- 1 Lignosulfonate functionalized kaolin-Ag hybrid catalyst for highly effective dye
- 2 decolorization
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Abstract: In this work, the imp on of silver nanoparticles on lignosulfonate 13 functionalized kaolin composite (LS-kaolin-Ag) was fabricated by a facile reduction 14 al reductant and stabilizer. Transmission electron microscopy, 15 method without ditio. X-ray powder diffection, and X-ray photoelectron spectroscopy, and Fourier 16 17 transform infrared spectroscopy (FTIR) were used to confirm the successful preparation of LS-kaolin-Ag composite. The catalytic reduction tests on both cationic 18 dye rhodamine B and anionic dye Congo red indicated the high catalytic activities of 19 this as-prepared LS-kaolin-Ag composite. Meanwhile, this catalyst showed good 20 21 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 22

efficient and cost-effective catalyst shows great application potential for thedecolorization of various organic dyes.

Keywords: Silver nanoparticles; Lignosulfonate functionalized kaolin; Dye
decolorization; Catalytic performance

27 1. Introduction

Environmental pollution is a serious threat on the economic development, ecosystem 28 diversity, and human health.(Ren et al., 2018a, b; Wang et al., 2018; Ye et al., 2017a, b) 29 Water bodies contaminated by various pollutants, such as heavy 30 als,(Long et al., 2011; Tang et al., 2018; Xu et al., 2012) organic pollutants 31 ny et al., 2018; Yang et al., 2018a, b; Yi et al., 2018; Zhou et al., 2018) dyes,(Gong et al., 2009; He et 32 al., 2018b; Joseph and Mathew, 2015) will e lac that the crisis of water resources. 33 Among those pollutants, organic dyes are one of the most observable pollutants that 34 and other industrial effluents, which have released from textile, leather, 35 te environment and human health due to their undesirable 36 caused adverse impacts on orgacs et al., 2004; Gong et al., 2009; He et al., 2018a) 37 diverse colors and oxi Great efforts have been made to deal with the problem of dye pollution, however, it is 38 39 still an urgent issue to be solved. In recent years, with the development of nanotechnology, nanocatalysis has been considered as superior technology for water 40 41 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 42 43 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 44

45 al., 2016)

Among various nanocatalysts, silver (Ag) nanoparticles as catalysts have been 46 47 attracting extensive scientific interest due to their fascinating properties and important catalytic performance in dye removal.(Ai et al., 2011; Joseph and Mathew, 2015) 48 49 However, the easy aggregation and difficult separation of Ag nanoparticles markedly restrict their catalytic activity and recyclability. In this regard, the incorporation of Ag 50 51 nanoparticles on insoluble supports has been verified as an efficient approach to enhance the dispersity and stability of Ag nanoparticles, there 52 improving their catalytic performance.(Dong et al., 2014; He et al., 2018c; 53 2012) Although various solid materials have been used as supports for Ag 54 ar., 2018c; Kurtan et al., 2016) it nanoparticles, (Goscianska and Pietrzak, 2015; He 55 is necessary to seek cheap and environmental-friendly support materials for their 56 ith the commercial and synthetic support production and application. Co 57 materials, clay minerals, which are widely distributed in nature, have an increasing 58 noparticle supports owing to their economic and 59 application as rioù environmental advantages.(Bagchi et al., 2014; Hashemian and Reza Shahedi, 2013; 60 Lin et al., 2014; Ramprakash Upadhyay and Srivastava, 2016; Zhou, 2011) 61 Furthermore, clay minerals can be used as efficient adsorbents for dye adsorption, 62 which is beneficial for the design and application of clay-based catalysts.(Rawtani and 63 Agrawal, 2012, 2013; Khatri et al., 2016; Adeyemo et al., 2017; Wang et al., 2017; 64 Peng et al., 2017) Kaolin is one of the most widely used clay minerals for 65 nanoparticle support due to its low-cost, abundance, eco-friendly, and exceptional 66

67	properties such as high versatility, thermal and mechanical stability.(Chen et al., 2012;
68	Hashemian and Reza Shahedi, 2013; Wang et al., 2011) Thus, kaolin shows great
69	potential as support of Ag nanoparticles. As is well-known, chemical reduction is one
70	of the powerful methods to fabricate Ag-based composite, which requires appropriate
71	reductant for the reduction of Ag ⁺ ions to form Ag nanoparticles.(He et al., 2018c;
72	Huang et al., 2017; Huang et al., 2018; Zhang et al., 2018a) Although the
73	incorporation of Ag nanoparticles on kaolinite has been reported, the reducing agent
74	of NaBH4 is hazardous and the application is missing. (Patakrilvi and Dekany 2003;
75	Patakfalvi et al., 2003) Thus, it is necessary to seek an effective and green reductant
76	for the synthesis and application of Ag-based compose.
77	Recently, lignosulfonate (LS), a non-toxic and ojocompatible macromolecule with
78	abundant functional groups such as hydroxy, sulfonic acid, and methoxy group, has
79	been reported as reductant and tavillar to synthesize Ag nanoparticles.(Gao et al.,
80	2018; Milczarek et al., 2010 A entative reduction mechanism has been proposed as
81	the reaction of Nyer-amminia complex with the -OH groups (phenolic-OH and
82	aliphatic-OH) on lignosulfonate molecules.(Milczarek et al., 2013) In addition,
83	lignosulfonate can also be used as surface modification molecules to enhance the
84	adsorption ability of raw adsorbent materials towards heavy metals due to their
85	combination with the functional groups on lignosulfonate chain.(Gao et al., 2018;
86	Yang et al., 2014) Inspired by the reduction and surface modification characteristics
87	of lignosulfonate, a hypothesis of utilizing lignosulfonate functionalized kaolin as a
88	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 89 nanoparticles onto lignosulfonate functionalized clay composite. In this work, a novel 90 91 LS-kaolin-Ag hybrid was fabricated by the utilization of lignosulfonate as reductant. Firstly, lignosulfonate was grafted onto kaolin surface to form lignosulfonate 92 functionalized kaolin, then Ag nanoparticles are generated by the reduction of Ag⁺ 93 94 ions. In order to evaluate the catalytic activity of as-prepared hybrid, the decoloration of model dye pollutants, rhodamine B (RhB) and Congo red (CR), were conducted. 95 Herein, we deem that this work can extend the development application of 96 Ag-based clay composite in wastewater treatment. 97 2. Materials and methods 98

99 2.1 Materials

100 Kaolin (Al₂Si₂O₉H₄), silver nitrate, and NBH₄ were purchased from Sinopharm 101 chemical reagent Co., Ltd. Sodum hanosulfonate (LS) was purchased from Xiya 102 reagent. 3-aminopropyl-trijletholysilane (APTMS), rhodamine B (RhB) and Congo 103 red (CR) were purchased from Sigma-Aldrich. Ultrapure water was used for the 104 preparation of solutions in all experiments.

105 2.2 Synthesis

The synthesis of LS-kaolin-Ag composite was based on the reduction nature of 106 lignosulfonate, 107 which has been reported in the synthesis of Ag nanoparticles.(Milczarek et al., 2013) The proposed synthetic process is illustrated in 108 109 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 2 h of ultrasonication, and 110

then 2 mL of APTMS was added into the mixture under stirring for 30 min at room 111 temperature. Afterwards, 400 mg of LS powder was added to the mixture and then 112 113 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 114 115 LS-kaolin composite. For the synthesis of LS-kaolin-Ag composite, silver ammonia solution $([Ag(NH_3)_2]^+)$ was used as Ag precursor, which was prepared by adding 116 dropwise ammonia solution into 10 mg/mL of silver nitrate until the precipitation just 117 disappeared. 400 mg of LS-kaolin was added into a flast 118 aining 200 mL untrapure water and 4 mL of prepared silver ammonia solu 119 inter stirring for 16 h at room temperature. The solid product was filtrated and washed with ultrapure water 120 for several times, and dried in a vacuum o °C overnight. The resultant 121 product was LS-kaolin-Ag composite. The apprepared samples were further used for 122 the following catalytic experime 123

124 2.3 Characteristic

mples was observed by using Transmission Electron 125 The morphology Microscope (TEM) VEOL, Japan) analysis. The chemical compositions of samples 126 were determined by X-ray photoelectron spectroscopy (XPS) on ESCALAB 250Xi 127 (Thermo Fisher Scientific, USA). X-ray powder diffraction (XRD) measurements 128 were recorded on a D8 Advance powder X-ray diffractometer (Bruker, German) with 129 a Cu Ka X-ray generator (40 kV, 100 mA). The samples for Fourier transform 130 infrared spectroscopy (FTIR) measurement were prepared by mixing the dried sample 131 powder with KBr (w/w 1:100) together and then compressed into thin pellets. The 132

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.

136 2.4 Catalytic reduction tests

The catalytic reduction tests of LS-kaolin-Ag composite towards RhB and CR with 137 the presence of NaBH₄ were carried out as follows. For the catalytic reduction of CR 138 solution, 20 mg of catalyst was added to 50 mL of CR solution with different 139 concentrations (50, 100, and 200 mg/L, respectively) and 0. 140 A NaBH₄ under stirring; 50 mL of 100 mg/L CR solution was mixed with 141 ferent catalyst dosages (10, 20, and 30 mg, respectively) and 10 mM NaBE under stirring. For the catalytic 142 reduction of RhB solution, 10 mg of catalys was added to 50 mL of RhB solution 143 with different concentrations (10, 20, and 4 mg/L, respectively) with 2 mM NaBH₄ 144 under stirring; 50 mL of 20 m solution was mixed with different catalyst 145 dosages (5, 10, and 20 mg respectively) and 2 mM NaBH₄ under stirring. With the 146 soler of dye solution gradually vanished due to the catalytic 147 reaction proceed the reduction. The catalytic activities of as-prepared samples were estimated by 148 monitoring the absorption spectra change at the maximum absorption wavelength of 149 dve with time using a UV-vis spectrometer (UV-2550, SHIMADZU, Japan). The 150 corresponding blank experiments without catalyst and comparative experiments with 151 LS-kaolin composite on dye decolorization were also conducted. 152

153 3. Results and discussion

154 3.1 Characterization studies

The characteristic analysis of kaolin has been reported in our previous study, (He et al., 155 2018b; He et al., 2019a, b) therefore, the main characteristics of as-prepared samples 156 157 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 158 (Fig. 1A), the smooth surface turned into rough and some thin flakes were observed 159 on the edge after the lignosulfonate modification on kaolin (Fig. 1B). On the other 160 hand, the color of raw kaolin was obviously changed from white to brown after the 161 modification (insets in Fig. 1), indicating the successful introduction 162 of lignosulfonate. Furthermore, it could be clearly seen from TEM image of 163 olin-Ag composite (Fig. 1C) that some small Ag nanoparticles were well dispersed on the material 164 surface. The EDX characteristic (Fig. 1D) fur de demonstrated the presence of 165 element of Ag in LS-kaolin-Ag composite. Overall, the differences of TEM images 166 ccessfully immobilized on the surface of suggested that Ag nanoparticle 167 LS-kaolin. 168

appointe formation was also analyzed by FTIR spectra 169 In addition, measurement (Fig. 2). The peaks at 472 and 577 cm⁻¹ that observed at kaolin, and 170 LS-kaolin, and LS-kaolin-Ag composite were corresponed to Si-O-Si and Si-O-Al, 171 respectively (Fig. 2 b, c and d).(Jin et al., 2015) After the LS modification, the typical 172 peak at 1043 cm⁻¹ (Fig. 2a), which was attributed to S=O symmetric stretching of the 173 $-SO_3$ group on the LS chains, was disappeared due to the interaction of $-SO_3^-$ with 174 NH₂ group.(Lü et al., 2010; Zhang et al., 2018b) In order to further confirm the 175 modification of lignosulfonate and the synthesis of Ag nanoaprticles on kaolin surface, 176

XPS analysis was used to determine the surface component and composition of 177 samples.(Chi et al., 2012) After modification, the characteristic elements of kaolin 178 179 such as Al and Si were still observed in the XPS survey spectra of LS-kaolin and LS-kaolin-Ag composites; however, their peak intensities decreased significantly as 180 181 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 182 introduction of lignosulfonate. The presence of N element was ascribed to the 183 application of APTMS as linkage. Compared with the XP ey spectrum of 184 LS-kaolin composite, an obvious peak of Ag3d was ob-185 n the XPS survey spectrum of LS-kaolin-Ag composite (Fig. 3A). Exhermore, the XPS spectrum of 186 Ag3d of LS-kaolin-Ag composite showed twe typical peaks at 368.3 eV for Ag3d_{5/2} 187 and 374.3 eV for Ag3d_{3/2}, respectively (Fig. 3B), indicating the metallic state of Ag in 188 LS-kaolin-Ag composite.(Chi ; Xu et al., 2017) This finding could be 189 further supported by the analysis of powder XRD pattern. As shown in Fig. 4A, the 190 could be readily indexed to face-centered-cubic structure of typical diffraction peak 191 metallic Ag according to JCPDS card NO.04-0783. Due to the low content of Ag 192 nanoparticles in the product as seen from EDX and XPS spectra, the XRD peak 193 intensities of Ag nanoparticles were not high.(Kurtan et al., 2016) Taking the above 194 characteristic analysis together, the immobilization of Ag nanoparticles on 195 lignosulfonate functionalized kaolin was successfully prepared. 196

197 Nitrogen adsorption-desorption isotherms of kaolin, and LS-kaolin-Ag samples
198 measured at 77 K is presented in Fig. 4B. The BET surface area of LS-kaolin-Ag was

199 16.223 m²/g, which was higher than that of kaolin (9.652 m²/g). The relatively higher 200 surface area could be beneficial for the contact of pollutant molecules with composite.

201 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 202 selected to investigate the catalytic activity of LS-kaolin-Ag composite in the 203 presence of NaBH₄. In order to determine the catalytic property of LS-kaolin-Ag 204 composite, LS-kaolin composite was firstly used in a control experiment for dye 205 removal. As shown in Fig. 5, no obvious peak changes of dyes we observed, which 206 was similar with the phenomena of catalytic reduction just 207 resence of NaBH₄, indicating that LS-kaolin composite had negligible catalytic activity towards dye 208 reduction when in comparison with LS-kaolin Accomposite in the following sections. 209 Therefore, a series of catalytic experiments were performed using LS-kaolin-Ag 210 composite as catalyst. 211

CR is a benzidine-based nione diazo dye with two –N=N– bonds on its molecular 212 biogegradable and toxic in aquatic environment.(Ganapuram structure, which 213 non et al., 2015; Vimons's et al., 2009) It was chosen as a model anionic dye indicator in 214 215 this study. The catalytic reaction was monitored by the changes of absorption spectra using UV-vis spectrophotometer. Similar with the previous reports, CR aqueous 216 solution shows the typical peaks at 498 nm ($\pi \rightarrow \pi^*$) and 343 nm ($n \rightarrow \pi^*$).(Ganapuram 217 et al., 2015; Vimonses et al., 2009) The effect of catalyst dosage on the decolorization 218 219 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, 220

the absorption spectra changed remarkably and dye color gradually vanished after 221 adding the LS-kaolin-Ag composite to CR solution. Thus, the incorporation of Ag 222 223 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 224 225 initiated catalytic process was attributed to the role of Ag nanoparticles that acting as electron relay to transfer the electrons from BH_4^- (donor) to the dye (acceptor) 226 molecule.(Khan et al., 2018) Meanwhile, the dye decolorization rate became much 227 faster with the increase of catalyst dosage in the mixture. When 228 catalyst dosage was 30 mg in 50 mL of 100 mg/L CR solution, the complete 229 catalytic reduction just required about 8 min (Fig. 6D), which took about 12 min at 20 mg catalyst at 230 same condition (Fig. 6C), whereas the dye reduction still proceeded after 30 min at 10 231 mg catalyst (Fig. 6B). At higher catalyst decage, the content of Ag nanoparticles in 232 ase the active sites on catalyst surface to composite was larger, which c 233 facilitate the electron transfer speed and thereby enhancing the catalytic reduction. 234 inet cs are commonly used to evaluate the reaction kinetics, The pseudo-first 235 der which can follow the equation: $\ln (A_t/A_0)$ =-kt, where A_t and A_0 are the absorbance of 236 CR at time t and 0, respectively, and k is the rate constant that can be calculated from 237 the slope of the linear plot.(Ai et al., 2011) As seen from Fig. 6F, the calculated rate 238 constants for CR reduction with LS-kaolin-Ag composite at 0, 10, 20, and 30 mg were 239 0.001, 0.049, 0.360, and 0.583 min⁻¹, respectively. This result further indicated the 240 241 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 243 color almost completely faded within 1 min at 50 mg/L of CR solution, whereas the 244 245 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 246 concentration of CR solution. At a fixed catalyst mass and NaBH₄ concentration in 247 solution, the electron transfer rate is finite. However, with the increase of dye 248 concentration, the competition among dye molecules to accept electrons from catalyst 249 increased, thereby decreasing the catalytic activity of catalys 250 RhB, a cationic dye, was also used to investigate 251 alytic activity of LS-kaolin-Ag composite in the presence of NaBH-under different catalyst dosages 252 and dye concentrations. Without the catalyst, the regime of maximum absorption peak 253 254 was insignificant, just at a very slow rate in the presence of NaBH4.(Kurtan et al., olin-Ag composite with certain mass can 2015) In contrast, the addition 255 talytic effectively enhance the c reaction as reflected in Fig. 8. The reduction 256 o at sibuled to the electron relay system.(Kurtan et al., 2015) As 257 mechanism was seen from Fig. 8F, the calculated rate constants for RhB reduction with LS-kaolin-Ag 258 composite at 0, 5, 10, and 15 mg were 0.007, 0.028, 0.443, and 2.067 min⁻¹, 259 respectively. The plots of $\ln (A_t/A_0)$ versus time showed a good linear correlation 260 (Table 1), indicating that the reactions conformed to pseuso-first kinetics. Similarly, 261 the high dye concentrations could inhibit the reaction process (Fig. 9). Herein, the set 262 263 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 264

as the CR reduction were observed. Thus, this as-prepared LS-kaolin-Ag composite is
an effective catalyst for dye decolorization.

267 3.3 Catalytic stability

A good stability and recyclability of catalyst is important for its practical application. 268 Investigations on the recyclability of LS-kaolin-Ag composite on CR and RhB 269 decoloration were carried out. After the completion of catalytic reaction, the catalyst 270 was filtered and washed with ultrapure water and ethanol and then dried for the next 271 cycle. Fig. 10 shows the recyclability of LS-kaolin-A 272 posite for the decolorization of two dyes in five successive catalytic r 273 Similar with the previous reports, the conversion percent of dyes t decreased a little after each 274 recycle, which may be attributed to the loss of cataly during recycling.(Kurtan et al., 275 2016; Kurtan et al., 2015) Therefore, mor efforts should be paid to improve the 276 stability of this as-prepared com 277

278 4. Conclusions

olin-Ag catalyst has been successfully fabricated by a 279 In summary, a f facile reduction roue without additional reductant, which was determined by the 280 281 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 282 RhB dyes in the presence of NaBH₄. Meanwhile, an appropriate catalyst dosage is 283 necessary for the rapid dye decolorization. Importantly, this catalyst remains good 284 285 stability and recyclability in dye wastewater treatment. These results indicate that this cost-effective catalyst has great potential in environmental applications. 286

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- 291 Compliance with ethical standards
- 292 Conflict of interest
- 293 The authors declare that they have no conflict of interest.
- 294 Ethical approval
- 295 This article does not contain any studies with human participants or animals
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