration. Furthermore, this composite also exhibited good catalytic performance on methylene blue, methyl orange, and Congo red. These results suggest that PDA-kaolin-Ag composites can be used as efficient and cost-effective catalyst for the decoloration of various organic dyes.

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1. Introduction

Environment pollution is a severe threat on ecosystem and human health (Ye et al., 2017; Ren et al., 2018a, 2018b; Wang et al., 2018a). Various contaminants released into water bodies have caused serious water pollution and water resource shortage (Xu et al., 2012; Tang et al., 2018; Wang et al., 2018b; Xiong et al., 2018; Yang et al., 2018a; Yi et al., 2018; Zhou et al., 2018). Organic dyes are a kind of common chemicals that are widely used in textile, paper, leather, and other industries. It is estimated that their annual production is over 7×10^5 ton and a portion of dyes will be inevitably discharged into water bodies during their production, usage, and transport (Gong et al., 2009; Adeyemo et al., 2017; He et al., 2018b). Consequently, multifarious undesirable colors appearing on water surface will impede the sunlight penetration, thereby endangering the survival of aquatic organisms(Yagub et al., 2014; He et al., 2018a). Owing to their undesirability, high visibility, and toxicity, therefore, it is imperative to solve this pollution challenge.

As is well-known, catalysis is a vital subject for water purification (Yang et al., 2018b). Nowadays, with the development of nanoscience, nanoscaled noble metal nanoparticles such as silver (Ag) and gold used as nanocatalysts have been attracting growing scientific interest in catalysis field (Ganapuram et al., 2015; He et al.,





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2018c; Qin et al., 2018). Hitherto, the application of Ag nanoparticles (Ag NPs) as catalyst for water purification, such as dye decoloration, organic compound reduction and degradation, has been widely reported due to its fascinating characteristics and important catalytic potential (Kurtan et al., 2015; Li et al., 2015; He et al., 2018c). Unfortunately, the easy aggregation of nanoparticles will impede their catalytic activity and practical application. To improve the dispersity of Ag NPs, the immobilization of Ag NPs on various support materials has been developed, which is beneficial to maintain its catalytic activity and facilitate the solid-liquid separation (He et al., 2018c). However, some support materials such as graphene materials and carbon nanotube are usually limited to apply due to their complicate preparation processes and high cost. In other words, seeking an appropriate material as support of Ag NPs for dye wastewater treatment is a significant subject.

Recently, clay minerals as nanoparticle supports have been attracting great attention due to their environmental and economical advantages in comparison with many other support materials such as graphene and carbon nanotube (Zhou, 2011; Lin et al., 2014; Ramprakash Upadhyay and Srivastava, 2016; He et al., 2018c). Kaolin, one of the common clay minerals, has been studied as the nanoparticle support owing to its low-cost, abundance, and eco-friendly (Chen et al., 2012; Hashemian and Reza Shahedi, 2013; Liu et al., 2013). In particular, its exceptional properties such as high versatility, thermal and mechanical stability make it important to act as nanocatalyst support (Wang et al., 2011). As one of the powerful methods, chemical reduction is usually applied to fabricate the Ag-based composites in the presence of reductants such as hydrazine, sodium borohydride (NaBH₄), sodium citrate, and dopamine (He et al., 2018c; Huang et al., 2018; Zhang et al., 2018). Nowadays, dopamine, a simple nontoxic organic chemical, has been widely used as green reductant for the synthesis of Agbased composites due to its dual-functional properties including reduction and self-polymerization (Zhang et al., 2013; Lin et al., 2014; Xie et al., 2014). It has been verified that dopamine can be polymerized into polydopamine (PDA) at weakly alkaline solution condition (Hu et al., 2014). The self-polymerization makes the substrate materials coated with abundant amine and hydroxyl groups, which is beneficial to the efficient bind with metal ions. Importantly, the in-situ reduction of the adsorbed metal ions occurred on the active surface of PDA (Yu et al., 2014). Therefore, dopamine has been employed as an effective and green reductant for the synthesis of Ag NPs rather than the hazardous reductants such as hydrazine and NaBH₄ (Zhang et al., 2013; Lin et al., 2014; Xie et al., 2014). However, the application of dopamine as reductant for the preparation of cost-effective PDA-kaolin-Ag composite has not been reported. Thus, this work was conducted to verify the application potential of this composite as catalyst for the removal of dye solution.

In this work, a novel PDA-kaolin-Ag catalyst was synthesized through a facile *in-situ* reduction route. In order to investigate the catalytic performance of this as-prepared composite on dye decoloration, Rhodamine B (RhB), a kind of common dye, was used as a model pollutant for the catalytic reduction tests. Herein, this catalyst exhibited excellent catalytic performance and good stability for dye decoloration, and could be used in environmental remediation.

2. Materials and methods

2.1. Materials

Kaolin ($Al_2Si_2O_9H_4$), dopamine hydrochloride, tris(hydroxymethyl) aminomethane (Tris), hydroxylamine hydrochloride ($NH_2OH \cdot HCl$), and silver nitrate ($AgNO_3$) used for the synthesis of catalyst were purchased from Sinopharm chemical reagent Co., Ltd. NaBH₄ was purchased from Sinopharm chemical reagent Co., Ltd. Rhodamine B (RhB), methylene blue (MB), methyl orange (MO), and Congo red (CR) were purchased from Sigma-Aldrich. Ultrapure water was used for the preparation of solutions in all experiments.

2.2. Synthesis of PDA-kaolin-Ag composites

Firstly, the PDA coated kaolin composite was prepared. 1.6 g kaolin powder was dispersed in 200 mL Tris-HCl buffer solution (10 mM, pH = 8.5) by ultrasonication for 2 h. Afterwards, 200, 400, and 800 mg dopamine hydrochloride were added into the mixture under stirring, resulting in the corresponding concentrations of dopamine hydrochloride were 1, 2, and 4 mg/mL, respectively. After stirring for 24 h at room temperature, the solid product was separated by filtration and washed with ultrapure water for three times. Then the obtained three PDA-kaolin samples were dried in a vacuum oven at 60 °C overnight.

For the synthesis of PDA-kaolin-Ag composites, three different PDA-kaolin powders (200 mg) were dispersed in 200 mL ultrapure water, respectively. And then 2 mL of silver ammonia solution (as Ag precursor solution) was added to the above reaction system under stirring for 12 h at room temperature. Herein, 10 mg/mL of AgNO₃ was prepared and ammonia solution was dropwise added to it until the brown precipitation just disappeared, then silver ammonia solution (10 mg/mL) was obtained. The solid products were separated by filtration and washed with ultrapure water for three times, and dried in a vacuum oven at 50 °C overnight. The resultant composites were named as PDA-kaolin-Ag/1. PDA-kaolin-Ag/2, and PDA-kaolin-Ag/4, respectively. The synthesis of kaolin-Ag without PDA was according to Leopold's method (Leopold and Lendl, 2003; Qi et al., 2014) In brief, 200 mg kaolin was dispersed in 100 mL ultrapure water, and 2 mL above silver ammonia solution was added into the mixture for stirring 12 h. Afterwards, 40 mg NH₂OH·HCl was added to the mixture under stirring for 4 h to obtain kaolin-Ag composite. For further comparison, different concentrations of silver ammonia solution were used for the synthesis of PDA-kaolin-Ag composites. Herein, 0.5 mL and 1 mL of silver ammonia solution were added to prepare PDA-kaolin-Ag/ 2(0.5) and PDA-kaolin-Ag/2(1) as the same procedure, respectively.

2.3. Characterization

The surface morphology and chemical compositions of asprepared samples were characterized using Transmission Electron Microscope (TEM) (JEOL, Japan) and X-ray photoelectron spectroscopy (XPS) on ESCALAB 250Xi (Thermo Fisher Scientific, USA), respectively. The crystal structures of samples were determined by X-ray diffraction (XRD) patterns that recorded on a D8 Advance powder X-ray diffractometer (Bruker, German) with a Cu K α X-ray generator (40 kV, 100 mA).

2.4. Catalytic performance of PDA-kaolin-Ag composite

To investigate the catalytic performance of as-prepared catalysts, a comparative experiment on the decoloration of RhB with PDA-kaolin and PDA-kaolin-Ag samples was firstly carried out. 10 mg sample was added into 50 mL RhB aqueous solution (10 mg/ L) under continuous stirring at room temperature, respectively. Then, 1 mL of fresh NaBH₄ solution (0.25 M) was rapidly injected into the mixture solution. With the reaction proceeding, 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 (in the range of 300–700 nm) at the maximum absorption wavelength of dye with a UV–vis spectrometer (UV-2550, SHIMADZU, Japan). Another comparative experiment on the decoloration of RhB with kaolin-Ag, PDA-kaolin-Ag/1, PDA-kaolin-Ag/2, and PDA-kaolin-Ag/4 was conducted to investigate the effect of dopamine concentration on the synthesis and catalytic performance of PDA-kaolin-Ag composites. Afterwards, PDA-kaolin-Ag/2 composite was further used to investigate the catalytic activity towards RhB solution under the conditions of different dye concentration and catalyst dosage. In addition, three other dyes including methylene blue (MB), methyl orange (MO), and congo Red (CR) were also used for the catalytic reduction tests.

3. Results and discussion

3.1. Synthesis and characteristics of PDA-kaolin-Ag composite

The PDA-kaolin was first prepared by mixing the kaolin powder into dopamine solution (10 mM, pH = 8.5) with stirring, and the PDA layers could be coated on the surface of kaolin due to the selfpolymerization of dopamine at weakly alkaline condition. Afterwards, silver ammonia solution was added, owing to the reducing ability of PDA, and then Ag NPs were deposited on the PDA layers by the *in-situ* reduction. The successful synthesis of PDA-kaolin-Ag composite has been verified by both the characteristic analysis and catalytic tests below. The facile synthesis process of PDAkaolin-Ag composite is presented in Fig. 1.

In order to determine the morphological feature of PDA-kaolin-Ag composites, TEM analysis was conducted. As shown in the TEM images (Fig. 2A and B), a thin PDA layer was obviously coated on kaolin surface. After the formation of Ag NPs, large amount of small black particles were well dispersed on the surface of PDA-kaolin without the agglomeration (Fig. 2D, E, F). However, the dispersity of Ag NPs was poor, and particles were aggregated to form larger size without PDA as stabilizer (Fig. 2C). These observations confirmed that PDA could act as an efficient reductant and stabilizer for the synthesis of Ag NPs on the clay support.

The composition and structure of kaolin have been characterized in our previous study (He et al., 2018b, 2019). Herein, a detailed characteristic description of PDA-kaolin-Ag composite was presented. The XRD patterns of kaolin-Ag and PDA-kaolin-Ag composites are shown in Fig. 3A. According to previous studies, the main diffraction peak of kaolin found at $2\theta = 26.5^{\circ}$ was ascribed to quartz, and some kaolinite peaks could also be seen at $2\theta = 45.8^{\circ}$ and 21.0° (Fig. S1a). (Ma et al., 2007; Zhao et al., 2011; Liew et al., 2012; He et al., 2014) Compared with the XRD patterns of kaolin and PDA-kaolin samples, in the case of kaolin-Ag and PDA-kaolin-Ag composites, several obvious diffraction peaks at $2\theta = 37.9^{\circ}$, 44.2° , 64.4° , and 77.3° that corresponded to the reflections of (111), (200), (220), and (311) crystalline planes were observed, which could be readily indexed to face-centered-cubic structure of Ag crystal according to JCPDS card No. 04-0783. Furthermore, the typical XRD peaks of Ag crystal revealed that the crystallized Ag NPs could be successfully incorporated on the surface of kaolin composite (Ai et al., 2011). With the increase of dopamine concentration, XRD peaks of Ag crystal in the PDA-kaolin-Ag composites were more intense and sharp, indicating that the dopamine mass was an important factor for the synthesis of Ag NPs. In addition, with the increase of Ag concentration, the intensities of typical Ag NPs XRD peaks of PDA-kaolin-Ag composite became stronger, indicating the relative amount of Ag NPs in PDA-kaolin-Ag/2 was higher than that in PDA-kaolin-Ag/2(1) and PDA-kaolin-Ag/2(0.5) (Fig. S1). In addition, the introduction of Ag NPs could not change the structure of kaolin.

Furthermore, XPS analysis was performed to further verify the composition of PDA-kaolin-Ag composites. The XPS survey spectra (Fig. 3B) showed that Ag element was emerged in the composite in addition to the characteristic elements of kaolin such as Al, Si, and O (Huang et al., 2016; He et al., 2018b). The element contents of kaolin-Ag and PDA-kaolin-Ag composites are listed in Table 1. Without PDA modification, the content of Ag atom was low (0.5%). Obviously, the increased contents of carbon and nitrogen atoms were attributed to the PDA modification. The contents of Ag atom were 1.79%, 2.02%, and 2.18% in PDA-kaolin-Ag/1, PDA-kaolin-Ag/2, and PDA-kaolin-Ag/4, respectively. The increased PDA content resulted in larger Ag content in PDA-kaolin-Ag composites. Thus, PDA modification on kaolin was beneficial for the synthesis of kaolin-Ag composites. The high-resolution scan of Ag3d spectrum of PDA-kaolin-Ag/2 revealed the presence of typical Ag3d_{5/2} and Ag3d_{3/2} peaks, which were centered at binding energy of 368.02 eV and 374.02 eV, respectively (Fig. 9) (Wei et al., 2015). Meanwhile, the binding energy gap of 6 eV suggested that the zero valence state of metallic Ag was deposited on the surface of PDA-kaolin (Cai et al., 2012; Wei et al., 2015; Gilea et al., 2018). Thus, the successful preparation of PDA-kaolin-Ag composite could be verified by taking the analysis of the characteristic results of XRD, TEM, and XPS together.

3.2. Catalytic performance

3.2.1. Catalytic activity of PDA-kaolin-Ag for RhB decoloration

To investigate the catalytic performance of PDA-kaolin-Ag on dye decoloration, herein, RhB was used as a model dye pollutant. Generally, the catalytic reduction process can be monitored by the variations of absorbance spectra with time, resulting from the dye color gradually vanishing after the addition of NaBH₄ and catalyst (Xie et al., 2014; Kurtan et al., 2016). Without Ag NPs in the



Fig. 1. The synthesis route of PDA-kaolin-Ag composite.



Fig. 2. TEM images of raw kaolin (A), PDA-kaolin (B), kaolin-Ag (C), PDA-kaolin-Ag/1 (D), PDA-kaolin-Ag/2 (E), and PDA-kaolin-Ag/4 (F). The blue circle indicates the PDA layer on kaolin. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



Fig. 3. (A) Powder XRD patterns and (B) XPS survey spectra of kaolin-Ag (a), PDA-kaolin-Ag/1 (b), PDA-kaolin-Ag/2 (c) and PDA-kaolin-Ag/4 (d).

Table 1	
Element composition,	atom ratios of kaolin-Ag and PDA-kaolin-Ag composites.

bumpies	Atom percentage (%)					
	C1s	N1s	01s	Si2p	Al2p	Ag3d
Kaolin-Ag PDA-kaolin-Ag/1 PDA-kaolin-Ag/2 PDA-kaolin-Ag/4	27.99 38.37 42.64 50.12	0.78 5.42 6.25 6.91	43.75 36.85 34.11 29.71	14.14 8.99 7.61 5.68	12.84 8.58 7.37 5.40	0.5 1.79 2.02 2.18

composite, only a slight decrease of absorbance spectra within 30 min was monitored (Fig. S2A, Supplementary information). Compared with PDA-kaolin composite, an obvious decrease trend of absorption peak could be observed as shown in Fig. S2B, indicating that the successful incorporation of Ag NPs on PDA-kaolin. Theoretically, the catalytic reaction involves the adsorption of dye

molecules and $BH_{\overline{4}}$ ions onto the catalyst surface and the electron transfer from the donor $BH_{\overline{4}}$ to the acceptor dye molecules, which has been collectively demonstrated in previous studies(Joseph and Mathew, 2015; Kurtan et al., 2015). Herein, the electrons donated by $BH_{\overline{4}}$ will transfer to the electron relay of Ag NPs, then RhB molecules can capture them from Ag NPs, thereby resulting in the redox reduction of RhB and generating its reduced form (leuco RhB) (Fig. 4).(Kurtan et al., 2015, 2016) Therefore, the presence of Ag NPs could enhance the decoloration of RhB.

Furthermore, the loading content of Ag could influence the catalytic activity on the dye decoloration. On one hand, the increase of PDA content could increase the Ag loading content (Table 1). The catalytic performance of kaolin-Ag, PDA-kaolin-Ag/1, PDA-kaolin-Ag/2, and PDA-kaolin-Ag/4 could be seen from Fig. 5. Obviously, the decoloration of RhB was much easier with PDA-kaolin-Ag/2 and PDA-kaolin-Ag/4 than that of kaolin-Ag and PDA-kaolin-Ag/1, owing to the higher content of Ag NPs on kaolin. On the other



Fig. 4. Proposed reduction mechanism of RhB by PDA-kaolin-Ag composite with the presence of NaBH₄.



Fig. 5. Successive UV-vis absorption spectra of RhB aqueous solution (50 mL, 10 mg/L) with in the presence of NaBH₄ (5 mM) and 10 mg of kaolin-Ag/A (A), PDA-kaolin-Ag/1 (B), PDA-kaolin-Ag/2 (C), and PDA-kaolin-Ag/4 (D).

hand, the increase of silver ammonia solution in the preparation of PDA-kaolin-Ag could enhance the catalytic performance (Fig. S3, Supplementary information). As shown in Fig. S3, the maximum absorbance peak of RhB was measured to be at 553 nm ($\lambda_{max} = 553$ nm). Obviously, the absorbance peak at 553 nm almost disappeared within 4 min in the presence of PDA-kaolin-Ag/2, which was more rapid than that of PDA-kaolin-Ag/2(0.5) (12 min) and PDA-kaolin-Ag/2(1) (6 min), indicating the better catalytic activity of PDA-kaolin-Ag/2 in dye decoloration. Therefore, choosing an appropriate Ag concentration for the preparation of Ag-based composites is necessary. Since PDA-kaolin-Ag/2 exhibited a satisfactory catalytic performance on RhB reduction, it was selected as catalyst for the following experiments.

3.2.2. Effect of dye concentration and catalyst dosage on the catalytic activity of PDA-kaolin-Ag/2 composite

To evaluate the catalytic activity of PDA-kaolin-Ag/2 composite towards RhB aqueous solution with different concentrations, three different concentrations (10 mg/L, 20 mg/L, and 40 mg/L) of RhB solution were used for the tests. As shown in Fig. 6, the decoloration time increased with the increase of RhB concentration. The intensity of maximum absorption peak dropped sharply within 1 min, 3 min, and 10 min after adding the catalyst into the corresponding RhB solution with concentration of 10 mg/L, 20 mg/L, and 40 mg/L, respectively. Furthermore, the complete decoloration of higher concentration of dye solution required more time at the same conditions. The increase of dye concentration would lead to



Fig. 6. Successive UV–vis absorption spectra of different concentration of RhB aqueous solution (50 mL) with (A) 10 mg/L, (B) 20 mg/L; (C) 40 mg/L, in the presence of NaBH₄ (5 mM) and PDA-kaolin-Ag/2 (10 mg). (D) Absorption rate curves of RhB aqueous solution with different concentration. Note: *2 indicates the double dilution of initial RhB solution before measurement.

the increased competition of electron capture among dye molecules, whereas the catalytic capacity was finite at a fixed mass of catalyst, thus the dye reduction decreased at a higher dye concentration.

The effect of catalyst dosage on the catalytic processes was also investigated. As shown in Fig. 7 it clearly indicated that the catalytic reduction of RhB was faster at the reaction system with higher catalyst dosage. Furthermore, the catalytic rate of RhB fitted by pseudo-first order reaction kinetic was applied to evaluate the catalytic activity. Herein, the kinetic equation was described as $ln(A_t/A_0) = -kt$, where A_t and A_0 are the absorbance of RhB at time t and 0, respectively, and k is the rate constant that can be calculated



Fig. 7. (a) Catalytic rate curves of RhB (20 mg/L, 50 mL) after the addition of catalyst with different dosage. (b) First-order kinetics plots of catalytic reduction of RhB with different catalyst dosage.

IdDle Z			
The catalytic kinetic	parameters	of cataly	tic reduction.

Catalyst mass	RhB solution	Rate constant	Correlation coefficient
5 mg	20 mg/L 50 mL	0.076 min ⁻¹	0.988
10 mg		0.643 min ⁻¹	0.990
15 mg		1.316 min ⁻¹	0.963



Fig. 8. Recycling of PDA-kaolin-Ag/2 catalyst for the RhB decoloration with NaBH₄.

from the slope of the linear plot.ln $\left(\frac{A_t}{A_0} = -kt\right)$. (Du et al., 2015).

The rate constants (k) were calculated to be 0.076 min^{-1} , 0.643 min^{-1} , and 1.316 min^{-1} at the corresponding catalyst dosage treatment of 5 mg, 10 mg, and 15 mg, respectively (Table 2). Obviously, the reaction rate increased with the increase of catalyst dosage due to the increased electron transfer ability. In addition, good linear correlation coefficient values of the plots can be observed from Table 2, indicating that the reactions could be well described by pseudo-first order kinetics. Thus, an appropriate catalyst dosage used for the dye reduction is necessary to make the reaction more effective. By comparison with the catalytic reduction of RhB using other different nanocatalysts (Ai et al., 2011; Kurtan

et al., 2015), we concluded that this as-prepared PDA-kaolin-Ag nanocatalyst showed a satisfactory catalytic performance on dye decoloration.

3.3. Catalytic stability

The stability and recyclability of catalyst are important for its application in wastewater treatment. As shown in Fig. 8, the conversion percentage just had a slight decrease after several reusing, indicating the good stability of PDA-kaolin-Ag catalyst. In order to determine the characteristic of recycled catalyst, XRD and XPS analyses were performed. As seen from Fig. 9A, the typical XRD diffraction peaks of crystallized Ag NPs were still prominent. Furthermore, it can be seen from Fig. 9B that there was no significant change on the valence state of Ag after the third cycles. These results are agreement with the previous report, which suggested that the PDA film played an important role in preventing the loss of Ag NPs (Xie et al., 2014; Ye et al., 2014). The good stability indicated that PDA-kaolin-Ag catalyst might has a satisfactory application in dye wastewater treatment.

3.4. Catalytic performance of PDA-kaolin-Ag towards other dye solutions

Undoubtedly, organic dye pollution has been a serious environment challenge. It is a pressing task to remove various dye pollutants from water bodies. In this study, the catalytic reduction tests toward other dyes including methylene blue (MB), methyl orange (MO), and Congo red (CR) by PDA-kaolin-Ag/2 composite were also carried out. Similarly, the color of dyes faded after the catalytic reduction. It can be seen from Fig. S4 that the maximum absorption peaks of three dyes dropped drastically within 20 min. These same reduction phenomena collectively reinforce the potential of PDA-kaolin-Ag composites as efficient catalysts for rapid dye decoloration in the presence of NaBH₄. The potential reduction mechanism could be explained by electron relay system as reported by previous studies (Kurtan et al., 2015, 2016). However, the reduction differences among various dyes could be noted by the comparison of reduction trends and rate constants, which might be ascribed to the different dve nature such as charge and hydrophobicity(loseph and Mathew, 2015; Kurtan et al., 2015). Therefore, more efforts should be paid to conduct a comprehensive research on a specific dye pollutant.



Fig. 9. The XRD (A) and XPS Ag3d patterns (B) of PDA-kaolin-Ag/2 catalyst used before (a) and after 3 recycles (b) for the catalytic reduction of RhB.

4. Conclusions

In summary, PDA-kaolin-Ag catalyst has been successfully fabricated by a facile *in-situ* reduction route without additional reductant, which was determined by the characteristic analysis of XRD, XPS, and TEM. The results show that appropriate dopamine concentration is important for the synthesis of PDA-kaolin-Ag composites and PDA-kaolin-Ag composites can be used as an efficient catalyst for the catalytic reduction of RhB dye in the presence of NaBH₄. Meanwhile, an appropriate catalyst dosage is necessary for the rapid dye decoloration. Importantly, this catalyst remains good stability and recyclability in dye wastewater treatment. In addition, PDA-kaolin-Ag composite also shows excellent catalytic activities toward other organic dyes such as MB, MO, and CR, indicating that this cost-effective catalyst has great potential in environmental applications.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2018.12.012.

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