



Effective treatment and utilization of hazardous waste sulfuric acid generated from alkylation by lignocellulose ester-catalyzed oxidative degradation of organic pollutants

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GRAPHICAL ABSTRACT



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ABSTRACT

Alkylation reaction catalyzed by concentrated H₂SO₄ generates hazardous waste H₂SO₄ containing a large amount of organic pollutants. This study focused on effective utilization and treatment of the waste H₂SO₄ for simultaneous consumption of H₂SO₄ and deep oxidative degradation of the organics. The waste H₂SO₄ could completely react with magnesium oxide ore to prepare crude MgSO₄ solution, and the organic pollutants in the solution were deeply degraded and mainly mineralized to H₂O and CO₂ with H₂O₂ as oxidant and sugarcane bagasse citrate (SBC), a kind of lignocellulose ester, as catalyst. The total amount of acidic groups of SBC significantly affected its catalytic activity, attributing to that these oxygen-containing functional groups adsorbed and immobilized metal ions on SBC to form catalytic active sites, which could activate and catalyze H₂O₂ to generate •OH and HO₂• radicals for effective degradation of the organics. The resulting purified MgSO₄ solution with color removal of 93.71% and total organic carbon removal of 85.89% under optimum catalytic reaction conditions was used to produce qualified MgSO₄·7H₂O product. These results highlighted the feasibility of using lignocellulose ester as effective catalyst for deep oxidative degradation of hazardous organic pollutants.

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1. Introduction

Economic, environmental, and technological criteria lead to the increased demand of high octane alkylates, which is commonly considered as an ideal blending components for gasoline. The most dominant technology for the current industrial production of the high octane alkylates is the alkylation of isobutane and C3 – C5 olefins catalyzed by concentrated H_2SO_4 (Sun et al., 2013). The spent H_2SO_4 catalyst is a viscous, thick, and black liquid with a pungent odour, and the main components are H_2SO_4 (~90%), organics (~7%), and H_2O (~3%). For producing one ton of alkylates, about 80 kg of waste H_2SO_4 is generated. Plenty of hazardous waste H_2SO_4 can pose serious threats to the ecological environment. Recently, the proven technology is using waste H_2SO_4 to generate SO_2 by high temperature pyrolysis, and the SO_2 is the feed gas for the production of fresh concentrated H_2SO_4 (Wang et al., 1999). But the major defect of this technology is the corrosive properties of waste H_2SO_4 and pyrolysis gas, resulting in high equipment investment and operating costs, which thus greatly reduce the economic feasibility. Direct utilization of waste H_2SO_4 to produce sulfate products can substantially reduce the investment cost, but the difficulty is how to completely degrade the organic pollutants with high chromaticity and strong pungent odour. Catalytic oxidation is an accepted method for deep degradation of the organics to CO_2 , H_2O , and other harmless small molecules (Boczkaj and Fernandes, 2017). To obtain the sulfate products meeting the requirement of purity standard, the oxidant and catalyst should not introduce any impurity into the reaction system (Cai et al., 2019). Choosing an appropriate method for the disposal of waste H_2SO_4 can effectively avoid serious hazards to the ecosystem and enhance economic efficiency for alkylated gasoline manufacturer.

Advanced oxidation processes (AOPs) have been widely demonstrated to be environment-friendly and economical technology for the treatment of organic pollutants. AOPs are powerful techniques for deep degradation of various hazardous or recalcitrant organic contaminants into CO_2 and H_2O (Duan et al., 2018). For chemical oxidation based AOPs, it is generally believed that highly reactive free radicals generated from various oxidants lead to the degradation of organics. Peroxide, ozone, persulfate, and high-valent transition metal species are usually used as oxidants (Wang et al., 2019; Guan et al., 2018; Huanosta-Gutiérrez et al., 2012; Yang et al., 2019; Feng et al., 2018). Among them, hydrogen peroxide (H_2O_2) is the most common oxidant for AOPs (Boczkaj and Fernandes, 2017; Guan et al., 2018; Ribeiro et al., 2016). Hydroxyl radicals ($\cdot\text{OH}$), as one of the most powerful oxidants with the supreme oxidation potential, is a strong oxidant for mineralization of organic compounds (Yang et al., 2013; Yu et al., 2018). In particular, a catalyst is essential for effective generation of $\cdot\text{OH}$ by catalytic decomposition of H_2O_2 . Most of the degradation of organics by H_2O_2 use metal-containing catalysts, especially the Fe (II)-containing catalysts (Lyu et al., 2015; Taran et al., 2015; Wang et al., 2017). However, metal-containing catalyst can introduce metal ion into the reaction solution and thus affect the purity of the product. It was reported that the materials with surface functional groups containing primarily oxygen can activate and catalyze H_2O_2 to generate $\cdot\text{OH}$, ascribing to that oxygen-containing functional groups act as electron acceptors to promote the decomposition of H_2O_2 (Yu et al., 2005; Wang et al., 2014; Zhang et al., 2014). It is significant to develop a green and effective catalyst which can adopt the oxygen-containing functional groups for AOPs without introducing extra metal ions to the reaction system.

Lignocellulose is composed of cellulose, hemicellulose, and lignin, which contain various oxygen-containing functional groups, such as aliphatic and phenolic hydroxyl, methoxyl, carbonyl, and carboxyl groups (Kai et al., 2016; Hendriks and Zeeman, 2009). It is hopeful to use these functional groups for activating and catalyzing H_2O_2 to generate $\cdot\text{OH}$. However, the hydroxyl groups can form inter- and intramolecular chain-stiffening hydrogen bonds, contributing to the

highly crystalline structure of cellulose (Klemm et al., 2005). As the stable supramolecular structure of lignocellulose with complex cellulose-hemicellulose-lignin matrix (Sun et al., 2016), these functional groups are in “passivation” state. In addition, lignocellulose contains plenty of hydroxyl groups but relatively fewer amounts of other oxygen-containing functional groups. It is considered that surface acidic functional groups play the main role for catalytic performance (Yu et al., 2005; Wang et al., 2014). Therefore, it is crucial to activate the “passive” functional groups and simultaneously introduce acidic functional groups to lignocellulose for enhancing its catalytic performance.

In this study, sugarcane bagasse (SB), a typical kind of lignocellulose derived from agro-industrial residue, was used to prepare lignocellulose-based AOPs catalyst for catalyzing the oxidative degradation of the organics in waste H_2SO_4 to prepare qualified sulfate product. As citric acid is a natural hydroxyl carboxylic acid with containing three carboxylic groups and is ubiquitous in natural waters (Wang et al., 2014), it is a desired green reagent for providing acidic functional groups to lignocellulose. A green, simple, and efficient technology, mechanical activation (MA)-assisted solid-phase reaction (MASPR), was adopted for the preparation of SB citrate (SBC) (Gan et al., 2018a). During the process of MASPR, SB was activated by MA and simultaneously reacted with citric acid in solid-phase condition without the use of organic solvents. The waste H_2SO_4 first reacted with magnesium oxide ore to prepare crude MgSO_4 solution, and then the organic pollutants in this solution were oxidized and degraded with H_2O_2 as oxidant and SBC as catalyst. The treated solution was crystallized to produce $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ with required purity. Moreover, the catalytic mechanism of SBC for the degradation of the organic pollutants was detailedly studied. The findings can develop a novel and efficient lignocellulose-based catalyst for deep oxidative degradation of hazardous organic pollutants, and develop a promising technology for effective treatment and utilization of waste H_2SO_4 .

2. Experimental

2.1. Materials

Waste H_2SO_4 , with H_2SO_4 content of 90.5%, was obtained from Qinzhou Tianheng Petrochemical Co., Ltd (Guangxi, China). Magnesium oxide ore (the chemical composition is listed in Table S1, and the main mineralogical structure and phase are shown in Fig. S1), with MgO content of 79.49%, was supplied by Guangxi Wuxing Chemical Group Co., Ltd, China. Sugarcane bagasse (SB) was obtained from Nanning Sugar Manufacturing Co., Ltd. (Guangxi, China). Chromatographically pure dimethyl-pyrroline-N-oxide (DMPO) was purchased from Sigma-Aldrich Corporation, USA. Citric acid, sodium hypophosphite, H_2O_2 (30 wt.% aqueous solution), tert-butyl alcohol (TBA), p-benzoquinone (PBQ), and other chemical reagents were obtained from commercial sources (analytical grade), used without additional purification. Deionized water was used throughout the work.

2.2. Preparation of SBC by MASPR

For the preparation of SBC by MASPR technology, a customized stirring ball mill was adopted as solid-phase reactor (Gan et al., 2018b). Typically, 500 mL of zirconia milling balls (5 mm diameter) was put into a jacketed stainless steel tank (1200 mL). Then, the mixture of 10.00 g of SB (dry basis), 11.85 g of citric acid, and 1.00 g of sodium hypophosphite (catalyst) was added into the tank. The mixture was subjected to milling and reacted at a speed of 300 rpm at 80 °C by circulating the thermostatic water in the jacket of the tank. After milling for different designed reaction time, the balls were removed from the powdered sample by a sieve. The sodium hypophosphite and unreacted reagents were removed by washing with distilled water to neutral, and then the sample was washed with absolute alcohol to remove water. After vacuum-dried at 55 °C for 24 h, the resulting SBCs

with different amount of acidic groups were obtained.

2.3. Determination of acidic groups in SBC

The amount of acidic groups (including carboxylic, carbonyl, lactone, and phenolic hydroxyl groups) was determined by Boehm titration method (Boehm, 2008; Goertzen et al., 2010), and the detailed experimental procedures are presented in Supplementary material. The total amount of acidic groups (n_{ag}) was the sum of the amounts of carboxylic groups (n_{RCOOH}), lactone groups (n_{RCOOCR}), phenolic hydroxyl groups (n_{ArOH}), and carbonyl groups (n_{RCOR}).

2.4. Experimental procedures for the treatment of waste H_2SO_4

The leaching experiment of waste H_2SO_4 and magnesium oxide ore was performed in a 2500 mL beaker. Firstly, 189 g of magnesium oxide ore and 1575 mL of deionized water were added in the breaker and stirred for 5 min to mix thoroughly. Then, the waste H_2SO_4 (225 mL) was slowly added into the breaker and reacted with the magnesium oxide ore. After finishing the addition of H_2SO_4 , the mixture was continuedly stirred to fully react for 10 min, and then the pH value of leaching slurry was measured by a pH meter. If the slurry was neutral, it was filtrated by a vacuum filter. The filtrate was crude $MgSO_4$ solution (1600 mL), stored in a sealed container for analysis and next experiments.

The oxidative degradation experiments of the crude $MgSO_4$ solution were carried out in a 250 mL three-neck flask, which was immersed in a thermostatic water bath for maintaining constant reaction temperature. In a typical experiment, 160 mL of the crude $MgSO_4$ solution was added in the flask and stirred for about 10 min to reach the required temperature, and then a certain amount of the SBC was added in the flask. A certain amount of H_2O_2 was added dropwise to the $MgSO_4$ solution for oxidative degradation of the organics, with a constant stirring speed of 100 rpm. After desired reaction time, the used SBC was removed from the solution by filtering. The resulting solution was evaporated under magnetic stirring. When the density of the solution reached 1.38 g cm^{-3} , the concentrated solution was cooled in room temperature for crystallization. After standing for 24 h, the magnesium sulfate crystals were separated from the solution, and the resulting $MgSO_4 \cdot 7H_2O$ product was obtained.

2.5. Characterization and analytical methods

X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, solid-state CP/MAS ^{13}C -NMR (cross-polarization/magic angle spinning ^{13}C -nuclear magnetic resonance), energy-dispersive X-ray fluorescence (XRF), ultraviolet/visible (UV/vis) spectroscopy, and electron paramagnetic resonance (EPR) were applied for the characterizations of the samples. The point of zero charge (pH_{PZC}) of the samples was measured by potentiometric titration. The total organic carbon (TOC) of the $MgSO_4$ solutions was analyzed by a TOC analyzer. The operating conditions for these analyses are described in Supplementary material.

3. Results and discussion

3.1. Catalytic activity of the SBC with different amount of acidic groups

To investigate the amount of acidic groups on the catalytic performance of lignocellulose ester, the SBCs with different n_{ag} prepared by MASPR were used to catalyze H_2O_2 to degrade the organics in crude $MgSO_4$ solution. As shown in Fig. 1a, the degradation efficiency of the organic pollutants (evaluated by the color and TOC removals of the $MgSO_4$ solution) remarkably enhanced with the increase of n_{ag} , implying that acidic functional groups in SBC exhibited the main catalytic activity. In the decomposition process, the acidic groups play the role of

electron transfer catalyst, relating to the oxidation and reduction of catalytic active sites (Zhang et al., 2014). The increase in the degradation efficiency of the organics can be due to that the acidic groups in SBC effectively enhanced the oxidation capacity of H_2O_2 .

The increase of n_{ag} in SBC was ascribed to the action of MA and the graft of citrate groups on SB. The amounts of different acidic groups in different samples are presented in Table S2. SB is composed of a certain amount of lignin (~23%), which contains a large number of functional groups (Laurichesse and Avérous, 2014). When subjected to MA, a series of free radical reaction could be induced by the instantaneous high temperature, and the reactions such as depolymerization/re-polymerization, demethylation, and redox were took place simultaneously, leading to the generation of different acidic groups in MA-treated SB (Zhao et al., 2016). In addition, the highly-ordered supermolecular structure of SB and the hydrogen bonds were destroyed by MA, and thus enhanced the reactivity of SB (Gan et al., 2018a). MA treatment induced the changes in the functional groups of SB, and the activated hydroxyl groups simultaneously reacted with citric acid to prepared SBC. The SBC with n_{ag} of $3.471 \text{ mmol g}^{-1}$ was applied for further and detailed investigations.

3.2. Effect of different factors on degradation efficiency of the organics in $MgSO_4$ solution

3.2.1. Effect of SBC dosage

Fig. 1b shows that the color and TOC removals greatly enhanced as the SBC dosage increased from 0 to 0.02 g/g waste H_2SO_4 in the oxidation system, indicating that the increased amount of SBC provided more acidic groups for effective catalytic activity. However, the degradation efficiency of the organics minimally increased when the SBC dosage was over 0.02 g/g waste H_2SO_4 , and a higher dosage of SBC was not beneficial to color and TOC removals. This phenomenon can be explained by the inhibition effect of excessive catalyst leading to scavenging of reactive radicals or competitive reactions that reduce the amount of radicals available (Rodrigues et al., 2017; Kang et al., 2018). This result suggests that excess dosage of catalyst could not lead to high catalytic performance but increased material consumption and the difficulty of post-processing. An optimum dosage of SBC catalyst was 0.02 g/g waste H_2SO_4 .

3.2.2. Effect of H_2O_2 dosage

As presented in Fig. 1c, H_2O_2 (30 wt.%) dosage had a significant effect on the degradation efficiency of the organics, and the color and TOC removals reached 89.41% and 59.46% respectively with the H_2O_2 dosage of 0.2 g/g waste H_2SO_4 . Continued increase of the H_2O_2 dosage did not lead to remarkable enhance of the color and TOC removals, implying that excess H_2O_2 reduced its oxidation capacity. This may be due to that H_2O_2 can act as scavenger to react with the generated hydroxyl radicals to form less reactive radicals like hydroperoxyls in high concentration of H_2O_2 (Boczkaj and Fernandes, 2017; Coleman et al., 2007). In addition, the formed hydroperoxyls could continue to consume H_2O_2 to generate water and oxygen (Zhang et al., 2014). Therefore, a H_2O_2 dosage of 0.2 g/g waste H_2SO_4 was considered as an appropriate value for effective oxidative degradation of the organics in $MgSO_4$ solution.

3.2.3. Effect of pH

As an important parameter in the catalytic process, pH can significantly affect the catalytic effect for impacting the charge of catalyst, H_2O_2 , and organic compounds in the solution. Fig. 1d shows that the color and TOC removals gradually increased as the pH increased from 1 to 5, but sharply decreased as the pH continually increased to more than 7. As a kind of weak acid, H_2O_2 is relatively stable in acidic media, but it is easy to decompose to oxygen and water in alkaline media. Therefore, the oxidation capacity of H_2O_2 was weak at $pH > 7$. At $pH < 7$, H_2O_2 with stable state could be catalyzed by SBC to generate

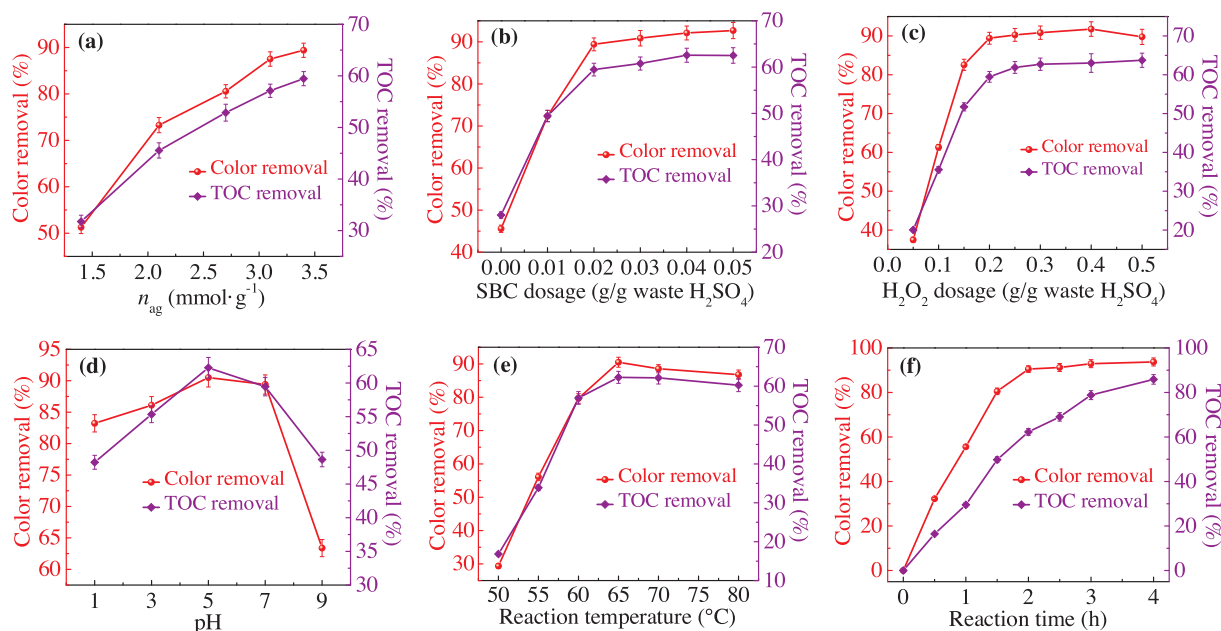


Fig. 1. Effects of (a) n_{ag} of SBC (SBC dosage of 0.02 g/g waste H₂SO₄, H₂O₂ dosage of 0.2 g/g waste H₂SO₄, pH = 7, reaction temperature of 65 °C, and reaction time of 2 h), (b) SBC dosage (n_{ag} = 3.471 mmol g⁻¹, H₂O₂ dosage of 0.2 g/g waste H₂SO₄, pH = 7, reaction temperature of 65 °C, and reaction time of 2 h), (c) H₂O₂ dosage (n_{ag} = 3.471 mmol g⁻¹, SBC dosage of 0.02 g/g waste H₂SO₄, pH = 7, reaction temperature of 65 °C, and reaction time of 2 h), (d) pH (n_{ag} = 3.471 mmol g⁻¹, SBC dosage of 0.02 g/g waste H₂SO₄, H₂O₂ dosage of 0.2 g/g waste H₂SO₄, reaction temperature of 65 °C, and reaction time of 2 h), (e) reaction temperature (n_{ag} = 3.471 mmol g⁻¹, SBC dosage of 0.02 g/g waste H₂SO₄, H₂O₂ dosage of 0.2 g/g waste H₂SO₄, pH = 5, and reaction time of 2 h), and (f) reaction time (n_{ag} = 3.471 mmol g⁻¹, SBC dosage of 0.02 g/g waste H₂SO₄, H₂O₂ dosage of 0.2 g/g waste H₂SO₄, pH = 5, and reaction temperature of 65 °C) on the color and TOC removals of the MgSO₄ solution.

reactive hydroxyl radicals to greatly improve its oxidation capacity. As the lifetime of hydroxyl radicals is extremely short, the organics were mainly degraded in the “reaction zone” of SBC, where the reactive sites of SBC, H₂O₂, and organics were the collective existence (Kan and Huling, 2009; Georgi and Kopinke, 2005). The SBC catalyst exhibited negative or positive charge when the solution pH greater or less than pH_{PZC} , respectively, and the pH_{PZC} of SBC was determined to be 2.2 (Fig. S2). H₂O₂ usually exhibits positive charge, thus the SBC catalyst with negative charge could lead to the electrostatic attraction and made H₂O₂ more easily diffused on the reactive sites of SBC, which improved the generation of hydroxyl radicals. In addition, SBC catalyst with negative charge contributed to the adsorption and immobilization of metal cations, which could play important role as the reactive sites for catalyzing H₂O₂ to producing hydroxyl radicals. As a result, a pH around 5 could be the point where a proper interaction force among SBC, H₂O₂, and organics, which contributed to the highest color and TOC removals.

3.2.4. Effect of reaction temperature

As presented in Fig. 1e, the increase of temperature could enhance the degradation of the organics with H₂O₂ as oxidant in the presence of SBC catalyst. In MgSO₄ solution, the high salinity inhibited the activity of H₂O₂ molecules in low temperature as the relatively high viscosity of the liquid phase and diffusion resistance (Bacardit et al., 2007). Obviously, the increase in reaction temperature could diminish the inhibitory effect of salt and promote the diffusion of H₂O₂ and organics onto the reactive sites of SBC (Kan and Huling, 2009). Moreover, the increase of temperature could accelerate the surface reaction rate, ascribing to that a higher temperature is good for the mass transfer process. At the temperature of 65 °C, the color and TOC removals almost reached the highest values. However, the degradation rate slightly decreased as the temperature greater than 65 °C. This may be due to that high temperature could accelerate the decomposition of H₂O₂ to oxygen and water, reducing the generation of active radicals for strong oxidative degradation of the organics. An optimum temperature of around

65 °C was chosen for the catalytic reaction.

3.2.5. Effect of reaction time

The results in Fig. 1f confirm that the organic pollutants were gradually degraded and mainly mineralized to CO₂ and H₂O catalyzed by SBC, as TOC and color removals decreased with the increase of reaction time. As increasing the reaction time from 0 to 2 h, both the color and TOC removals increased significantly, reaching 90.50% and 62.26%, respectively. This result also indicates that the removal rate of color was faster than that of TOC. As increasing the reaction time from 2 to 4 h, the removal efficiency of color only increased by 3.21% and reached 93.71%, but that of TOC increased by 23.63% and reached 85.89%. This suggests that the chromogenic macromolecular organics were quickly degraded to small molecular organics, and then gradually mineralized to CO₂ and H₂O. Therefore, the degradation of the macromolecular organics went through several steps, and maintaining a longer reaction time was more beneficial to the deep oxidative degradation of the organic pollutants. The change in the color of the solution could directly reflect the degradation degree of the chromogenic macromolecular organics, but the removal efficiency of TOC could be considered as an indicator for evaluating the complete degradation and removal of all the organics in the solution.

3.3. Characterization of the SBC samples before and after catalysis

3.3.1. FTIR analysis

Fig. 2a shows the FTIR spectra of original SB and the SBCs before and after catalytic reaction. In Fig. 2a-1, the spectrum of original SB shows the characteristic peaks of cellulose at 3426, 2916, 1425, 1376, 1250, 1162, and 1050 cm⁻¹, assigned to stretching vibration of -OH, stretching vibration of C-H, CH₂ bending, C-H bending, OH in-plane bending, antisymmetric bridge stretching of C-O, and skeletal vibration of C-O-C pyranose ring, respectively (Sun et al., 2005). The characteristic peaks of lignin are presented at 1602, 1511, 1460, and 1425 cm⁻¹, attributed to aromatic skeleton vibrations (Zhou et al.,

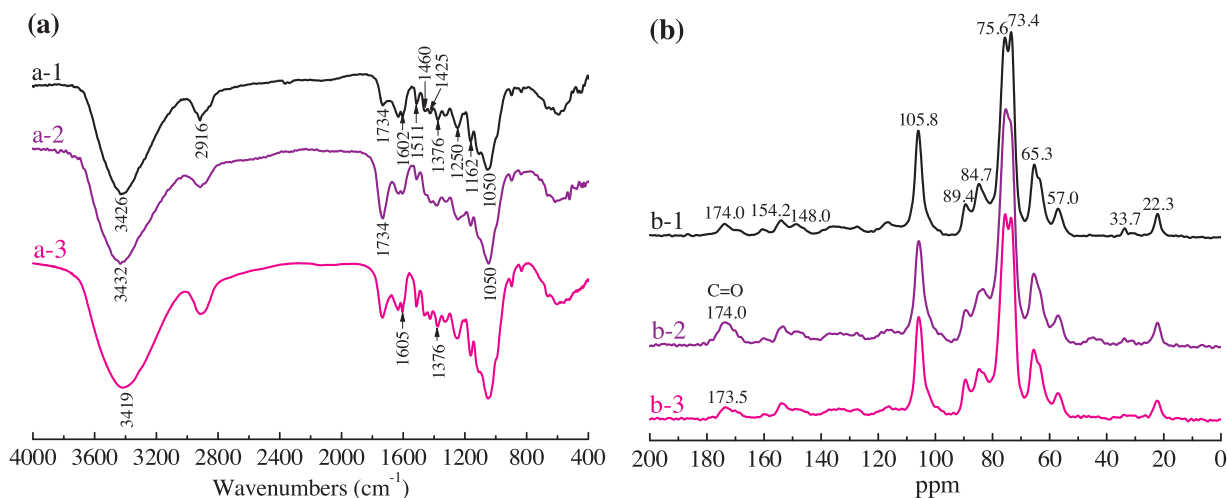


Fig. 2. (a) FTIR spectra and (b) CP/MAS ¹³C NMR spectra of (1) SB, (2) SBC before catalytic reaction, and (3) SBC after catalytic reaction.

2015). A peak at 1734 cm⁻¹ is ascribed to the characteristic polysaccharides in hemicellulose (Sun et al., 2004). FTIR analysis could further confirm the introduction of citrate groups in SBC by MASPR, as the significant increase in the intensity of characteristic peaks of ester carbonyl and carboxyl groups at 1734 cm⁻¹ (Fig. 2a-2). After catalytic degradation of the organics in MgSO₄ solution with H₂O₂ as oxidant and SBC as catalyst, the peak intensity at 1605 and 1376 cm⁻¹ in SBC became stronger, implying that metal ions were adsorbed on the carboxyl carbonyl groups to form carboxylate. Moreover, the stretching vibration of O–H in the SBC before and after catalytic reaction shifted from 3432 to 3419 cm⁻¹ (Fig. 2a-3), which showed a strong evidence for the chelating interaction between the functional groups (mainly hydroxyl and carboxyl groups) and metal ions induced by the formation of complexes (Ahmad et al., 2018; Wang and Wang, 2018).

3.3.2. Solid state CP/MAS ¹³C NMR analysis

The CP/MAS ¹³C NMR spectra of original SB and the SBCs before and after catalytic reaction are shown in Fig. 2b. In the spectrum of original SB (Fig. 2b-1), the signals at 65.3, 73.4, 75.6, 84.7, 89.4, and 105.8 ppm are attributed to C-6, C-5, and C-2,3 of crystalline cellulose, C-4 of amorphous cellulose, C-4 and C-1 of crystalline cellulose, respectively (Vaidya et al., 2016); the characteristic signals at 33.7, 100–155, and 165–180 ppm are assigned to methylene bridges between aromatic nuclei, aromatic carbons, and carbonyl units in lignin, respectively (Gan et al., 2018a); the signals at 22.3 and 174.0 ppm correspond to the inherent acetylation of hemicellulose and acetyl, uronic, and ferulic ester groups of the polysaccharides, respectively. In the spectrum of the MASPR-prepared SBC before catalytic reaction (Fig. 2b-2), the peaks at 65.3, 84.7, and 89.4 ppm became weaker, and the peaks at 73.4 and 75.6 ppm overlapped to one peak, which indicate that MA destroyed the crystal structure of SB and thus improve its accessibility and reactivity (Gan et al., 2018a). In addition, the increase in the intensity of the signal at 174.0 ppm assigned to C=O confirmed the introduction of citrate groups in SB to prepare SBC by MASPR. In contrast, the intensity of the characteristic peak of C=O in the spectrum of SBC decreased after catalytic reaction, and the peak shifted from 174.0 to 173.5 ppm (Fig. 2b-3), which could be ascribed to the interaction between carboxyl groups and metal ions, corresponding to the result of FTIR analysis.

3.3.3. Elemental analysis

Elemental analysis of magnesium oxide ore, original SBC, and used SBC was performed by XRF, and the result is presented in Table S1. As comparing the elements in the original and used SBC samples, it shows that the contents of some elements in the used SBC were greater than

those in the original SBC and some new elements exhibited in the used SBC, such as Mg, Fe, Mn, Cu, etc. This might be due to that the acidic groups in SBC could adsorb some metal ions from the crude MgSO₄ solution during the process of catalytic reaction, resulting in the enrichment of metal ions on the surface of SBC, which could form catalytic active sites in SBC. The metal ions adsorbed onto the acidic groups of SBC were the main active sites. In addition, SBC could simultaneously adsorb the organic compounds by its abundant functional groups. As a result, the adsorbed organic pollutants could be quickly degraded at the catalytic active sites on SBC.

3.4. Analysis of the MgSO₄ solutions during the process of oxidative degradation

3.4.1. The changes in color of the MgSO₄ solutions with different reaction times

To investigate the degradation efficiency of the organic pollutants catalyzed by SBC, the MgSO₄ solution samples with different oxidation times were detected by UV/vis spectroscopy (Fig. 3). The absorption peak sharply decreased as the increase of oxidation time, corresponding to remarkable changes in the color of MgSO₄ solution, which clearly indicate that the chromophoric organics were significantly destroyed and degraded. After catalytic oxidation, the UV/vis spectra of MgSO₄ solution showed blueshift and this phenomenon was more remarkable as the increase of reaction time, ascribing to the destruction of auxochrome by oxidative degradation. This result suggests that SBC could

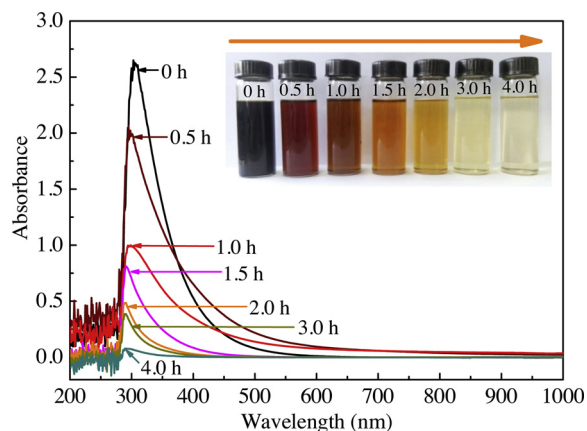


Fig. 3. UV/vis spectra of the MgSO₄ solution samples with different catalytic reaction times.

effectively activate and catalyze H_2O_2 for deep degradation of the organic pollutants in MgSO_4 solution.

3.4.2. Determination of radicals

To further demonstrate the detailed actions of H_2O_2 and SBC in the system, color removal efficiencies of the MgSO_4 solution samples with different treatments were compared. SBC exhibited a good catalytic activity for oxidative degradation of the organic pollutants with H_2O_2 as oxidant. H_2O_2 can be converted to three free radicals: $\cdot\text{OH}$, $\text{HO}_2\cdot$ and $\cdot\text{O}_2^-$ via the following equations (Duan et al., 2018):



It is significant to validate whether reactive radicals were generated induced by SBC catalyst during the oxidation reaction. Herein, tert-butyl alcohol (TBA; scavenger of $\cdot\text{OH}$) and was applied to determine the generation of hydroxyl radicals (Fig. 4a) (Kim et al., 2014). SBC showed adsorption capability for the organic pollutants in MgSO_4 solution, as the color removal gradually increased with the time and reached 8.83% after 4 h. The addition of only H_2O_2 also led to a good degradation of organics, ascribed to that the metal ions in solution could catalyze H_2O_2 to enhance its oxidation capacity. With both SBC and H_2O_2 in the reaction system, the oxidative degradation capacity of H_2O_2 was significantly improved by SBC catalyst. The metal cations adsorbed onto SBC provided catalytic active sites for H_2O_2 , and SBC could simultaneously adsorb the organics, which thus accelerated the oxidative degradation. In addition, p-benzoquinone (PBQ; scavenger of $\text{HO}_2\cdot$) was applied to test whether superoxide radicals were generated during the reaction (Fig. 4b). Clearly, the color removal efficiency reduced with the addition of PBQ, indicating that the generation of $\text{HO}_2\cdot$ radicals in the solution were rapidly trapped by PBQ and thus weakened the oxidative degradation ability of H_2O_2 . Both $\cdot\text{OH}$ and $\text{HO}_2\cdot$ radicals were generated in this reaction system, and $\cdot\text{OH}$ played a major role in the degradation of the organics.

DMPO spin-trapping EPR technique was used to further verify the generation of $\cdot\text{OH}$ (Lyu et al., 2018). As shown in Fig. 5, the addition of only SBC in the reaction system did not exhibit any signals, implying that no radicals generated in the SBC system. After the addition of H_2O_2 , a quartet of signals with relative intensities of 1:2:2:1 were detected from the DMPO- $\cdot\text{OH}$ adducts during the reaction process, indicating that $\cdot\text{OH}$ radicals were formed in the H_2O_2 system (Wang et al., 2014). Although without the addition of catalyst, H_2O_2 could be catalyzed to generate $\cdot\text{OH}$ as the presence of metal ions in the MgSO_4

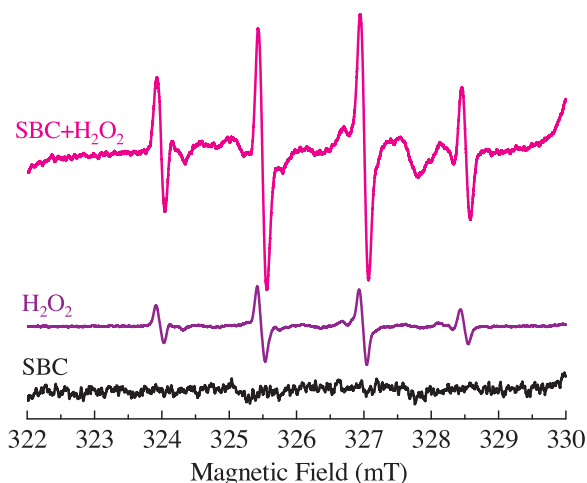


Fig. 5. DMPO spin-trapping ESR spectra of the MgSO_4 solution samples in different systems ($n_{\text{ag}} = 3.471 \text{ mmol g}^{-1}$, SBC dosage of 0.02 g/g waste H_2SO_4 , H_2O_2 dosage of 0.2 g/g waste H_2SO_4 , pH = 5, reaction temperature of 65 °C, and DMPO dosage of 100 mmol L^{-1}).

solution, especially Fe, Mn, Cu, etc., which usually exhibit good catalytic performance (Lyu et al., 2015, 2018; Huang et al., 2017; Ma et al., 2018). In comparison, SBC + H_2O_2 system exhibited very strong DMPO- $\cdot\text{OH}$ signals, which was approximately 3 times higher than that in the H_2O_2 system. This result demonstrates that the acidic groups in SBC and the adsorption of the metal ions on SBC could provide plenty of catalytic active sites for efficiently catalyzing H_2O_2 to form abundant reactive $\cdot\text{OH}$, which promoted the degradation of organic pollutants with high utilization efficiency of H_2O_2 . The DMPO-trapped EPR results confirm that the important role of SBC in catalytic reaction, which were consistent with the results of forementioned analyses.

3.5. Identification of the product

The resulting treated MgSO_4 solution with color removal of 93.71% and TOC removal of 85.89% was obtained under the catalytic reaction conditions of SBC dosage of 0.02 g/g waste H_2SO_4 , H_2O_2 dosage of 0.2 g/g waste H_2SO_4 , pH = 5, reaction temperature of 65 °C, and reaction time of 4 h, and then the purified MgSO_4 solution was used to prepare $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ product. The prepared product was determined by chemical assay and XRD analysis to verify its composition and crystalline phase, respectively. The percentage of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in the product was 99.5%, containing less than 0.005% of iron and < 0.5% of other impurities without harmful heavy metals, which met the requirements of industrial magnesium sulfate. XRD pattern (Fig. 6a) of the prepared product exhibits obvious characteristic diffraction peaks

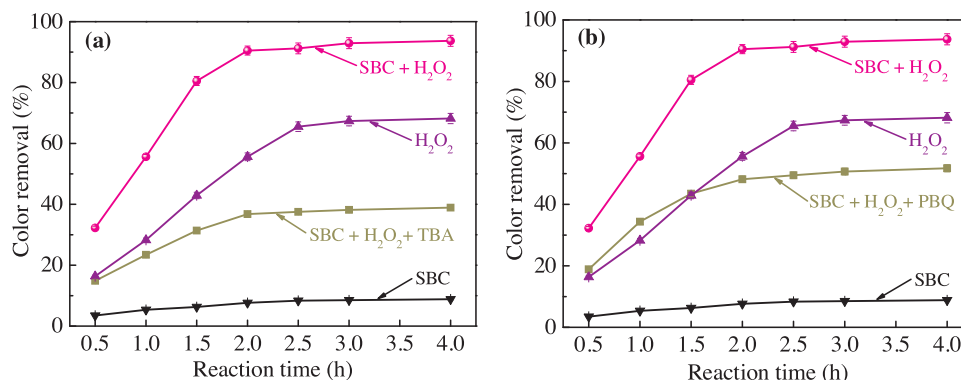


Fig. 4. Color removal of the MgSO_4 solution in different systems ($n_{\text{ag}} = 3.471 \text{ mmol g}^{-1}$, SBC dosage of 0.02 g/g waste H_2SO_4 , H_2O_2 dosage of 0.2 g/g waste H_2SO_4 , pH = 5, and reaction temperature of 65 °C).

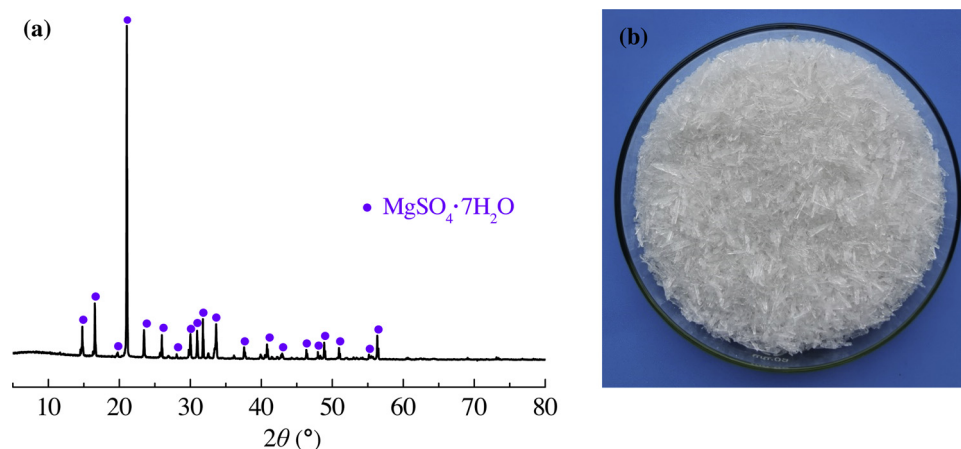


Fig. 6. (a) XRD pattern and (b) photograph of the prepared magnesium sulfate product.

of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, indicating the successful production of magnesium sulfate using waste H_2SO_4 . Additionally, the apparent morphology of the product (Fig. 6b) shows the white and transparent crystals, which further confirms that the prepared product was qualified $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. After the separation of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ crystals, the remaining MgSO_4 solution with a small amount of organics was returned to crude MgSO_4 solution for recycled treatment and utilization. Therefore, the waste H_2SO_4 was successfully utilized by reacting with magnesium oxide ore and efficiently treated by deep oxidative degradation of the organic pollutants.

4. Conclusions

In summary, simultaneous consumption of waste H_2SO_4 and deep oxidative degradation of the organics in waste H_2SO_4 were successfully performed with MASPR-prepared SBC as an effective catalyst. The waste H_2SO_4 could completely react with magnesium oxide ore to prepare crude MgSO_4 solution, and the organic pollutants in the solution were deeply degraded and mainly mineralized with H_2O_2 as oxidant and SBC as catalyst. The total amount of acidic groups of SBC significantly affected its catalytic activity, attributing to that these oxygen-containing functional groups adsorbed and immobilized metal ions on the SBC to form catalytic active sites, which could activate and catalyze H_2O_2 to generate $\cdot\text{OH}$ and $\text{HO}_2\cdot$ radicals for effective degradation of the organics. The resulting purified MgSO_4 solution with color removal of 93.71% and total organic carbon removal of 85.89% under optimum catalytic reaction conditions was used to produce qualified $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ product. Consequently, this novel technology showed great application prospect in the removal of hazardous organic contaminants using esterified agro-industrial residue as effective catalyst, which achieved the effect of treating waste by waste.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jhazmat.2019.120892>.

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